



From Electrode Design to K-Ion Full Cell Optimization : Electrochemical Performance and Interface Phenomena Investigations

Badre Larhrib

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UNIVERSITE DE PAU ET DES PAYS DE L'ADOUR

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by **Badre LARHRIB**

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Field of Specialization: Physics & Chemistry

From Electrode Design to K-Ion Full Cell Optimization : Electrochemical Performance and Interface Phenomena Investigations

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A wise man once said :

“Don’t be afraid to start over again. This time, you’re not starting from scratch. You’re starting from experience”

Abstract

Renewable energy production growth has motivated research into new stationary storage technologies based on abundant and inexpensive elements. After the success of the Na-ion batteries, the K-ion technology has caught the interest of the scientific community. Indeed, the physical-chemical properties of potassium should allow the development of high energy and high power batteries. First, the initial phase of this PhD thesis seeks to qualify effective electrode materials, both for negative and positive electrodes, through the optimization of composition, structure, and electrochemical performance. Two groups of positive electrodes will be explored: i) polyanionic materials and Prussian Blue analogues as cathodes, and ii) the use of graphite as the anode, initially, with subsequent exploration of alternatives like hard carbons. Expanding upon the improved electrodes design, the subsequent phase of our study will concentrate on the optimization of full cells. Developing on the optimized full cell, the final part delve into comprehending the mechanisms governing the formation of cathode and solid electrolyte interphases in the selected K-ion battery. Various techniques, including Raman and X-ray Diffraction will be employed for ex situ analysis. Furthermore, ex situ X-ray Photoelectron Spectroscopy, will provide an in-depth exploration of the parameters that govern electrode/electrolyte interfaces.

Résumé

La croissance de la production d'énergie renouvelable a encouragé les chercheurs vers de nouvelles technologies de stockage stationnaire basées sur des éléments abondants et peu coûteux. Après le succès des batteries au sodium-ion, la technologie au potassium-ion a suscité l'intérêt de la communauté scientifique. En effet, les propriétés physico-chimiques du potassium devraient permettre le développement de batteries à haute énergie et puissance. De ce fait, la première phase de cette thèse de doctorat vise à qualifier des matériaux d'électrodes efficaces en optimisant leur composition, leur structure et leurs performances électrochimiques. Cela inclut l'exploration de deux groupes d'électrodes positives : i) les matériaux polyanioniques et les analogues du bleu de prusse en tant que cathodes, et ii) l'utilisation du graphite en tant qu'anode initialement, avec des recherches ultérieures sur des alternatives telles que les carbones durs. En élargissant la conception des électrodes améliorées, la phase suivante de notre étude se concentrera sur l'optimisation des cellules complètes. Suite à la conception optimisée des cellules complètes, la dernière partie vise à comprendre les mécanismes gouvernant la formation des interfaces cathode-électrolyte et électrolyte solide dans la batterie au potassium-ion sélectionnée. Diverses techniques, dont la spectroscopie Raman et la diffraction des rayons X, seront utilisées pour des analyses ex situ. De plus, la spectroscopie de photoélectrons aux rayons X ex situ, permettra une exploration approfondie des paramètres qui gouvernent les interfaces électrode/électrolyte.

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General Introduction

The projection of a huge increase in global energy consumption between 2020 and 2050 has raised significant concerns about climate change. To limit temperature rise, the international climate agreement signed in Paris in 2015 aimed to limit the increase to no more than +2°C by 2100 [1]. In 2018, the Intergovernmental Panel on Climate Change (IPCC) warned that without action, a 1.5°C increase was likely before 2050. However, a new report in August 2021, considering recent global consumption trends, suggests that a 1.5°C increase may occur by 2030 [2]. Recently, the IPCC's Sixth Assessment Report provides a thorough analysis of climate change, covering its impacts on ecosystems, biodiversity, and global and regional communities. It assesses vulnerabilities and the ability of both nature and society to adapt. The report emphasizes the availability of multiple, practical solutions to reduce greenhouse gas emissions and cope with human-induced climate change [3]. The Synthesis Report for this assessment was published on March 20, 2023.

To address these challenges and meet the international climate agreement, ecological measures include exclusive production of electric vehicles by 2040 and a preference for renewable energy production [4]. Europe aims for at least 80% of its energy production to be renewable by 2050 [5]. This ambitious goal involves dealing with the intermittent nature of renewable energy sources due to climatic conditions (such as wind and solar power). Effective energy storage systems are essential.

To support the development of such systems, collaborative networks exist at both European and national levels, like Alistore and the National Network on Electrochemical Energy Storage (RS2E). The “Université de Pau et des Pays de l’Adour” (UPPA) has also received national excellence recognition for its Solutions for the Energy and Environment (E2S) project, which brings together research teams from eight laboratories (including two international ones) to address energy transition issues. These networks facilitate knowledge sharing and research collaboration to enhance electrochemical system performance.

The electrochemical devices under consideration include batteries, supercapacitors, and fuel cells. The goal is to achieve high energy density, long lifespan, and significant efficiency. Lithium-ion

batteries possess all the required characteristics for stationary storage of renewable energy and are already being developed in this field [6,7]. In fact, their importance is highlighted by the fact that the 2019 Nobel Prize in Chemistry was awarded to three of its inventors [8]. However, the extensive and growing use of this technology raises concerns, particularly regarding the supply chain challenges associated with lithium.

In search of an alternative, other alkali metals have been considered. Sodium-ion technology, with chemical and physical properties similar to lithium, has shown promise and commercial viability. One advantage is the abundant availability of sodium in the Earth's crust, being approximately 1000 times more abundant than lithium [9]. Following sodium, potassium is now receiving increasing attention. As abundant as sodium in the Earth's crust, potassium-ion batteries (KIBs) could potentially serve as a relevant alternative [10].

KIBs have gained significant and rapidly growing interest due to their chemical and economic advantages. From a chemical perspective, it has been demonstrated that the potential of K^+/K in carbonate ester electrolytes is low (-2.93 V vs. standard hydrogen electrode) [11]. This low voltage indicates the potential for high energy density when using K ions as charge carriers and a reduced risk of potassium plating. Additionally, K ions exhibit high ionic conductivity and fast diffusion rates in carbonate ester electrolytes like propylene carbonate [12].

Economically, potassium resources are virtually inexhaustible and widely distributed [13], resulting in the comparatively lower fluctuation and cost of potassium carbonate (750 euros per tonne, compared to 20800 euros for lithium carbonate) [14,15]. Furthermore, the most effective KIB electrode materials discovered thus far do not contain costly elements such as cobalt, nickel, or other high-price transition metals. KIBs also have the advantage of being able to use aluminium as an anode current collector in place of the more expensive copper since potassium does not form thermodynamically unfavourable intermetallic compounds with aluminium, reducing manufacturing costs. In addition, KIBs can be produced using existing facilities in the lithium- and sodium-ion battery (LIB and NIB, respectively) industry, facilitating a continuous transition to commercial production.

The chemistry of potassium batteries is highly diverse, offering a range of materials with exceptional performance characteristics. Positive electrodes can be designed from Prussian blue analogues, layered transition metal oxides, and polyanionic compounds, each exhibiting

competitiveness in various aspects of performance, including voltage, capacity, rate capability, safety, and cycle life. Unlike sodium battery chemistry, graphite stands out as a prime material for potassium battery anodes, often used in combination with various graphitic and non-graphitic carbons. This diversification of electrode materials paves the way for diverse manufacturer profiles and target markets.

The immense potential of KIBs has prompted an announcement from a battery startup based in Austin, Group1, which plans to commercialize a Prussian White cathode material for KIBs, aiming to benchmark the LiFePO_4 cathode used in LIBs. They aspire to launch this product on a large scale by 2027 [16]. Beyond private sector initiatives, significant research efforts from academia have been dedicated to KIB development over the last five years. Numerous worldwide publications have emerged from several countries that have prioritized research projects related to potassium batteries [17–19].

The development of KIBs is currently carried out in two stages. The first part focuses on studying positive and negative electrode materials in a half cell configuration to qualify and identify promising materials, where the studied electrode faces potassium metal. In contrast, the high potassium metal reactivity induces the migration of electrode degradation species toward the surface of the working electrode, thereby compromising the reliability of solid electrolyte interphase (SEI) studies in half cells [20]. The second part involves work in a full cell to mitigate the impact of potassium metal and understand the behaviour of cells in a configuration similar to commercial batteries. For initial tests in a full cell, a three-electrode assembly is generally preferred to assess the performance of the positive and negative electrodes using a reference electrode with potassium metal, which theoretically should not interact with the other electrodes. As previously mentioned, K-ion technology presents several challenges, including the qualification of positive electrodes for industrial applications (i.e., capacity, average potential, tap density, one or two-step synthesis, and safety), the high reactivity of potassium metal, electrode and electrolyte design, and further analysis of full cells toward a K-ion prototype in the coming years. This leads us to the primary objectives of this thesis: to comprehend the behaviour of specific electrode materials and investigate the phenomena taking place at the electrode/electrolyte interfaces in order to evaluate their impact on cell performance.

This thesis was conducted at the “Institut des sciences analytiques et de physico-chimie pour l'environnement et les matériaux” (IPREM - UMR 5254 UPPA/CNRS), known for its expertise in the field of surface and interface phenomena in Li-ion battery electrodes for many years. Given their reactivity and thinness, studying the properties (chemical composition, homogeneity, and so on...) of electrode/electrolyte interfacial layers that requires the use of surface analysis techniques such as X-ray Photoelectron Spectroscopy (XPS). In the course of this work, three main collaborations were established: with the “Institut Charles Gerhardt Montpellier” (ICGM - UMR 5253 - CNRS/UM/ENSCM), with the “Institut de Chimie de la Matière Condensée de Bordeaux” (UMR 5026 - CNRS/University of Bordeaux/Bordeaux INP), and with the “Institut de Science des Matériaux de Mulhouse” (IS2M - UMR 7361 - CNRS/UHA), all of which are members of the Energy Electrochemical Storage Network, just like IPREM. Some missions were occasionally conducted at ICGM (Montpellier), which has a fully equipped laboratory for materials characterizations and cycling studies. Furthermore, the positive electrode materials studied in this thesis were synthesized by ICMCB (Bordeaux). Finally, the hard carbon materials studied in this thesis were synthesized in IS2M (Mulhouse).

This thesis manuscript is a part of the ANR TROPIC (grant ANR-19-CE05-0026) project. Containing four chapters, this manuscript presents a structured exploration of the research findings, with some results presented in the form of integrated publications within their respective sections.

Chapter 1 provides an overview of the state of the art in metal-ion batteries, particularly potassium-ion batteries. It focuses on electrode materials, electrolyte components, and their properties.

Chapter 2 outlines the negative and positive electrodes design. Special attention is given to the impact of electrode formulation and pyrolysis of hard carbon synthesis on electrochemical performance in half cell configuration.

Chapter 3 explores the current literature of full cells for KIBs and a guideline toward reliable K-ion full cells. This investigation addresses the lack of knowledge about full cells in K-ion batteries compared to well-documented cases in Li-ion batteries.

Chapter 4 investigates the impact of various parameters on the electrochemical performance of $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ /graphite full cells, highlighting the significance of solid electrolyte SEI

preformation, optimal passivation layer conditions, and the potential influence of vanadium dissolution on capacity fading. The aim is to enhance the understanding of SEI growth mechanisms, leading to reliable XPS analysis of the SEI in KIBs and facilitating practical passivation layer characterizations.

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Chapter 1

Metal-ion batteries: State of the art

I. From primary voltaic cells to K-ion batteries

The development of metal-ion technologies has resulted in nearly 200 years of electrochemical research. The first primary battery was designed by Alessandro Volta (1800), the works and law of Michael Faraday (1831), the cell Daniell (1836), the first rechargeable lead acid systems discovered by Gaston Planté (1859), and improved for industrialization by Camille Fauré (1881), the Leclanché battery by French engineer Georges Leclanché (1866), Waldemar Jungner (1899) developed nickel-cadmium accumulators, Thomas Edison (1901) created nickel-iron accumulators, and Stanford Ovshinsky (1967) developed the nickel metal hydride technology that replaced nickel-cadmium batteries [1]. Then, the oil shock and digital revolution of the early 1970s and 1990s highlighted the limits of energy densities of secondary Nickel-Cadmium- and Nickel-metal hydride batteries (Figure 1). This new interest in batteries with embedded applications, both for mobile technologies and for electric vehicles, led to an acceleration of research in the field of batteries. It was in this context that the first Li-ion accumulators appeared.

Sony first introduced Li-ion batteries (LIBs) in 1991. Since the digital revolution, this technology has been used by users of mobile computing devices (smartphones, tablets, laptops, and so on) because it provides a long lifespan compared to the aforementioned technologies [2]. Li-ion batteries today reach high energy densities by volume and mass, up to $735 \text{ Wh}\cdot\text{dm}^{-3}$ and $275 \text{ Wh}\cdot\text{kg}^{-1}$ [3]. Lithium has on the one hand a very low potential ($-3,04 \text{ V}$ versus the standard hydrogen electrode (SHE)), and on the other hand a very low molar weight ($6,941 \text{ g}\cdot\text{mol}^{-1}$) and a low ionic radius ($0,76 \text{ \AA}$). This makes it possible to store large energy in a minimum volume and weight [4]. In addition, the low ionic radius induces rapid diffusion of Li^+ ions at interfaces involving high-power batteries. LIBs present the best performance among commercial secondary batteries, and current research is focused on continuing to improve battery performance in terms of energy, power (fast charging), cost, environmental impact, safety, and lifespan. However, the challenges changed at the turn of the 21st century: the challenge now is to develop an energy-sustainable society, including through the development of renewable energy. The specifications for grid energy storage systems have several requirements such as long lifetime, high efficiency, and superior safety [5]. It is still possible to develop LIBs in line with these specifications, but a new issue has emerged related to the low abundance of lithium in the earth's crust combined with an irregular distribution worldwide. The risk of an unstable supply and fluctuating market price for lithium, which is mainly

concentrated in Australia and Latin America, may be worrying [6]. For example, the price of the Li_2CO_3 precursor had risen from 15,000€ per ton in early 2017 to about 65,000€ in February 2023 [7]. Thus, demand for energy storage systems remains high, requiring further research into the development of new technologies.

A few years later, novel electrochemical storage technologies beyond LIBs (i.e., Na- and K-ion batteries) are highly required to meet the growing demand of the transport and electricity-grid [8]. These technologies often suggest several advantages; unlike lithium, potassium - like sodium - is distributed uniformly throughout the world and is among the most abundant elements in the earth's crust (1.5%) [9]. The costs of carbonate precursors (M_2CO_3), alkali metal, and alkali salts used in electrolyte formulations decrease according to $\text{Li} \gg \text{K} > \text{Na}$, making potassium and sodium attractive. These two alkalis also have the advantage of not forming any alloy with aluminum, which is a lightweight material and less expensive than copper: aluminum can therefore be used as a current collector [10]. In a similar way to LIBs, and unlike Na-ion ones, the reversible electrochemical intercalation of K^+ into graphite was experimentally demonstrated by Komaba et al. in 2015[11], which was the beginning of the K-ion batteries (KIBs) trend. Although it may be thought at first that the use of sodium or potassium would significantly reduce costs, in contrast, a recent study [12] has shown that by taking into consideration the battery lifespan the use of potassium could not have a significant advantage over the overall cost of the battery. However, the annual cost (a real determining factor) would be amortized if the developed potassium-ion batteries could reach a very long lifetime. If the lifetime was 1500 cycles (about 4 years full charge per day), so at this point, the annual cost of a K-ion battery would become lower than that of a Li-ion battery. These cost estimates are related to scientific advances as well as fluctuations in market material costs, which are influenced by demand and various geopolitical factors.

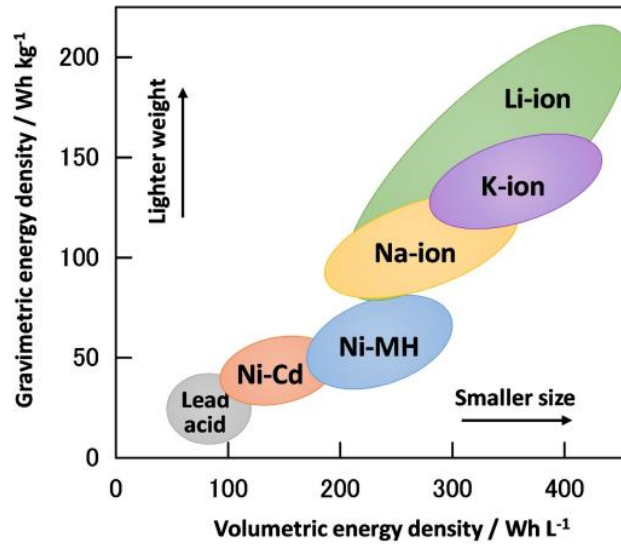


Figure 1. Energy density of the main rechargeable battery technologies [4].

II. Metal-ion battery basics

Generally, a battery is a system that enables energy stored in an electrochemical form to be restored in electricity. For this, electrochemical reactions, specifically oxidation-reduction reactions, occur at the electrodes, generating an ionic movement via the electrolyte and a movement of the electrons via the external circuit (also called electric current). These electrochemical reactions are associated with redox couples, the potentials are given by the Nernst formula. If the electrochemical reactions are irreversible, the cell is referred to as the primary battery, and cannot be recharged. If the electrochemical reactions are reversible (i.e., both half-equations are reversible), the rechargeable cell is known as a secondary battery, or accumulator [13].

II.1 Metal-ion battery components

The four main battery parts are the two electrodes facing each other, physically separated by an electrolyte-soaked separator.

II.1.1 Electrodes

The so-called composite electrodes are manufactured from a mixture of powder of active material and additive(s) (percolating electronic conducting agent, binder) coated on a current collector [14]. Each element is chosen to meet a special specification.

- Current collector. It must be chemically inert and an excellent electrical and thermal conductor to ensure the rapid transfer of electrons while avoiding excessive heating. It is usually a thin metal foil made of copper or aluminum, which is therefore solid and facilitates electrode handling.
- Active material. This is a source material for M^+ ions or a host material that can accommodate them. The active material of the positive electrode includes the redox couple(s) of higher potential(s) than the M^+ / M^0 couple; it is often a transition metal oxide. The active material of the negative electrode comprises the redox couple(s) of lower potential(s) versus the M^+ / M^0 couple, the most used being graphite. The electrodes thus made of these materials are called respectively "cathode" (positive electrode material) and "anode" (negative electrode material) [15].
- Percolating electronic conductive agent (additive). It ensures electronic conductivity by passing electrons from the current collector to the different active material particles. It is generally a carbon black (nanometric primary particles), which has the main advantage of having a high electronic conductivity of the order of 10^3 S m^{-1} , thus facilitating charge transfer within the active material [16].
- Polymer binder (additive). It maintains the formation of a homogeneous film, and it above all ensures a mechanical strength between the active material, the carbon additive, and the current collector. It, therefore, improves on the one hand the adhesion with the current collector and prevents possible delamination, and on the other hand the mechanical strength which must be appropriate to support the volume expansion of the electrode when the ions are inserted into the active material. Since the close contact between the binder and the various electrode components, a polymer with high anodic and cathodic stability is required. The binder is generally a polymer such as polyvinylidene fluoride (PVDF) for the positive electrode or carboxymethylcellulose (CMC) for the negative electrode, which is solubilized in N-methyl pyrrolidone (NMP) and water, respectively [17].

II.1.2 Separators

The separator is inserted between the anode and cathode. It prevents the two electrodes from being physically in contact, which may lead to a short circuit. It must present high mechanical properties, as well as a low thickness (in the specifications of commercial LIBs the separator must not exceed

25 μ m). The separator must be permeable to the electrolyte and should have a high porosity to allow the ions to move without constraints during cycling. It is generally made of polymer (the best electrochemical stability is found for separators made of polypropylene and/or polyethylene). Some separators play an active role in safety by being impermeable to ions above a certain temperature, which collapses the separator pores in case of a thermal runaway. However, as this phenomenon is irreversible, it also means that the battery will no longer be able to perform [18].

II.1.3 Electrolytes

The electrolyte wets the separator and electrode porosities. During battery cycling, it ensures the transport of M^+ ions from one electrode to the other, and more precisely to the surface of the particles of active material; it thus forms an ionic percolating network and is thus a determining component in the performance and safety of the battery [19]. Ideally, the electrolyte should present a :

- High ionic conductivity ($> 10^{-4} \text{ S cm}^{-1}$).
- Low electronic conductivity ($< 10^{-10} \text{ S cm}^{-1}$).
- High thermal stability.
- Good compatibility with the battery components (electrodes, separators, and collectors).
- High electrochemical stability within the operating potential window of the battery to prevent degradation during cycling. However, standard solvents reduce on the surface of the active material particles of the negative electrode below $\sim 1 \text{ V}$ (versus M^+ / M^0 , with $M=\text{Li, Na or K}$), i.e., in the operating potential window of the negative electrode (0 to 2V). Therefore, standard solvents oxidize on the surface of the cathode active material particles, above $\sim 3 \text{ V}$ versus M^+ / M^0 . It should be noticed that the use of a coating on the active material decelerates/limits the electrolyte degradation but does not eliminate it. It is therefore important to optimize the protective passivation layer (called SEI, Solid Electrolyte Interphase) directly formed by the decomposition products of the electrolyte [20]. The SEI, at the center of this thesis work, is detailed at the end of this state of the art chapter.

II.2 Fundamental principles of metal-ion battery

Active material reactions during charge and discharge are oxidation-reduction reactions. The operating principle of a cell is shown graphically in **figure 2**. During the charge, the M^+ ions are extracted from the active material of the positive electrode (oxidation of the transition metals): the electrons then generated circulate in the external circuit while the metal ions (M^+) migrate through the electrolyte, towards the active material of the negative electrode where they will be stored (reduction of this material). It should be noted that, depending on the material used, several storage mechanisms are possible (insertion, alloying, and conversion). These mechanisms are briefly detailed for K-ion batteries in IV and V sections of this chapter. The reverse reactions occur during discharge: the metal ions stored in the negative electrode migrate through the electrolyte to the active material of the positive electrode, while the electrons flow from the negative electrode to the positive electrode in the external circuit. Considering an M-ion battery consisting of graphite (C_y) at the negative electrode and a transition metal oxide (MTO_2) comprising one alkali at the positive electrode, the following reactions are involved [21]:

- During the charge :
(+) $M_1TO_2 \rightarrow M_{1-x}TO_2 + x M^+ + x e^-$
(-) $C_y + x M^+ + x e^- \rightarrow C_yM_x$
- During the discharge :
(+) $M_{1-x}TO_2 + x M^+ + x e^- \rightarrow M_1TO_2$
(-) $C_yM_x \rightarrow C_y + x M^+ + x e^-$

It should be mentioned that for practical reasons, the electrochemical devices used in the laboratory to test the electrochemical performance of an electrode material (positive or negative) are frequently "half cells", using metallic lithium, sodium, or potassium as reference electrode. As well, due to the high reducing power of alkali metal, this electrode must be the counter electrode (negative electrode) of the device, with the lowest potential. Thus, the materials tested in half cells all become the positive electrode of the device.

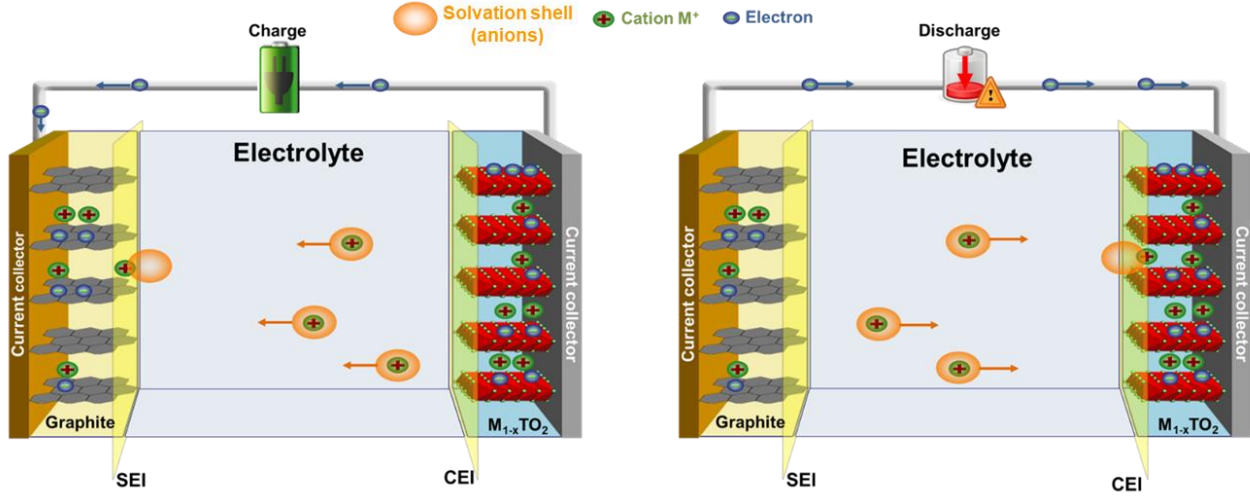


Figure 2. Schematic illustration on working principle of a metal-ion battery.

II.3 Nomenclature and electrochemical characteristics of metal-ion battery

In order to ensure a good understanding of the nomenclature, the main characteristic terms used for metal-ion batteries are defined in this section. It should be noted that in the scientific literature, these characteristics are often a function of the electrochemical materials, whereas for the final application and practical use, a more inclusive approach considering the mass or volume of all the components is to be preferred.

- Energy density

The energy density of the battery (ED) is defined as the capacity (Q, or sometimes noted C) times the working potential (average or operating potential). It is expressed in $Wh\ kg^{-1}$ or $Wh\ dm^{-3}$ [15].

$$ED = Q \times U$$

To make an efficient battery, it is necessary to maximize this energy density. For this, the cell operating potential E and the capacity of the electrode materials must be as high as possible.

- Electrode potential and cell operating potential.

The electrode potential can be evaluated from the Nernst equation as a function of the redox couple involved [15]:

$$E_{electrode} = E_0 + \frac{RT}{nF} \ln \frac{a(Ox)}{a(Red)}$$

With E potential of the electrode, E_0 standard potential of the redox couple, R molar gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T temperature in Kelvin, n number of electrons exchanged, F Faraday constant ($\sim 96500 \text{ C mol}^{-1}$), and $a(Ox)$, $a(Red)$ activities of redox species.

The cell working potential is the difference in chemical potentials across the battery, expressed in volts (V) according to:

$$E = E_{cathode} - E_{anode}$$

Thus, to make a high cell working potential, it is necessary that the cathode potential is as high as possible, and the anode potential is as low as possible.

In practice, there are phenomena of ohmic drop in conductive materials (ionic and electronic), and phenomena of surface overpotential and concentration at the electrodes. Surface overpotential arise from the kinetics of charge/mass transfer at the electrode/electrolyte interfaces, concentration overpotentials are produced by the presence of alkali concentration gradients across the electrodes, and the ohmic drop is due to the ionic resistance of electrolyte. Because of these phenomena, the operating potential (U) during discharge is always lower than the value E ($U < E$) [15].

- Theoretical capacity and practical capacity of electrode materials.

The theoretical mass capacity (in mAh g^{-1}) of an active material can be calculated from the number of moles or electrons exchanged using Faraday's formula:

$$Q_{theoretical} = \frac{F \times n}{3.6 \times M}$$

With M the molecular weight of the active material (g mol^{-1}) and F Faraday's constant. Knowing the theoretical capacity obviously allows us to compare the theoretical performance of the studied materials and to estimate the full cell capacity, but it also allows us to quickly define the galvanostatic cycling rate.

The practical capacity Q of the cell is the charge amount that the battery can give back when fully discharged at constant current, under standard temperature conditions. It is defined by the integral of current versus time and is expressed in mAh:

$$Q = \int_0^t i(t) dt$$

In the half cell configuration, the negative electrode (alkali metal) is a "limitless" tank of M^+ ions thus theoretically not bridging the capacity of the positive electrode; the experimentally measured capacity is thus associated to the positive electrode capacity.

In addition, the specific mass and volume capacities provide access to the amount of energy stored or delivered by the material (cathode or anode) per unit mass or per unit volume, according to:

$$Q_m = \frac{Q}{m} \text{ for the mass capacity}$$

$$Q_v = \frac{Q}{v} \text{ for the volume capacity}$$

It should be kept in mind that the mass/volume capacity of the cell depends on several factors (temperature, formulation of electrodes and electrolytes, current rate, aging of the battery, and so on ...), thus making comparisons between different studies complex [22].

- Galvanostatic cycling and associated characteristics.

The measurement of the electrochemical behavior of a material can be carried out thanks to a galvanostatic cycling with potential limitation. This mode of cycling allows to apply a constant current (I) and to follow the evolution of the potential according to time. The reaction is then "compelled" since the material does not have time to return to its equilibrium state. On the one hand, a negative current is applied to discharge the battery (or a positive current to charge it), and on the other hand, the potential controls are fixed between two limit values. To apply the current, we can define a current density (in mA g^{-1}) or a rate (C/n). In this thesis work, C/n is a measure of the time (n , in hours) required to provide the theoretical capacity of the battery (or the common practical capacity). In other words, the theoretical or practical capacity should be obtained during a total discharge or charge of n hours. The calculation of the current to be applied (in mA) is expressed by :

$$I = \frac{Q_{\text{reversible}} \times m}{t}$$

With m mass of active material in gram, $Q_{\text{reversible}}$ capacity of the material in mAh g^{-1} and t duration of the charge or discharge in hour. Thus, to obtain the experimental specific capacities Q_{charge} and $Q_{\text{discharge}}$ (in mAh g^{-1}), it is necessary to note the experimental time of the charge and discharge period:

$$Q_{charge} = \frac{I \times t_{charge}}{m} \quad \text{and} \quad Q_{discharge} = \frac{I \times t_{discharge}}{m}$$

From a galvanostatic cycling, the coulombic efficiency (%) corresponds to the ratio between the reversible capacity and the overall capacity (irreversible and reversible capacities). The coulombic efficiency must be as close as possible to 100%, and is expressed according to :

$$CE = \frac{Q_{reversible}}{Q_{reversible} + Q_{irreversible}} \times 100$$

- Capacity retention.

The capacity retention is the ratio of the reversible capacity of the n^{th} cycle and that of the 1st cycle. the capacity retention allows to define the life of the battery, which corresponds in general to the number of cycles for which the restored energy is at least 80% of its nominal value.

- Power density.

The power density P is the energy density delivered times the period in hours, according to:

$$P = \frac{ED}{t}$$

With ED the energy density of the cell (Wh kg^{-1} or Wh dm^{-3}) and t the period in hours. The power density is expressed in Watts per kilogram (W kg^{-1}). Corresponding to the ability of a battery to store energy in a period of time, the power depends on the active materials used since it is linked to the kinetics of the oxidation-reduction reactions taking place within the battery, but also to the mobility of the M^+ ions through the electrodes and the electrolyte, as well as to the charge/mass transfer at the electrode/electrolyte interfaces [15].

- Polarization or overpotential.

The difference between the charge and discharge working potentials is called the polarization voltage, or overpotential. In this thesis, we will discuss the measurement of the polarization from galvanostatic curves. In theory, the equilibrium potentials of the battery during charge and discharge do not vary according to the different cycles. In practice, the measurement of the average potentials during a complete charge and discharge cycle are not necessarily equal: we can observe a hysteresis on the galvanostatic curves between

charge and discharge. In this manuscript, polarization is defined as the difference between the average charge and discharge potentials, as shown in **figure 3**.

The origin of polarization is complex and is sometimes debated. Generally, it is associated with an internal electronic impedance: different redox processes between charge and discharge, kinetic limitation of the active material if the applied current is too high, bad contact and/or degradation of the electronic contact between the particles of active material during cycling or limited charge transfer due to the SEI [23]. An important polarization has a direct impact on the values of the various characteristics of the battery involving the potential (practical capacity, power, coulombic efficiency, and so on...): indeed, the cut-off potential is reached before the cell is completely charged/discharged.

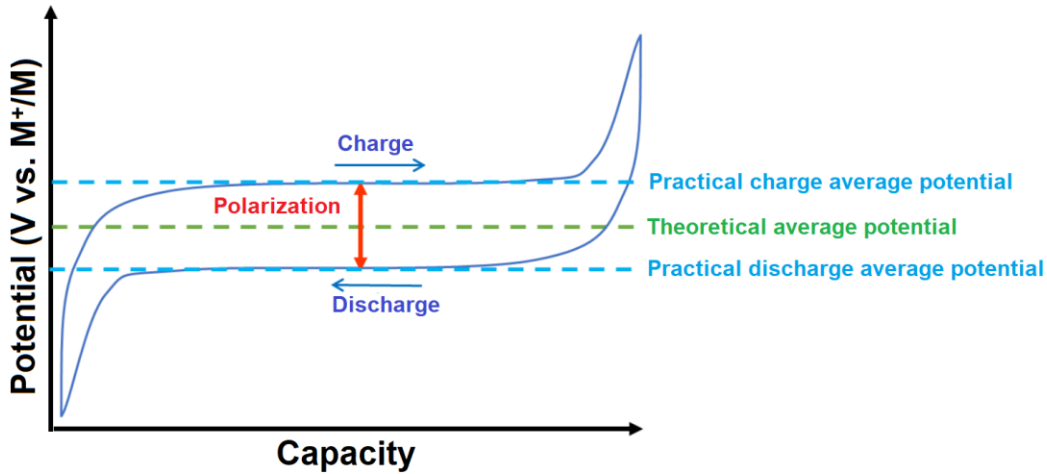


Figure 3. Polarization measurement from galvanostatic curve.

III. Advantages and limitations of K-ion batteries

K-ion batteries have recently acquired regard as a low-cost alternative, only in the case where the full KIB exceeds 1500 cycles, and the capacity retention is over 80% [12]. As well, **figure 4a** depicts the abundance of elements in the Earth's crust. The mass fractions of Li, Co, Cu, and Ni, which are commonly used in high-energy LIBs, are about 0.002% in the Earth's crust, whereas those of Al, Fe, Na, and K are greater than 1%. In terms of elemental abundance, K-based batteries, like Na-based batteries, but unlike LIBs, have a significant advantage for large-scale energy storage applications. Researchers have been motivated to realize high-energy and -power KIBs that are free of the rare elements [24–28]. Furthermore, KIBs are expected to operate at higher voltages

than NIBs and even LIBs [10,11]. **Figure 4b** depicts the potential windows showing the electrochemical stability of LIBs, NIBs, and KIBs with carbonate standard electrolyte solution (0.5M KPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC)). The negative potential value of E^0 (K⁺/K), also known as E^0 (Li⁺/Li), suggests that the negative electrodes in KIBs have a lower potential limitation than those in LIBs, allowing for high-voltage KIBs. As a result, choosing a suitable negative electrode that takes advantage of the low-potential limitation without potassium plating is critical. To achieve practical high-voltage battery performance, battery components such as high-potential positive and low-potential negative electrode materials, electrolytes, binders, and current collectors must be developed. Unfortunately, this approach typically results in oxidative decomposition of the electrolyte solution as well as structural instability at the active material/electrolyte interface especially at high potential. For instance, current LIBs can be charged to 4.5 V, which are limited by oxidative decomposition of the electrolyte on the positive electrode side, which involve a degradation of electrolyte and electrode material surface. According to this viewpoint, developing novel oxidation-resistant electrolytes (>5 V vs Li⁺/Li) is critical for realizing high-voltage KIBs [29]. **Figure 4b** compares the available potential regions for LIBs, NIBs, and KIBs based on the different standard potentials of Li, Na, and K and the assumption that the same anodic limit of electrolyte decomposition is maintained. KIBs have the widest voltage window (4.6 V) without metallic potassium plating compared to the respective Li (4.5 V) and Na (4.2 V) systems. This unique feature of high-voltage operation comparable to that of LIBs motivates researchers to improve KIBs.

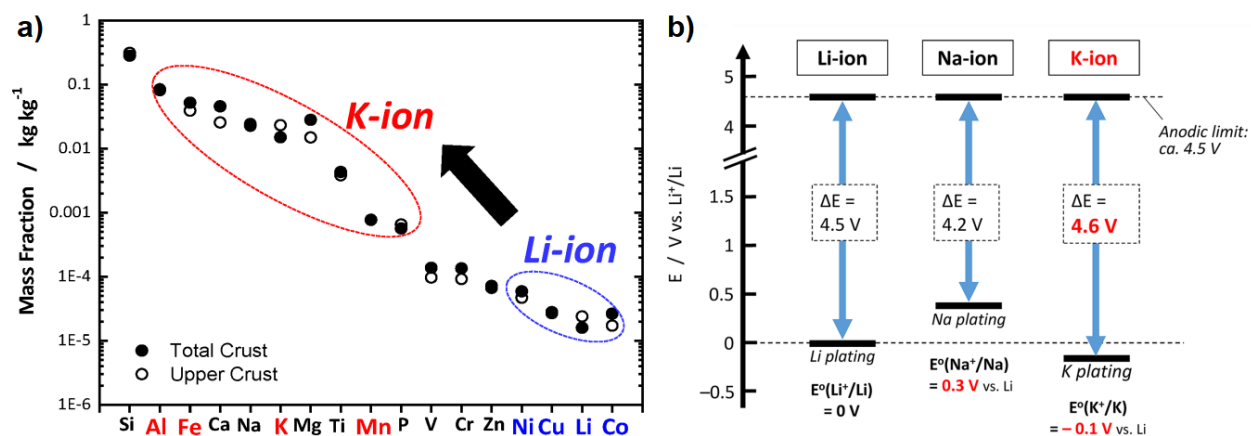


Figure 4. a) The abundance of elements in the Earth's crust, along with the most used elements in Li- and K-ion technologies b) Voltage windows of Li-, Na-, and K-based batteries deduced from a cyclic [10].

In contrast, the main limitations of sodium and potassium compared to lithium are their relatively high molar masses and their larger ionic radii, as shown in **table 1** [10,12]. Indeed, lower mass and volume energy densities are expected. If potassium metal as a negative electrode should allow to obtain very high energy density batteries, K metal electrodes should be banned for uses in conventional liquid electrolyte based battery because of its high reactivity [30]. However, for safety concern, when KIBs are overcharged, K metal may act as an internal fuse, cutting the short-circuit before the severe thermal runaway of the battery, because of the low melting point of this metal (**Table 1**). Nevertheless, in organic solvents, studies agree that the large size of the ions combined with their low Lewis acidity leads to a weak interaction between non-aqueous solvents and K ions, and thus lead to a high ionic conductivity, which would allow high power densities to be obtained [21]. Other physical and chemical properties of potassium have significant advantages, including its low desolvation energy compared to Li⁺ and Na⁺.

To summarize, while KIBs offer several advantages, including the abundance of potassium, the potential for high energy density and high-power output, and the low cost associated with the use of inexpensive aluminum foil as a current collector on the negative side, there are still some limitations that need to be addressed. These include the need to develop stable and effective solid electrolyte interphases and the identification of suitable cathode materials. However, despite these challenges, KIBs remain an attractive technology with the potential to significantly improve the

performance, sustainability, and cost of batteries at specific conditions, and they continue to be an active area of research and development [12].

Table 1. Comparison of the physical and chemical properties of Li^+ , Na^+ , and K^+ .

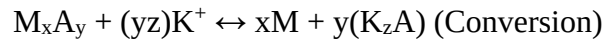
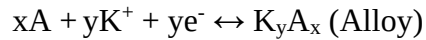
	Li^+	Na^+	K^+	Ref
Atomic mass	6.9	23.0	39.1	-
$E^0 (\text{A}^+/\text{A}_{\text{PC}}) \text{ V vs. Li}^+/\text{Li}$	0	0.23	-0.09	[31]
Ionic radii	0.76	1.02	1.38	[32]
Stokes radii in PC (Å)	4.8	4.6	3.6	[33]
Desolvation energy in PC (kJ mol^{-1})	215.8	158.2	119.2	[34]
Limiting molar ionic conductivity in PC ($\text{S cm}^2 \text{mol}^{-1}$)	8.3	9.1	15.2	[33]
Melting point ($^{\circ}\text{C}$)	180.5	97.8	63.4	[10]

IV. Negative electrode materials

Recently, KIBs have also gained attention due to a development on the anode side: the discovery that potassium can intercalate into graphite, which opens new possibilities for the use of graphite as a negative electrode material in KIBs. As a result, this section will explore research on various materials that can be used as negative electrode materials for KIBs, including conversion materials, metal alloys, intercalation compounds, and carbon anodes.

IV.1 Alloying and conversion materials

For these materials, there is no problem of slow diffusion of potassium ions in the crystalline structure because the electrochemical process forms new species containing potassium as phase transitions occur, according to the following general mechanisms:



While the size of the K ion is not expected to play a significant role, it does directly impact volume expansion, which can be up to four times greater than that observed with a lithium alloy. The combination of alkali metals with other elements has been identified as a promising approach to create high-capacity anodes for Li and Na batteries [35,36]. These anodes leverage the ability of

certain elements to alloy with Li, Na, and K, resulting in significantly higher specific capacity compared to carbon-based anodes. Using first principles DFT calculations, the energetics of alloying K and Na with various anode materials were computed and compared. Sb, Sn, and P were found to undergo K alloying reactions experimentally [37]. A Sb-C composite anode has been shown to reversibly alloy with K over 10 cycles, forming cubic K_3Sb with a capacity of approximately 650 mAh g^{-1} [38]. A ball milled Sn-graphite nanocomposite anode for KIBs was found to sustain a capacity of $150\text{-}170 \text{ mAh g}^{-1}$ for approximately 10-15 cycles, whereas bulk Sn is electrochemically inactive [39]. Phosphorus has a high theoretical capacity of 2594 mAh g^{-1} assuming that K_3P can be formed. The $Sn_4P_3\text{-C}$ composite anode achieved a reversible capacity of approximately 380 mAh g^{-1} over 50 cycles with good rate capability [40]. However, the huge volume expansion of K-alloying reactions will present challenges from a cell energy density perspective. Conversion anodes, which reduce oxides to their metallic state, have long been used in LIBs [41]. However, the utilization of composite $Co_3O_4\text{-}Fe_2O_3$ as a conversion anode for KIBs has only recently been shown [42]. Despite the lower reversible capacity of 220 mAh g^{-1} at 50 mA g^{-1} for 50 cycles, which is 2 times lower than that obtained for a similar material in Na cells (440 mA h g^{-1}).

IV.2 Intercalation materials

In this subsection, we will focus on intercalation materials excluding carbon anodes. Compounds based on titanate, such as $Li_4Ti_5O_{12}$ and $Na_3Ti_2O_7$, have been extensively studied as anodes for non-graphitic intercalation in Li and Na systems for power application [43,44]. For KIBs, $K_2Ti_4O_9$ has been proposed as a suitable compound due to its layered structure with an interlayer spacing that can host K^+ . It has a theoretical capacity of 129 mAh g^{-1} and a practical capacity of 97 mAh g^{-1} at 0.2 C [45]. $K_2Ti_8O_{17}$, another titanate compound, has a similar framework to $K_2Ti_4O_9$. This oxide presents a reversible capacity of 181.5 mAh g^{-1} at 20 mA g^{-1} [46]. The NaSICON-type (Na superionic conductors) structure has also been studied as an anode for KIBs [47]. The carbon-coated $KTi_2(PO_4)_3$ delivers a capacity of 75.6 mAh g^{-1} at 0.5 C [48]. The relatively high average voltage and low capacity of these intercalation materials is a significant limitation for their use in KIBs, despite their promising results and good capacity retention over 100 cycles.

IV.3 Carbonaceous materials

Carbon materials are composed of graphene layers (sp²-hybridized carbon) distributed in a less ordered manner, or even rolled up on themselves in the form of a nanotube [49]. The more disordered the graphene layers are distributed, the more numerous the surface sites capable of accommodating ions are present, resulting in a higher specific capacity. There is both intercalation of ions in the graphitized areas, that is, between the planes of graphene linked by Van der Waals bonds, and their adsorption in the microporosity [50]. One strategy to improve the specific capacity of these materials, which hardly exceeds 300 mAh.g⁻¹, is to dope them with heteroatoms such as nitrogen, phosphorus, boron or sulfur: doping creates defects, which increases the number of active sites for ion adsorption, leading to a pseudo-capacitive behavior [51–56]. Carbon anodes can be differentiated based on their composition and level of graphitization, as elaborated in the subsequent paragraphs.

- Soft and hard carbon have differing degrees of structural disorder, with soft carbon having a lower degree of disorder compared to hard carbon. Both types of carbon comprise of graphene sheets that are unevenly distributed. While soft carbon can undergo graphitization via high-temperature heat treatment, which results in the formation of graphite, hard carbon cannot undergo this process, even at extreme temperatures exceeding 3000°C [57]. Furthermore, Hard carbon has a high electrical conductivity, while soft carbon has a high specific capacity but low conductivity. Thus, Jian et al. [58] propose that the combination of these materials in a composite structure could lead to a material with high capacity, high rate capability, and long cycling stability.
- Carbon nanofibers (CNFs) are 1D nanostructures used as electrode materials for batteries. They have a complex network of fibers with diameters ranging from a few nanometers to several hundred nanometers and high surface area. CNFs have high electrical conductivity, high reversible capacity of 270 mAh g⁻¹, and can adsorb more K ions into a given volume. However, their high surface area can lead to significant electrolyte decomposition, resulting in low coulombic efficiency in the first cycle of battery operation. Further research is needed to address these challenges [59,60].
- Graphite carbon has an ordered structure, it consists of a stack of graphene layers, with the sheets perpendicular to the c-axis. Regardless of the crystal form of graphite, whether

hexagonal (ABAB stacking, thermodynamically more stable) or rhombohedral (ABCABC stacking), the C-C distance is the same: 1.42 Å in the graphene planes and 3.35 Å between the graphene layers [61–63]. Furthermore, studies using theoretical and experimental methods have proposed different mechanisms for the formation of K-graphite intercalation compounds (K-GICs). Ex situ X-ray diffraction (XRD) has suggested the following mechanism: $C \rightarrow KC_{36}$ (stage III at 0.3–0.2 V) $\rightarrow KC_{24}$ (stage II at 0.2–0.15 V) $\rightarrow KC_8$ (stage I at 0.15–0.01 V) [50]. KC_8 then leads to graphite during depotassiation, and following cycles this carbon-type structure suffers from structural damage due to high-volume expansion (~60%) [50]. Another mechanism proposed using density-functional theory (DFT) calculations and ex situ XRD and Raman showed: $C \rightarrow KC_{24}$ (stage III, between 0.35 and 0.18 V) $\rightarrow KC_{16}$ (stage II at 0.14 V) $\rightarrow KC_8$ (stage I at 0.01 V) [64]. A mechanism starting from a dilute stage was proposed using in situ XRD and Raman as well as DFT: KC_{60} (stage V) $\rightarrow KC_{48}$ (stage IV) $\rightarrow KC_{36}$ (stage III) $\rightarrow KC_{24}/KC_{16}$ (stage II) $\rightarrow KC_8$ (stage I) [65]. The theoretical capacity of full potassiation of graphite leads to KC_8 corresponding to a 279 mAh g⁻¹ theoretical capacity. However, conventional graphite delivers about 65% of its capacity between 0.25 V and 0.01 V, and power performance could be limited in half cells by the large K metal plating/stripping polarization [17,66]. For instance, this polarization is about 0.1 V higher with 0.8 M KFSI (Bis(Fluorosulfonyl)Imide potassium salt) EC:DEC (Ethylene carbonate : Diethyl carbonate) compared to 0.8 M KPF₆ (Hexafluorophosphate potassium salt) EC:DEC, which explains the lower rate performance generally observed with KFSI [60,67]. Note that a co-intercalation (intercalation of ions and solvent molecules) has also been observed for ether-based electrolytes, resulting in reduced capacity. This co-intercalation can be avoided by using concentrated electrolytes [68–70]. Thus, graphite electrodes still suffer from several drawbacks (i.e., low rate performance and high volume expansion). These issues will be considered in chapter 2.

In summary of this section, the most significant discovery in the early stages of researching KIB anodes has been the intercalation of K⁺ into graphite. When appropriate binders and electrolytes are used, graphite has demonstrated reasonable electrochemical performance. Although other carbon forms have been shown to store K ions, they are unlikely to be as

effective as graphite in terms of specific energy (i.e., Hard and soft carbons present a higher average potential compared to graphite) [58]. Alloying anodes may not be a suitable choice for KIBs, as the same issues that affect them in LIBs and NIBs are worsened in KIBs, resulting in a significantly reduced energy density. On the other hand, intercalation anodes have been shown to be stable for long-term cycling, but candidates with higher capacity and low voltage are still needed. Finally, conversion anodes anode materials are still in the early stages of development and require further evaluation for practical application.

V. Positive electrode materials

V.1 Organic materials

Organic materials, including small organic molecules, polymers, and organometallic complexes, are promising candidates for cathode materials in K-ion batteries due to their low cost and reduced energy consumption during the synthesis process [71]. However, they require an additional pre-potassiation step before use. Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and polyanthraquinone sulfide (PAQS) are two organic cathode materials with high capacity, but PTCDA requires annealing at 450°C to improve its electronic conductivity and cycling performance, while PAQS has slow ion migration and dissolution issues at high current densities [72,73]. The major drawbacks of organic materials are their high solubility in commonly used solvents and low electronic conductivity. Nevertheless, organic cathode materials still offer the potential for high capacity and good cycling performance in solid-state batteries, despite their low operating potential [74].

V.2 Layered oxides

Layered oxide compounds have a high energy density and are commonly used as cathodes in LIBs and sodium-ion batteries NIBs. These 2D compounds can be classified by an alpha-numeric expression that describes the coordination of alkali sites and oxygen stacking sequences [75]. In the crystal structure of layered oxides, transition metals (T_M) and alkali ions are segregated into alternating blocks that allow for rapid alkali ion migration. $K_{0.3}MnO_2$ was the first layered K-cathode used in KIBs that delivers a reversible capacity of $\sim 125 \text{ mAh g}^{-1}$ with an average voltage of $\sim 2.7 \text{ V}$ [76]. There have been numerous other layered K-cathodes developed since then, including P3-type $K_{0.5}MnO_2$ and P2- and P3-type K_xCoO_2 [77–79]. Mixed TM oxides have been investigated, but they did not improve energy density because of a decrease in operating voltage.

The stoichiometric O₃-type KCrO₂ is the only layered oxide synthesized without K deficiency and displays a reversible capacity of $\sim 93 \text{ mAh g}^{-1}$ with an average voltage of $\sim 2.73 \text{ V}$ [80]. However, layered K-compounds have a low working potential and steeper voltage curves, as well as more voltage steps compared to Li and Na systems due to the long-ranged repulsive interaction between alkali ions, which is not useful for practical application.

Moreover, the maximum allowable voltage for most K-layered oxides is restricted due to the inherent structural instability, which causes a decline in their capacity during overcharge [81]. This limitation is evident upon depotassiation of K_xMnO₂ and K_yCrO₂, resulting in a significant decrease in the crystallinity of the electrodes, as confirmed by ex situ X-ray diffraction analysis [77,80]. This loss in structural integrity is irreversible, particularly at low K content, which hinders the use of a broader range of K de/intercalation. The reasons behind this irreversible structural alteration require further investigation to overcome this limitation.

V.3 Prussian blue and their analogs

Prussian blue (PB) is a compound with the chemical formula Fe₄[Fe(CN)₆]₃(H₂O)_x, and Prussian blue analogues (PBAs) represent a family of metal hexacyanoferrates whose general formula is A_xT_{M1}[T_{M2}(CN)₆]_y·n(H₂O) (with A=Li, Na or K; x varying from 0 to 2; T_{M1} and T_{M2}=transition metals such as Fe, Ni, Co, and so on.) [10]. Unlike the cathode materials mentioned above, the use of PB and PBA for K-ion batteries is not based on the excellent performance of their lithium counterparts. On the contrary, their low capacity compared to layered oxides or polyanionic materials has dampened researchers' interest in using these materials as cathodes for LIBs. The practical utility of such a material became apparent when it came to storing large ions: the three-dimensional structure consists of alternating T_{M1}N₆ and T_{M2}C₆ octahedra linked together by cyanide ligands (-C≡N-), forming a rigid organometallic framework. This framework presents large interstitial sites creating ion flow channels along the (100) direction, allowing the rapid insertion of cations of various sizes, including Li⁺, Na⁺, K⁺, NH₄⁺, and so on. The study of the reaction mechanism by ex situ X-ray diffraction (XRD) has been carried out by Bie et al. [24] on the material K₂Mn[Fe(CN)₆] which displays good electrochemical performance in full cell (80 mAh g⁻¹ after 60 cycles at 30 mA g⁻¹), or by He et al. [82] on the material K_{1.7}Fe[Fe(CN)₆]_{0.9}. The impact of the size of the active material particles on the electrochemical performances (the best performance was 140 mAh g⁻¹ being associated with 20 nm particles) [82]. The electrochemical

performance is indeed dependent on the chemical composition, morphology, and particle size, as well as the amount of interstitial water. Even if all these parameters must be optimized to obtain better performance, PBAs have the advantages of being stable, having a high ionic diffusion coefficient allowing to support high current densities upon cycling, and displaying working potentials generally that may reach 3.9 V in K-ion cells, which is globally higher than working potentials in LIBs [70,81].

V.4 Polyanionic compounds

Polyanionic compounds are a family of materials with a general formula $M_xT_y(XO_4)_z$, where M = Li, Na, or K; T = transition metal; X = P, S, As, Si, Mo, and W; and $(XO_4)_z$ is the polyanionic framework. These structures often have M-O-X bonds, so the inductive effect of the $(XO_4)_z$ groups implies a strong polarization between the oxygen ions and the M cation, decreasing the covalence of the M-O bond [83,84]. Polyanionic compounds have good thermal and structural stability, operate at high potential, and, like PBA, diverse polyanionic compounds have open 3D structures allowing for rapid ion diffusion. However, they generally have low practical capacity and poor coulombic efficiency. Moreover, they have low electronic conductivity due to the presence of XO_4 insulating groups between transition metals, which inhibits electron propagation via d-orbital overlap. Among polyanionic compounds, those based on vanadium and phosphates or fluorophosphates have been actively studied and have shown good electrochemical properties for K-ion batteries (as in the case of Li- and Na-ion batteries). **Figure 5** summarizes the most well-known polyanionic materials, some of which will be discussed later.

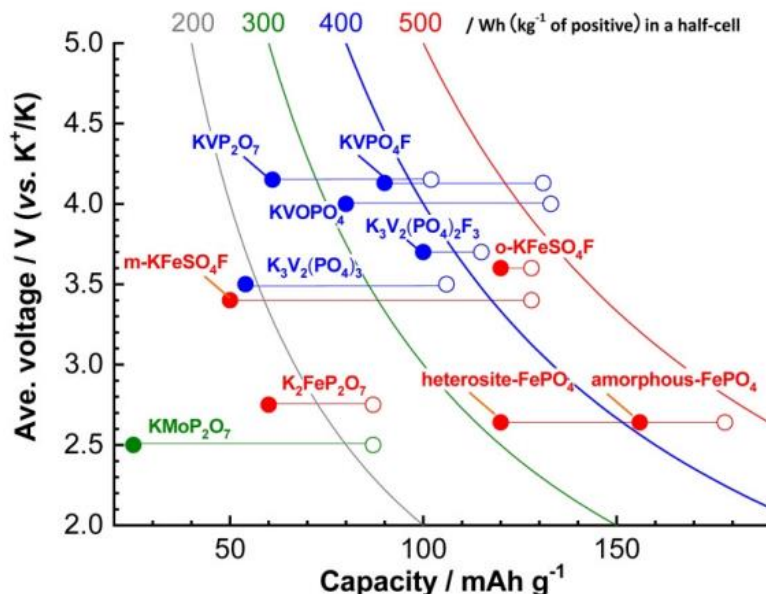


Figure 5. Average potential and energy density (Wh kg^{-1}) versus gravimetric capacity (mAh g^{-1}) of reported polyanionic compounds for KIBs. Average voltage and the energy density were calculated by assuming electrode active material mass in K-half cells. Filled circles and empty circles represent practical and theoretical capacity of the materials, respectively technologies [85].

Several structures can be distinguished for polyanionic compounds:

- The NASICONs with the general formula $\text{M}_x\text{T}_2(\text{XO}_4)_3$ are a class of polyanionic compounds that have gained significant attention as promising electrode materials for energy storage devices. The first realized compound of this family, $\text{NaZr}_2(\text{PO}_4)_3$, was synthesized in 1967 by Sljukic et al. [86] and its structure was subsequently elucidated by Hagman et al. [87]. The structure of $\text{NaZr}_2(\text{PO}_4)_3$ consists of a three-dimensional chain of PO_4 tetrahedra and ZrO_6 octahedra. As a result, the oxygen atoms in this compound belong to both the PO_4 and ZrO_6 groups, which gives rise to its unique properties. The working potential of NASICONs makes them ideal candidates for use as cathode or anode materials in energy storage devices. However, their molecular weight is very high, and the potential does not exceed 4 V for K-ion battery cathodes, which may limit their practical applications. Additionally, the electronic conductivity of these materials is low, on the order of $10^{-12} \text{ S cm}^{-1}$, which may impede their performance as electrodes [88,89]. To overcome this limitation, a carbon coating is often employed to improve electronic conductivity. This approach has shown promising results in enhancing the electrochemical performance of

NASICONs as energy storage materials. Further research is required to optimize the synthesis, characterization, and performance of NASICONs to advance their practical applications in energy storage devices.

- The olivine family of materials with the chemical formula $MTPO_4$ has gained significant attention in recent years due to their remarkable properties for energy storage applications, with lithium iron phosphate ($LiFePO_4$ or LFP) being the most widely used material in commercial Li-ion batteries due to its safety. This breakthrough was made possible thanks to the discovery of the intercalation/deintercalation properties of lithium ions in 1997 by Padhi and Goodenough [90]. The structure of these materials consists of a network of FeO_6 octahedra and PO_4 tetrahedra linked by vertices and edges. The octahedral sites create one-dimensional channels along the (001) direction, allowing for efficient diffusion and storage of ions [91]. However, in the case of K-ion batteries, ion diffusion in the material can destabilize the structure, limiting their effectiveness. One solution to this problem is the use of amorphous materials, which can avoid this issue. However, the working potential of the electrode is too low (<2.5 V) for these materials to be an attractive alternative in KIBs [92].
- Tavorite compounds with the formula $MT(XO_4)Y$ ($Y = O, OH, \text{ or } F$) have a unique structure composed of TO_4Y_2 octahedra that are linked together by Y- anions, forming infinite chains $[Y-TO_4-Y]_n$. These chains are further linked to the XO_4 poly-anionic groups in such a way that each oxygen atom belongs to a different octahedra. The specific structure of tavorite varies depending on the inductive effect of the Y anion and the XO_4 poly-anionic group. The surrounding environment of the transition metal has an impact on the potential of the redox couple involved. More specifically, a higher electronegativity of the anion results in a more ionic metal-ligand bond, leading to a reduction in the energy of the antibonding orbital and an increase in the potential difference of the $T^{x+}/T^{(x-1)+}$ redox couple compared to Li^+/Li . An example of this effect is observed in $LiFePO_4Y$, where the working potential of the Fe^{3+}/Fe^{2+} redox couple increases from 2.6 V ($LiFePO_4OH$) to 2.9 V ($LiFePO_4F$) versus Li^+/Li [93]. Tavorites based on fluorophosphate and vanadium are of particular interest for use in LIBs due to their high operating potential (~ 4.06) and high theoretical energy density, which is comparable to that of $LiFePO_4$.

The potassium equivalent, KVPO₄F, also has a high working potential (4.3 V), which was explored by the research group of S. Komaba [94] in 2017. This study also investigated KVOPO₄, which is a complete substitution of fluorine by oxygen. The specific capacity of KVPO₄F was found to be approximately 92 mAh g⁻¹, compared to 84 mAh g⁻¹ for KVOPO₄. Upon charging the material up to 5 V, the unit cell volume of KVPO₄F decreased by 5.8%, whereas KVOPO₄ showed a decrease of only 3.3%. Additionally, these materials exhibited good cycling performance at high current densities, with KVPO₄F and KVOPO₄ showing 90.7% and 93.9% capacity retention, respectively, over 25 cycles at 5 C.

Recently, R. Wernert et al. [95] created mixed anion phases KVPO₄F_{1-y}O_y with varying compositions ($y = 0, 0.25, 0.5, 0.75, 1$) and analyzed their crystallographic and electronic structures. Their experiments showed that the substitution of O²⁻ anions with F⁻ occurs as a solid solution throughout the composition domain. The vanadium ions exhibit complex and diverse local environments due to the different distortions in the cis and trans octahedra caused by the vanadyl bond. The presence of both ionic V^{III}-F bonds and covalent (V^{IV}=O)²⁺ vanadyl type entities significantly impacts the electrochemical properties and potassiation/depotassiation mechanisms upon cycling. Ultimately, these results indicate that KVPO₄F_{0.5}O_{0.5} is a promising positive electrode material with high capacity (105 mAh g⁻¹), working potential (4.2 V vs K⁺/K), sloping electrochemical curve, and low polarization, as shown in **figure 6a and b**.

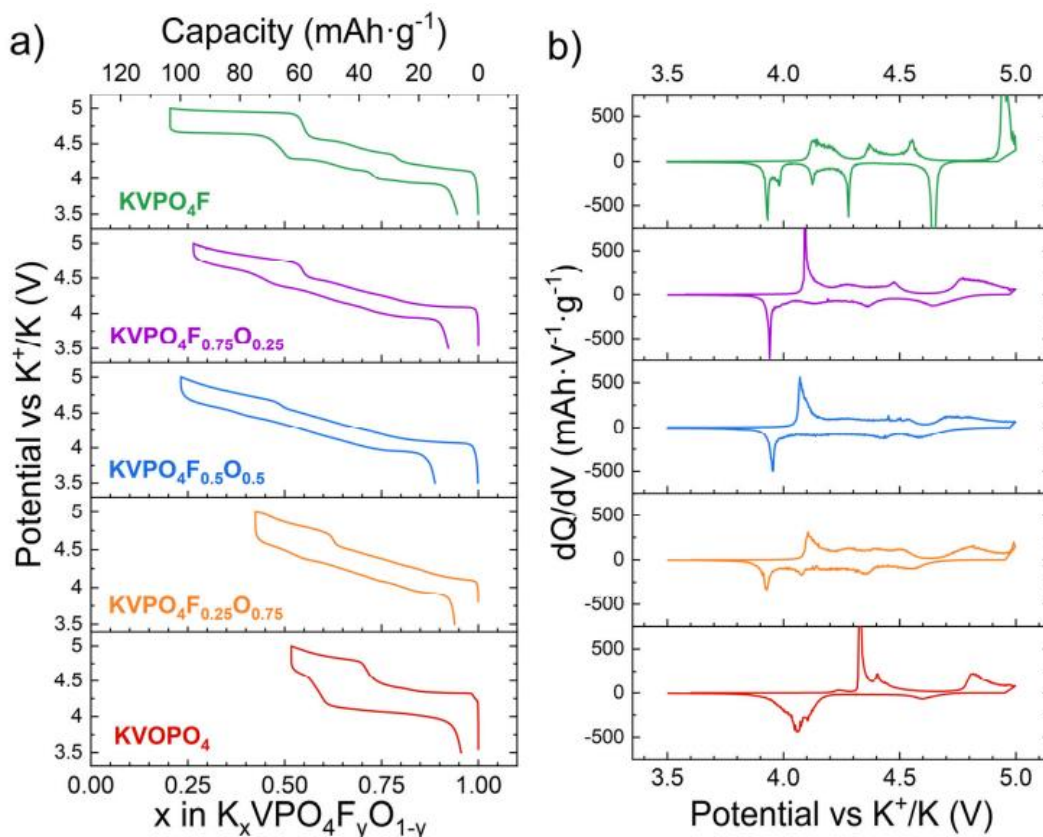


Figure 6. a) Galvanostatic charge/discharge profiles (2nd cycle) obtained for all materials in K metal half cells at C/20. b) Corresponding derivative curves [95].

In brief, regarding polyanionic materials, their use as cathode materials is advantageous due to their high working potential. However, optimizing synthesis methods, chemical composition, and morphology of active material particles is necessary to improve their performance. $KVPO_4F_{0.5}O_{0.5}$ material will be studied in detail in upcoming chapters.

VI. Non-aqueous electrolytes

VI.1 Overview

Figure 7 presents an overview of the electrolyte salts and solvents used in 223 studies on K-ion batteries published up to 2020. KPF_6 and KFSa were the most commonly used electrolyte salts, with KPF_6 -based electrolytes used in about 80% of the studies. KFSa-based electrolytes were mainly used for studying negative and positive electrode materials operating at potentials below 4 V vs. K^+/K due to their tendency to promote Al foil corrosion at high potentials. However, KFSa (also called KFSI) electrolytes were found to improve the Coulombic efficiency and cyclability of the negative electrode in some studies. Carbonate ester solvents such as ethylene carbonate

EC:DEC mixtures were the most commonly used solvents for both KPF_6 and KFSA electrolytes due to their high electrochemical stability and solubility of K salts. Ether solvents and ionic liquid electrolytes containing K^+ ions were also used in some studies. However, among 223 studies, there are only 9 on Full k-ion cells, showing the lack of reliable work on the practical use of this technology. The selection of electrolyte salts and solvents is discussed in detail in the following sub-section.

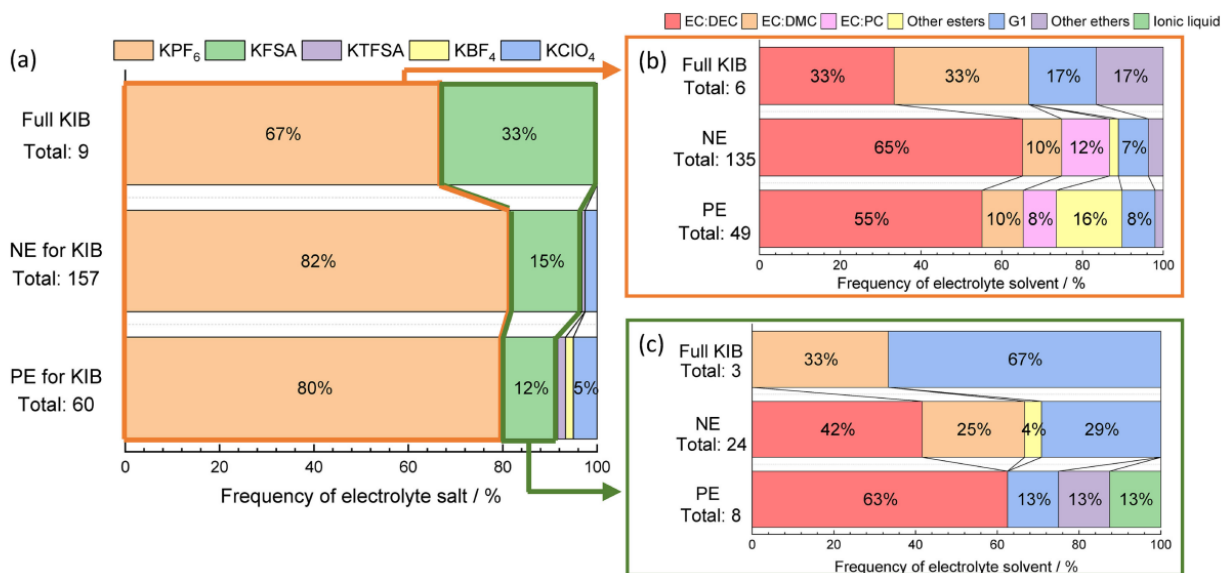


Figure 7. salts and solvents of the electrolytes used in 223 studies on full K-ion battery (KIB), half cell negative electrode (NE), and half cell positive electrodes (PE) for KIBs: a) using frequency of electrolyte salts of KPF_6 , $\text{KN}(\text{SO}_2\text{F})_2$ (KFSA), $\text{KN}(\text{SO}_2\text{CF}_3)_2$ (KTFSA), KBF_4 , and KClO_4 , b) using frequency of solvent types for KPF_6 -based and (c) KFSA -based electrolytes grouped by (ethylene carbonate) EC:DEC (diethyl carbonate), EC:DMC (dimethyl carbonate), EC:PC (propylene carbonate), other carbonate esters, monoglyme (G1), other ethers/glymes, and ionic liquids [96].

VI.2 Electrolyte development strategies

Compared to lighter alkali metal ions such as Li^+ and Na^+ , K^+ ions have weaker Lewis acidity and display weaker interactions with Lewis bases such as anions and solvents. As a result, the solubility of potassium electrolyte salts in non-aqueous solvents tends to be lower than that of equivalent Li and Na salts. The solubility of these salts can be described by the Born-Haber cycle, where the

Gibbs free energy of dissolution (ΔG) is equal to the difference between the solvation Gibbs energy and the lattice Gibbs energy. K ions show lower solvation energy than Li and Na ions for both aqueous and non-aqueous systems, resulting in their lower solubility [34]. However, K salts with a low lattice energy can be highly soluble, and the presence of a large counter anion is advantageous for high solubility. The size of the counter anion tends to increase in proportion with the size of the cation in sufficiently soluble salts. Indeed, typical electrolyte salts with large anion sizes are amide salts, such as KFSA. The solubility of KFSA in a PC solvent is >3 M due to weaker ionic association between the K^+ and FSA^- anion [69]. Moreover, K salts impact the charge-discharge performance, especially the coulombic efficiency (CE) of graphite electrodes. **Figure 8a and 8b** show the charge-discharge curves and CEs of K-graphite cells filled with 0.75 mol kg^{-1} $KPF_6/EC:DEC$ electrolyte and 1 mol kg^{-1} $KFSA/EC:DEC$ [96,97]. Both cells showed an initial discharge capacity of $>250 \text{ mAh g}^{-1}$, whereas the KFSA electrolyte cell had a lower initial irreversible capacity than the KPF_6 electrolyte cell. Furthermore, the KFSA electrolyte cell showed a higher Coulombic efficiency than the KPF_6 electrolyte cell in subsequent cycles. These results highlight that the type of electrolyte salt has a significant impact on the graphite electrode performance in KIBs. To overcome the Al corrosion issue observed with KFSA-based electrolytes, highly concentrated KFSA electrolytes and KFSA-containing ionic liquids (ILs) can be used (**Figure 8c**) [27,98–100]. On the other hand, most KPF_6 electrolytes exhibit low Coulombic efficiencies with graphite electrodes because of insufficient SEI passivation. This issue can be resolved by using a KPF_6 -KFSA binary salt electrolyte with an appropriate salt ratio. This electrolyte will realize both Al passivation and high Coulombic efficiency. Overall, the physical and transport properties of K electrolyte salts, such as solubility and conductivity, can be optimized by selecting appropriate counter anions and by using binary salt electrolytes with an appropriate salt ratio. These findings have implications for the design of KIBs, where the choice of electrolyte salt has a significant impact on the performance of the battery.

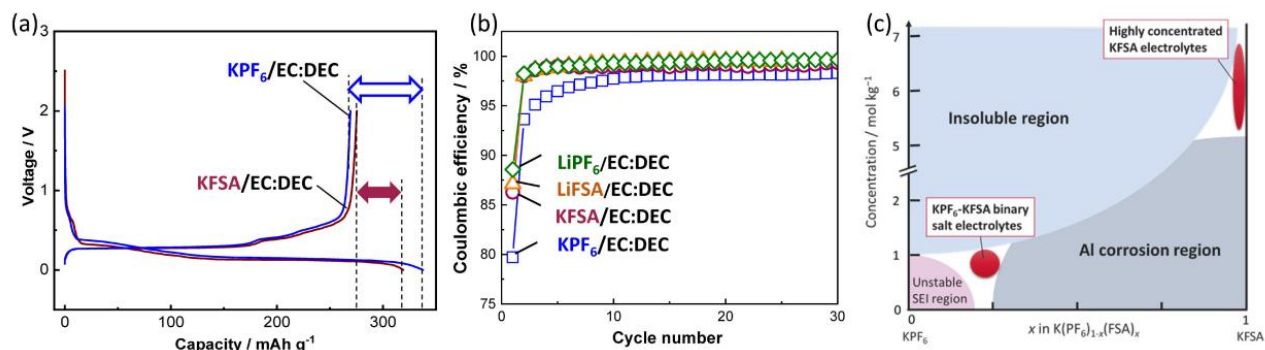


Figure 8. (a) 1st Charge-discharge profiles for graphite//K cells filled with KPF₆/EC:DEC and KFSA/EC:DEC electrolytes. (b) Coulombic efficiencies of graphite//Li and K//Li cells filled with MPF₆ and MFSA (M = Li and K) electrolytes. (c) Plot of binary KPF₆-KFSA molar ratio vs. concentration for K-ion electrolytes [96].

Various highly concentrated KFSA solutions are studied by Hosaka et al. [69] using common electrolyte solvents, such as monoglyme, PC, and γ -butyrolactone (GBL), and their ionic conductivities and viscosity were evaluated. The KFSA/monoglyme solution demonstrated higher ionic conductivity and lower viscosity than the other solutions, and its potential window was evaluated through cyclic voltammetry. The highly concentrated KFSA/monoglyme showed Al passivation and stable performance with the positive and negative electrodes of high-voltage KIBs. The graphite electrodes in 7 mol kg⁻¹ KFSA/monoglyme showed an improved rate performance compared to those in 0.8 mol dm⁻³ KPF₆/EC:DEC, despite the viscous nature of the electrolyte at higher concentrations. The SEI formed on graphite electrodes in the highly concentrated KFSA/monoglyme electrolyte showed suppressed surface layer thickening compared to that in the KPF₆/EC:DEC electrolyte [98]. The presence of SEI components derived only from FSA enables high Coulombic efficiency, indicating less deposition of organic species on the graphite surface. The use of highly concentrated KFSA/monoglyme electrolyte in graphite electrodes has demonstrated high CE and enabled Al passivation, but monoglyme decomposition on high-potential positive electrodes limits its application in high-voltage KIBs. To increase oxidation stability, long chain glymes such as diglyme and triglyme were utilized as they form stable complexes with K ions [101]. These highly concentrated KFSA/diglyme and KFSA/triglyme solutions showed higher oxidation stability than KFSA/monoglyme, and Raman spectroscopy revealed that more than 70% of glyme molecules were coordinated to K ions [98]. The highly concentrated solutions exhibited high anodic stability due to the higher stability of the solvate complexes of diglyme and triglyme [96]. The electrochemical performance of K//Mn-based PBA

cells filled with highly concentrated KFSA/diglyme and KFSA/triglyme solutions showed higher coulombic efficiency than that of KFSA/monoglyme electrolyte cells due to less electrolyte decomposition [98]. Although the aforementioned advantages, concentrated electrolytes are not recommended for practical applications from a gravimetric energy density point of view (the device energy density takes into consideration the entire battery component weights).

In 2020, S. Komaba group [27] introduced a KFSA-based ionic liquid (IL) composed of $K[N(SO_2F)]$ -[N-methyl-N-propylpyrrolidinium][$N(SO_2F)_2$], abbreviated as $K[FSA]$ -[C₃C₁pyrr][FSA].

This IL has a wide potential window and high ionic conductivity, making it a promising candidate for use in batteries. When used as an electrolyte at 1 mol dm⁻³, the IL allowed the graphite electrode to achieve a higher coulombic efficiency than a carbonate electrolyte. While both cells showed an irreversible capacity in the first cycle due to electrolyte decomposition and SEI formation, the IL electrolyte had a higher Coulombic efficiency of 65% compared to the EC:DEC electrolyte cell's 60%. The IL electrolyte also had an initial discharge capacity of 265 mAh g⁻¹, which is 95% of the theoretical capacity for KC₈. In subsequent cycles, the IL electrolyte maintained a higher Coulombic efficiency than the EC:DEC electrolyte cell. The chemical components of the SEI formed by the IL and conventional carbonate electrolyte were compared using Hard X-ray Photoelectron Spectroscopy (HAXPES) analysis. The IL electrolyte cell showed different peaks for -C=O and -C N- near 286-287 eV, indicating the deposition of [C₃C₁pyrr] cation and [FSA] anion decomposition products on the graphite electrode. In contrast, the EC:DEC electrolyte cell showed peaks for R-C(=O)-R, R-C(=O)-O-R, and RO-CO-O-R, indicating deposition of EC and DEC derived decomposition products. Thus, ionic liquids are considered as a good candidate to enhance electrochemical performance and to prevent thermal runaway, but they suffers from several drawback including high viscosity and cost [102].

Another promising improvement strategy was studied, which is the use of a binary on KPF₆-KFSA-based salt while varying the molar ratio to overcome the Al foil corrosion issue [97]. The performance of binary salt electrolytes with graphite electrodes in K-graphite cells filled with KFSA, $K(PF_6)_{0.75}(FSA)_{0.25}$, $K(PF_6)_{0.9}(FSA)_{0.1}$, and KPF₆ electrolytes was evaluated, and the results were compared. The cells exhibited high reversible capacities of over 270 mAh g⁻¹ (**figure 9a**),

with excellent capacity retention and negligible capacity fading upon cycling. However, there were significant differences in their irreversible capacities and CE. The KPF_6 electrolyte displayed a large irreversible capacity and a low Coulombic efficiency (80%) at the initial cycle, whereas the $\text{K}(\text{PF}_6)_{0.75}(\text{FSA})_{0.25}$ and $\text{K}(\text{PF}_6)_{0.9}(\text{FSA})_{0.1}$ cells showed lower irreversible capacities and, therefore, higher Coulombic efficiencies close to 90%. During subsequent cycles, the CEs of binary salts approached 99.5% (**figure 9b**), which was higher than that of the KPF_6 electrolyte (approximately 98%-99%). This improvement was attributed to the addition of KFSA, which seemed to enhance the SEI stability and minimize irreversible reactions, resulting in higher coulombic efficiency and improved rate performance. The HAXPES analysis of the graphite electrodes cycled in $\text{K}(\text{PF}_6)_{0.9}(\text{FSA})_{0.1}$ and KPF_6 electrolytes confirmed that the SEI of main components consisted of C, O, K, and F. However, the $\text{K}(\text{PF}_6)_{0.9}(\text{FSA})_{0.1}$ SEI showed a higher relative K content than KPF_6 , while the amounts of C, O, and F were lower. This result indicated a change in the SEI composition when FSA was added to the electrolyte. Additionally, the total atomic ratio of the sp² carbons on the graphite surface in the $\text{K}(\text{PF}_6)_{0.9}(\text{FSA})_{0.1}$ electrolyte decreased to 80% of that in the KPF_6 electrolyte, suggesting the formation of a thinner SEI layer on the graphite surface cycled in the KPF_6 -KFSA electrolyte.

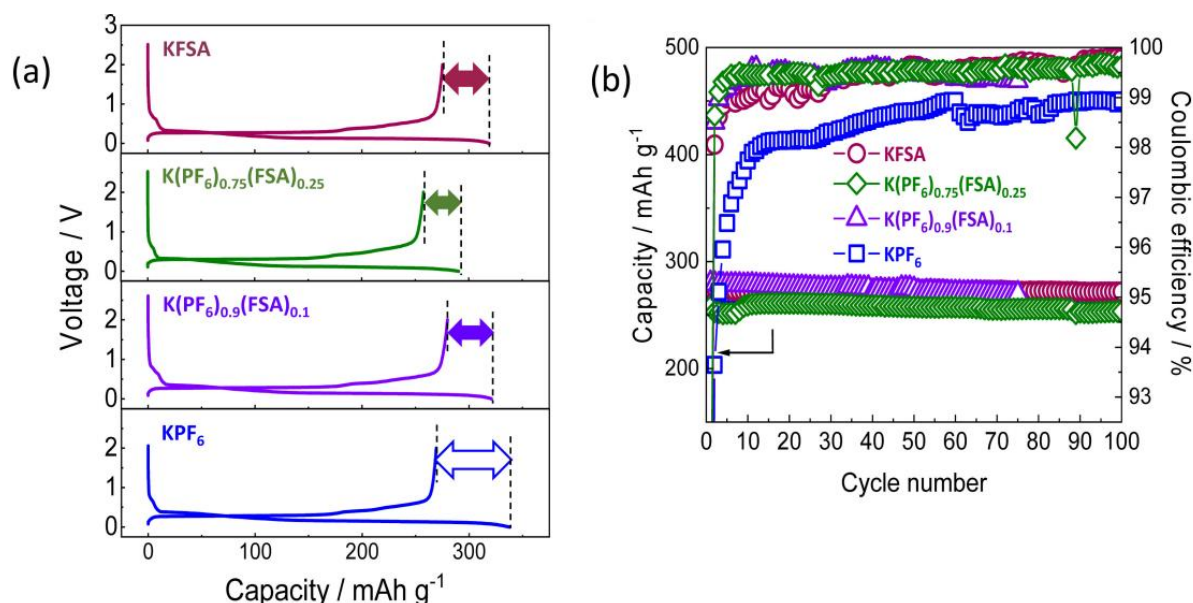


Figure 9. (a) First cycle charge-discharge curves of graphite electrodes in K cells containing 1.0 mol kg⁻¹ KFSa (red line), 1.0 mol kg⁻¹ K(PF₆)_{0.75}(FSA)_{0.25} (green line), 0.75 mol kg⁻¹ K(PF₆)_{0.9}(FSA)_{0.1} (purple line), or 0.75 mol kg⁻¹ KPF₆ (blue line) in EC:DEC. (b) Reversible capacities and CE over 100 cycles. Current density : 25 mA g⁻¹ upon cycling. Reproduced from [97].

As with lithium technology, there is the way of improvement via additives, which are added to improve battery performance by increasing reversible capacity and cycling performance. They act in particular by (i) limiting the dissolution of certain elements of the electrodes, (ii) influencing the solvation of the cation, the viscosity or wettability of the electrolyte, and thus the ionic conductivity and the transfer kinetics at the electrode/electrolyte interface, (iii) trapping traces of water or acid, (iv) preventing electrolyte degradation at the electrode surface, (v) improving the SEI growth during charge/discharge cycles, which is its most frequent function, (vi) limiting the overpotential and impedance [103–105]. In this case, the goal is for the additive to be preferentially reduced or oxidized and form a better quality (more homogeneous, more stable, more passivating) passivating layer than if the electrolyte had been reduced/oxidized. They therefore generally have a higher reduction potential than the solvents in the electrolyte, and vice versa in oxidation. Fluoroethylene carbonate (FEC) and vinylene carbonate (VC) are commonly used for Li-ion batteries, and in 2017, an initial study reported improved coulombic efficiency with the addition of FEC (2%) for a battery using a Prussian blue (KMnFe) analog at the cathode and 0.7M KPF₆/EC:DEC as the electrolyte [24]. However, the cell polarization also increased. Other studies have followed, but none have

been able to show a clear improvement without a trade-off [82]. One study comparing different additives states that the addition of FEC or ethylene sulfite (ES) has no positive effect on polarization during potassium metal plating/stripping [66,106]. However, another study suggests that a beneficial effect of FEC would come from a good passivation of the potassium metal surface [107]. Thus, the real impact (beneficial or not) of the addition of an additive has not been demonstrated with certainty, either in the case of potassium metal in the half cell or in the full cell case.

VII. Solid electrolyte interphase and cross-talk

VII.1 Overview

Since the 1970s, the SEI layer has been considered a crucial component of non-aqueous secondary batteries [108]. Indeed, during cycling, different reactions can occur at the electrode surface that consume electrons and M^+ cations. These reactions can cause the degradation of the electrolyte (salt and/or solvent), which is evident from the electrochemical curves that show significant irreversible capacity during the first few cycles. As a result, insoluble degradation products lead to a layer on the electrode surface called SEI for the negative electrodes, and CEI (cathode electrolyte interphase) or SPI (solid permeable interface) for the positive electrodes [109,110]. Ideally, this SEI should form quickly, be stable, and passivating to reduce electron transport while allowing M^+ cations to pass during cycling process. This, in turn, slows down the electrolyte degradation. However, it is worth noting that not all parasitic reactions that consume electrons are related to the formation or repair of SEI. Some reactions are completely undesirable and result in a capacity fade and power without any advantage [20,111]. The degradation of the electrolyte, implying SEI growth, can occur during storage (cell left at rest) or during cycling due to chemical reactivity between the electrolyte and electrode components [112]. The solvent instability in operating potential window of the battery is the reason behind this degradation. In other words, the redox potential of the active electrode materials should be within the electrochemical potential window defined by the energy limits between the LUMO (Lowest Unoccupied Molecular Orbital) and HOMO (Highest Occupied Molecular Orbital) of the electrolyte, as illustrated in **figure 10a**.

If the electrolyte LUMO energy is lower than the electrochemical potential of the negative electrode, electron transfer from the negative electrode to the LUMO occurs, resulting in the spontaneous reduction of the electrolyte. It is interesting to note that the LUMO of carbonate-based

electrolytes is higher than the Fermi level of metallic electrodes, graphite, or oxides, all of which have potentials lower than 1 V versus M^+/M ($M=Li, Na, \text{ or } K$). Therefore, the SEI is known to form spontaneously on these materials when in contact with carbonate-type electrolytes [20,113,114]. On the other hand, if the electrolyte HOMO energy is higher than the electrochemical potential of the positive electrode, electron transfer from the HOMO to the positive electrode occurs, leading to the spontaneous oxidation of the electrolyte. Although the term "SEI" strictly applies to the electrode/electrolyte interface, regardless of the electrode, the term "CEI" or "SPI" has been introduced to distinguish the cathode/electrolyte interface (**Figure 10b**) [109,110,115].

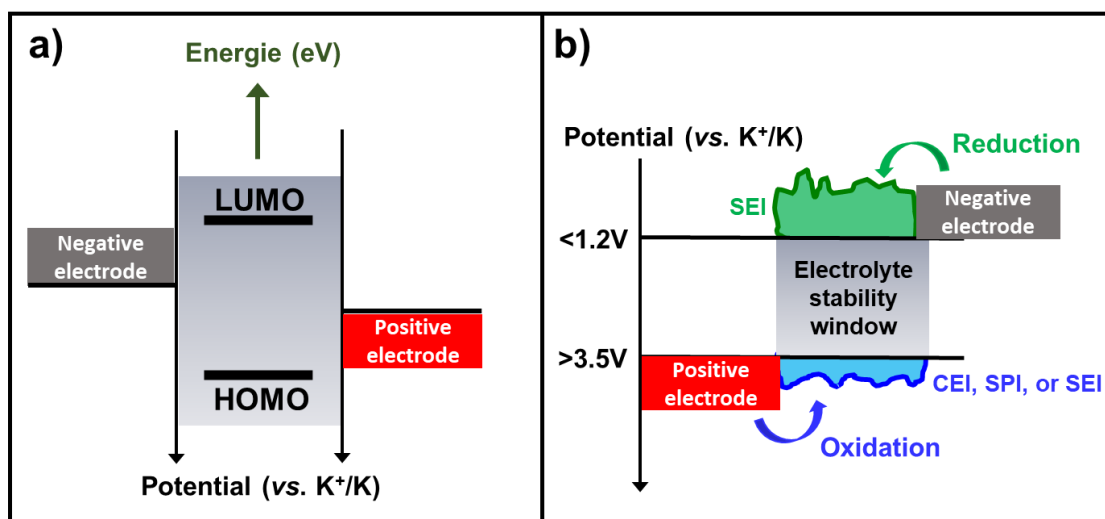


Figure 10. Thermodynamics of electrolyte reduction and oxidation illustrating a) Energy states of the electrodes and electrolyte, leading to the formation of the SEI and cathode electrolyte interphase (inspired from ref [116]) b) SEI formation in K-ion batteries.

Although DFT calculations can determine the energies of the HOMO and LUMO orbitals of the solvent, it has also been shown that the formation of cation-solvent complexes leads to a decrease in the energies of the HOMO and LUMO orbitals [117,118]. As a result, the electrolyte's resistance to oxidation increases, but its resistance to reduction decreases. Similarly, DFT calculations have been used to compare the energy of the LUMO orbital and the energy of the same orbital after the addition of an electron (HOMO) [118]. This electron comes from the metal electrode (half cell configuration) during discharge. A small energy difference between the HOMO and the LUMO indicates some similarity between the orbitals, facilitating electron transfer and thus less stability of the solvent. Based on these results, it appears that DME is less likely to degrade, while EC, the

most commonly used solvent for KIBs, is more likely to degrade. In addition to the formation of cation-solvent complexes, other catalytic phenomena, or adsorption phenomena on the surface of active materials during the desolvation step can also modify the energy of the HOMO and LUMO orbitals [20,119,120]. Among the solvents used, Li et al. [65] demonstrated that the use of a linear alkyl carbonate without a co-solvent is not suitable for stabilizing the electrolyte. Their study, based on K//K symmetric cells using KPF_6 salt, shows that only cells containing EC (solvent or co-solvent) can maintain "plating/stripping" cycles. It should be noted that the use of KFSI still allows "plating/stripping" cycles with only a linear alkyl carbonate as solvent, but the polarizations vary and are much higher compared to those obtained with EC.

Their hypothesis regarding such a difference between KFSI and KPF_6 is based on a complementary DFT study, showing that the FSI^- anion is physically closer to K^+ than the PF_6^- anion: this spatial configuration will, on one hand, decrease the electronegativity of solvents, and on the other hand, keep the solvent molecules away from the cation, thus preventing solvent decomposition. The FSI^- anion is therefore preferentially reduced compared to the PF_6^- anion. Additionally, in the case of an EC:DEC mixture, the study reports that the cation is preferentially surrounded by EC molecules; the cation would thus be in an environment that is globally like that of a cation in EC only, which justifies the similarities between the plating/stripping results when EC and EC:DEC solvents are used. It should also be noted that the model used for these studies justifies the better solubility of KFSI: the FSI^- anion being close to the cation, it plays a solvent role. This model is the most elaborate for K-ion batteries and is part of the few theoretical studies that take into consideration the anion impact on the stability of electrolyte. Generally, models are based only on the stability of the molecules' reduction or even on the stability of the cation-solvent complexes' reduction. However, the study of more complex systems is essential for understanding interfacial phenomena, the impact of the anion on electrochemical performance and the composition and structure of the SEI having been demonstrated for years for all M-ion technologies [65,111]. Furthermore, Caracciolo et al. [30] pointed out the higher reactivity of K metal and its impact on the SEI growth. Therefore, to ensure accurate SEI studies, it is necessary to work with full cell configurations to reduce the contamination caused by K metal. In chapters 3 and 4, we will investigate in detail the influence of various full cell parameters on SEI formation.

VII.2 SEI models

The ideal SEI should effectively passivate and cover the electrode surface to minimize any reaction with the electrolyte, preventing rapid capacity loss. Additionally, it should remain stable without continuous formation to avoid any further capacity loss. The SEI should also possess some flexibility to accommodate any possible volume expansion of the electrode. Originally, the SEI was regarded as an electronic insulating that selectively filtered out solvent molecules, anions, or other electrolyte compounds that could react with the anode while allowing the conduction of lithium, sodium, and potassium ions via the presence of alkyl carbonates ROCO_2^- [121,122]. Inorganic and organic compounds are distinguished as they play different but complementary roles in SEI formation. The organic component of the SEI is impregnated by the electrolyte, and solvent molecules can potentially degrade the electrode. Therefore, the inorganic portion of the SEI must prevent any contact between the electrolyte and the electrode to ensure the passivation of the electrode. In 1979, Peled [123] initiated the study of negative electrode/electrolyte interfaces and developed the concept of SEI, based on the alkali and alkaline earth metal electrode. Since then, the concept has been generalized to all negative and positive electrodes, and several models have been proposed, divided into two main types.

- The various models proposed for carbonaceous materials have shed light on the nature and formation of the SEI, a crucial component that determines the electrochemical performance and safety of metal-ion batteries. Dahn's [124] model, which suggests that the SEI is a two-dimensional passivating film resulting from surface reactions, has been foundational in this field. However, Besenhard's [125] and Aurbach's [126] models have expanded on this concept by proposing that the SEI is a 3-dimensional passivating film generated through a combination of solvent co-intercalation and surface reactions. Besenhard's model postulates that the SEI is formed through co-intercalation of the solvent between the graphene planes, resulting in the formation of graphite intercalation compounds. In contrast, Aurbach's model proposes that the SEI is also the result of surface reactions, in addition the co-intercalation of the solvent between the graphene layers. Both models provide valuable insights into the mechanisms underlying SEI formation and highlight the importance of the interplay between solvent and surface reactions.

- Other generic models, including the mosaic model of Peled [123] and the model of Ein-Eli [127], also propose that the SEI is a 3-dimensional passivating film generated by surface reactions. The mosaic model suggests that the SEI is composed of micro-regions of different nature, while the model of Ein-Eli suggests that the SEI functions as a double layer capacitor, with some components of the electrolyte adhering to the negative electrode via coulombic interactions.

Although these models differ in significant ways, it can be generally stated that the Solid Electrolyte Interphase is a three-dimensional film that forms on the surface of the electrode, comprising products of solvent and salt degradation. Ideally, the SEI should present high electronic resistivity and good ionic conductivity. However, achieving a high-performing SEI is extremely challenging because passivating compounds poorly conduct M^+ ions (lithium, sodium, or potassium) while ionic conductive compounds are less effective at passivating [128–131]. Therefore, it is important to avoid using exclusively organic layers and instead use a composite, mainly inorganic layer. However, the complex composition of the SEI is controversial in the literature, especially for potassium-ion batteries which have been studied for a shorter period, especially in half cell configurations. So, there is a lack of comprehensive research in the existing literature regarding full cell SEI studies, which is essential to obtain dependable insights into SEI and effectively restrict the reactivity of potassium metal. Therefore, additional research is necessary to fill this gap and improve our understanding of SEI behavior in KIBs.

VII.2 Cross-talk in M-ion batteries

The previous two sub-sections were dedicated to explaining the SEI formation. However, studies of the electrode/electrolyte interface do not take into account the influence of metallic potassium. In fact, a phenomenon of cross-contamination (so-called "cross-talk") has been reported several times in the case of Li-ion cells [132–134]. Chemical or electrochemical side reactions at one electrode of a battery produce compounds that react chemically or electrochemically at the other electrode, a process known as electrode cross-talk. cross-talk understanding is essential for cell longevity for three reasons. First, any side effect leads to capacity fade. In advanced batteries, capacity fade is caused by a combination of cyclable M^+ loss, active material loss, and increased impedance. Numerous cell cycling analyses and post-mortem studies have concluded that cell failure is dominated by loss of cyclable Li (LCL) at the anode in both mature and emerging

chemistries [132,135]. Side reactions disrupt the stoichiometric balance between the electrodes, resulting in incomplete charge and discharge. Because LCL is caused by an imbalance between electrodes, it can only be noticed in full cells with two intercalation electrodes. Although many side reactions can cause LCL, the continuous growth of the SEI on the anode is the most common [136–138]. Second, cross-talk has magnified the effects on coulombic efficiency. This metric is still the most accurate single predictor of battery lifetime. CE, when measured precisely, can be used to screen different designs in weeks rather than months [139–141]. However, because it cannot distinguish between competing reactions, it does not scale uniformly with lifetime. Several groups have suggested that the electrolyte can decompose into soluble products that can shuttle between electrodes reversibly [142–145]. This redox shuttles would reduce CE without affecting lifetime. Finally, the physical and chemical nuances of cross-talk significantly increase the complexity of battery reaction networks, necessitating a highly empirical theory for determining cell lifetime. Therefore, cross-talk reactions are naturally dependent on both the anode and cathode materials, data-driven lifetime models must be qualified and validated separately for each electrode combination. Although electrochemical models can reduce the number of experiments required to predict battery lifespan [146,147]. The oxidation of the electrolyte is more significant when the potential is high, which promotes interactions between the cathode and the anode at high potential, making it challenging for the development of K-ion batteries. Previous studies have already shown a main issue for KIBs, indicating an interaction between the metal electrode and the working electrode even when no current was applied [112].

Conclusions

The abundance of potassium, its high ionic conductivity, as well as the low standard potential of the K^+/K couple which favors the development of high-power and -energy density batteries, has motivated research KIBs. Through the various types of cathode and anode materials, it has been observed that research on electrode materials has been inspired by equivalent Li-ion and Na-ion systems. The large size of the K^+ ion is particularly well-suited to polyanionic materials (positive electrode), but is more problematic in the case of carbonaceous electrodes commonly used as negative electrodes (i.e., graphite suffers from its high volume expansion ~60%). It has appeared essential to carry out this study on graphite formulation to better volume expansion management and good electrochemical performance, so a part of chapter 2 is devoted to this study.

It has been observed that making full cells in KIBs is essential to overcome the potassium metal reactivity. Furthermore, the surface of the electrodes can be contaminated by degradation products of the electrolyte resulting from the quasi-systematic use of potassium metal as a negative electrode in half cells (cross-talk contamination impact). To provide knowledge on this subject, the way toward reliable full cells in KIBs is the subject of chapter 3.

It has been noticed that varying different full cell parameters and their impact on SEI growth is well documented for Li-ion batteries but still missing in K-ion literature, so chapter 4 is dedicated to these investigations.

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Chapter 2

Negative and positive electrodes for KIBs

Introduction

Carbon-based materials have attracted significant attention as promising electrode materials for potassium-ion batteries due to their high theoretical capacity, low cost, and environmental friendliness. Graphite, hard carbon, and soft carbon are the most investigated among various types of carbon-based materials. In this chapter, we will study the optimization of electrode formulation for graphite, the physical-chemical and electrochemical performance of hard carbons synthesized at different temperatures, and the selected positive materials for power (i.e., Fluorophosphate) and energy (i.e., Prussian blue analogue) applications.

Graphite has been widely used as an anode material for lithium-ion batteries due to its high capacity and stable cycling performance. However, graphite suffers from several drawbacks when used as an anode material for potassium-ion batteries, including high-volume expansion and low-rate performance [1]. To address this last issue, the graphite electrode formulation was optimized by managing the ionic and electronic percolating networks and introducing binary binders to enhance its electrochemical performance. The results relating to this part are described in the next section of this chapter and are presented in the form of a publication published in the periodical “Electrochimica Acta” in 2022.

Hard carbon is another type of carbon-based material that has been extensively investigated as an anode material for potassium-ion batteries. The physical-chemical properties of hard carbons, such as their close porosity, active surface area, specific surface area, defect sites, oxygen-based functional groups, and crystallinity play a critical role in determining their electrochemical performance. Therefore, the correlation between the physical-chemical properties and electrochemical performance was investigated. So, in the second section of this chapter, we will compare the electrochemical performance of graphite and hard carbons (using another composition). This study was conducted within the framework of the TROPIC ANR project in collaboration with ICGM and IS2M (my contribution involved conducting electrochemical tests and their subsequent discussions).

However, to complete the missing pieces of the puzzle, we have to identify candidates for positive electrodes that offer high capacity, high average potential, as well as robust chemical and electrochemical stability. As mentioned in the first chapter, the leading candidates exhibiting superior electrochemical performance and scalability are $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ and PBAs. In the third

section of this chapter, we will delve into the electrochemical performance of $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ and exploring the impact of the coating process, electrode composition, and electrolyte on the electrochemical properties of PBA .

Thus, by understanding the advantages and limitations of each type of negative and positive materials, we can design and develop high-performance electrode materials for potassium-ion batteries.

I. Published paper: Optimized electrode formulation for enhanced performance of graphite in K-ion batteries.

Correction notice : It has come to our attention that there was an error in reporting the composition of the materials used. The correct optimal composition is 85/5/8/2 wt.% of graphite/CB/CMC/SBR instead of the indicated 95/5/8/2 wt.%.



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Optimized electrode formulation for enhanced performance of graphite in K-ion batteries

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volume expansion

ABSTRACT

Potassium ion batteries (KIBs) are emerging notably due to the reversible K^+ intercalation into graphite. So far, optimization of graphite electrode formulation remains, however, to be investigated. This work thus proposes to optimize ionic (porosity) and electronic percolation networks as well as mechanical properties of graphite electrodes for KIBs. To do so, carbon black amount (CB) and electrode calendaring is first adjusted. Then carboxylated styrene butadiene rubber (SBR) is used, with different amount and functional groups contents, as co-binder with carboxymethyl cellulose (CMC—Na). The best electrodes, made of 95/5/8/2 wt.% of graphite (SLP30)/CB(C65)/CMC—Na/SBR (Synthomer) with 2.4 mg cm^{-2} loading and 35% porosity, deliver $\sim 250 \text{ mAh g}^{-1}$ during depotassiation at 5C with only $\sim 0.3 \text{ V}$ polarization and 205 mAh g^{-1} during potassiation at 1C (3-electrodes configuration). In addition, no capacity loss is observed after 55 cycles at C/5 potassiation/1C depotassiation due to a low electrode volume expansion (11%) compared to 24% without SBR after only 35 cycles. These results highlight that appropriate SBR significantly improves the electrode structure/cohesion/elasticity (i.e. volume expansion management), leading to better power performance and capacity retention of graphite electrodes for KIBs. Finally, considering that further improvements are expected by tuning electrolyte formulation, this work will benefit to the development of high energy KIBs.

1. Introduction

Potassium-ion batteries (KIBs) are considered as an attractive technology due to the K abundance (2.1 wt.% of the Earth's crust) [1] and low standard redox potential of K^+/K (-2.93 V vs. SHE), which is close to that of Li^+/Li (-3.04 V vs. SHE). In addition, K^+ presents the smallest Stokes' radius ($3.6 \text{ \AA}$) in propylene carbonate compared to Li^+ ($4.8 \text{ \AA}$) and Na^+ ($4.6 \text{ \AA}$) so that electrolytes with higher ionic conductivity are expected in KIBs (i.e. high power cells) [2]. More importantly, similarly to Li^+ and contrary to Na^+ , the electrochemical intercalation of K^+ into graphite interlayers was experimentally demonstrated by Komaba et al. [3], thus allowing its use as active material for negative electrode in KIBs. However, compared with the size of Li^+ ($0.76 \text{ \AA}$), the oversize of K^+ ($1.38 \text{ \AA}$) leads to a much higher volume expansion (60% compared to 13% with Li^+) so that during the potassiation/depotassiation processes, both graphite structure damages and electrode pulverization/delamination may occur [4]. In the latter case, it is thus of great interest to evaluate and control the volume expansion of the electrode upon

cycling.

Regarding the formation of the so-called K-graphite intercalation compounds (K-GICs), studies based on both theoretical and experimental approaches have proposed different mechanisms. Based on *ex situ* X-ray diffraction (XRD), the following mechanism was proposed: $C \rightarrow KC_{36}$ (stage III at $0.3\text{--}0.2 \text{ V}$) $\rightarrow KC_{24}$ (stage II at $0.2\text{--}0.15 \text{ V}$) $\rightarrow KC_8$ (stage I at $0.15\text{--}0.01 \text{ V}$). Then, depotassiation KC_8 leads back to graphite while in following cycles, XRD showed structural damage of the graphite explained by the high-volume expansion (60%) [5]. Based on density-functional theory (DFT) calculations and *ex situ* XRD and Raman, a slightly different mechanism was proposed: $C \rightarrow KC_{24}$ (stage III, between 0.35 and 0.18 V) $\rightarrow KC_{16}$ (stage II at 0.14 V) $\rightarrow KC_8$ (stage I at 0.01 V) [22]. Based on *in situ* XRD and Raman as well as DFT, a mechanism starting from dilute stage was proposed: KC_{60} (stage V) $\rightarrow KC_{48}$ (stage IV) $\rightarrow KC_{36}$ (stage III) $\rightarrow KC_{24}/KC_{16}$ (stage II) $\rightarrow KC_8$ (stage I) [6]. Overall, full potassiation of graphite leads to KC_8 (60% volume expansion) corresponding to a 279 mAh g^{-1} theoretical capacity. However, conventional graphite delivers about 65% of its capacity

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between 0.25 V and 0.01 V so that power performance could be limited if the K^+ mobility is low during graphite potassiation, which still need to be confirmed. So far, power performance of graphite in half-cells are significantly altered by the large K metal plating/stripping polarization [7,32]. For instance, this polarization is about 0.1 V higher with 0.8 M KFSI EC:DEC compared to 0.8 M KPF₆ EC:DEC, which explains the lower rate performance generally observed with KFSI [8,9].

It is thus of high interest to better evaluate and control the parameters that govern the energy and power performance of graphite-based electrodes in KIBs. So far, most of the studies focused on the electrolyte formulation (solvents and salt(s) ratios) to form a stable/passivating solid electrolyte interphase (SEI) without hindering the power performance [10–15]. However, half-cells results should be taken with caution as the highly reactive K metal was proved to significantly affect electrochemical performance (K metal polarization) [3,7,8,32] as well as the SEI formation (cross talking mechanism) [16,17,33]. Considering the electrode materials and formulation, i.e. the graphite structure, the conductive additives, binders, active material loading and calendaring pressure, only a limited number of studies have been performed. Indeed, studies about carbon additives and calendaring pressure effects are still missing in the literature while they are expected to critically impact both ionic and electronic percolation networks (power performance), similarly to Li-ion batteries (LIBs) [18]. In particular, the use of carbon black with nanoscale primary particles size (compared to microscale for graphite) is mandatory to form an efficient/durable percolating electronic network. Calendaring will also affect the cohesion and adhesion between graphite particles and binder(s) as well as with the current collector, which are critical parameters regarding the graphite volume expansion issue [19]. Regarding the graphite structure (interlayer distance and defects), polynanocrystalline graphite, made by chemical vapor deposition on a nanoporous graphenic carbon matrix, was used to increase the capacity retention thanks to the presence of disorder at nanoscales but strict order at atomic scales [20]. Expanded graphite with enlarged interlayer spaces have also been proposed to boost the potassium ion diffusion with a capacity up to $\sim 175 \text{ mAh g}^{-1}$ at 200 mA g^{-1} rate (for 2 $\text{mg}_{\text{graphite}} \text{ cm}^{-2}$ electrode) compared to $\sim 40 \text{ mAh g}^{-1}$ for a conventional graphite [21]. Ball milling during electrode slurry preparation was also reported to increase capacity retention due to gentle graphene layers exfoliation and defects formation [22]. The aim of these graphite structure modification is to mitigate graphite structural damages induced by the volume expansion. A study showed, however, that graphite electrodes (with, however, unknown graphite supplier, type and loading) can cycle more than 2000 times as C/3 with nearly no capacity loss while the same graphite electrodes with a 28.56 mg cm^{-2} loading also showed no capacity loss after 60 cycles at C/14 [13]. Despite missing information about the graphite electrodes, these results suggest that both structural damages and/or electrode pulverization induced by the volume expansion may not be an issue. Regarding the binders (amount and type), their roles are to obtain good mechanical properties (especially for the electrode processing) as well as to maintain the electrode cohesion / limit the electrode volume expansion upon cycling. So far, polyvinylidene fluoride (PVDF), sodium polyacrylate (sodium polyacrylic acid, PAA-Na) and sodium carboxymethylcellulose (CMC-Na) have been tested in graphite electrode for KIBs. Among them, PAA-Na and CMC-Na showed significant increase of the coulombic efficiency (CE) due to a pre-formed SEI induced by the binders while PAA-Na led to higher capacity retention due its lower swelling property [3,23]. Another study also pointed out that generally, binder amount higher than 4 wt.% (literature data), for instance 8 wt.% (their data with a 1:1 wt ratio of CMC-Na/PAA), significantly increases the capacity retention of graphite electrodes for KIBs [24].

However, styrene-butadiene rubber (SBR, especially carboxylated ones), frequently used as high elasticity binder with good mechanical properties for graphite electrodes in LIBs [5,25,26,34], has never been tested in KIBs so far. Additionally, the combination of SBR with CMC is known to produce more homogeneous and less microporous graphite

electrodes [27] due to an increase of the graphite surface charge, as established by electrokinetic measurements [28]. In addition, both SBR and CMC are water-soluble binders with low cost and pollution as well as fast-drying kinetics in electrode fabrication [29]. Overall, the literature thus highlights that electrode formulation (conductive additive and binder(s) amounts as well as graphite loading and calendaring pressure...) is the key towards high performance graphite electrodes for KIBs. However, the concomitant study of these electrode formulation parameters is still missing so far, and especially for KIBs.

To fill this gap, this work evaluates the effects of the carbon black amount together with the electrode calendaring on the electrochemical performance of graphite electrodes with two different loadings for KIBs. Subsequently, the impact of SBR with different amount and functional groups contents as co-binder with CMC—Na are also investigated. At each step, a focus is performed on the CE, capacity retention and more importantly on polarization / rate capability. Overall, the aim of this study is to get high-capacity Gr/K cells with enhanced cycling performance in order to develop high energy KIBs in the future.

2. Experimental

2.1. Materials and electrodes preparation

Graphite SLP30 (Gr, from TIMCAL), carbon black Super C65 (CB, from MTI) and CMC—Na (noted CMC thereafter, Sigma-Aldrich, Mw $\sim 250,000$) were used as active material, conductive additive, and binder, respectively. Two carboxylated SBR binders (noted SBR, kindly provided by nanografi and SBR(2), kindly provided by Synthomer) were also used as co-binders with CMC (see Table S1 for their physical and chemical properties). Electrode slurries were prepared by mixing different amounts of materials (Fig. 1) in distilled water using mechanical planetary ball milling (PULVERISETTE 7) at 500 rpm for 1 h. Slurries were coated on an aluminum current collector foil with a 15 nm thickness using the doctor blade method with a blade thickness of 125 or 200 μm for the 2.4 mg cm^{-2} and 4 mg cm^{-2} graphite loading, respectively. Films were then dried at room temperature for 1 night. Electrodes were then cut out with a 12.7 mm diameter using a precision punch and dried again in a vacuum oven at 80 °C for 12 h.

The strategy to optimize the Gr electrodes formulation is presented in Fig. 1. In the first step, the CMC amount was kept constant (10 wt.%)

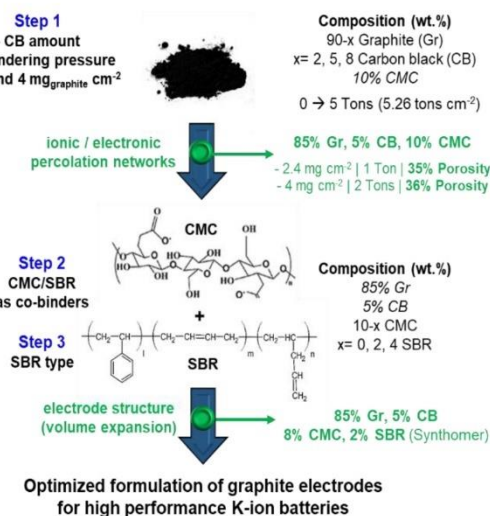


Fig. 1. Schematic representation of the approach followed in this work to optimize the graphite electrodes for KIBs. For each step, the goal and optimized results obtained in this study are highlighted in green.

while the Gr/CB amounts (in wt.%) were varied as follow: 88/2, 85/5 and 82/8. For each composition, two loadings (2.4 and $4 \text{ mg}_{\text{graphite}} \text{ cm}^{-2}$) were prepared with different uniaxial calendaring loads (1, 2, 3, 4 and 5 tons, i.e. 1.05, 2.10, 3.18, 4.21 and 5.26 tons cm^{-2} , respectively) in order to obtain optimal ionic(porosity)/electronic percolation networks. In the second step, the effect of CMC/SBR as co-binders on the electrode structure and mechanical properties was evaluated (Fig. 1). To do so, the optimal Gr/CB contents, graphite loading, and calendaring pressure were selected and only the CMC/SBR contents were varied as follow: 10/0, 8/2, 6/4 (in wt.%). In a third step, another SBR (Synthomer one) was used with the previously optimized CMC/SBR contents in order to evaluate the impact of the SBR nature (i.e. functional groups contents and despite that such information is not available for this SBR, Table S1) on the electrochemical performance. Finally, to evaluate the impact of two SBR on the electrode volume expansion, electrodes thickness was measured before and after cycling using a micrometer (Mitutoyo with an accuracy of $\pm 1 \mu\text{m}$).

2.2. Electrochemical experiments

Electrochemical tests were performed by assembling CR2032 coin half-cells as follow: graphite (Gr) electrodes, microporous trilayer (PP/PE/PP, from Celgard) and glass fiber (GF/D, from Whatman) membranes as separator, K metal (Alfa Aesar, 99.95%) as reference with 0.8 M KPF₆ (Sigma-Aldrich, $\geq 99\%$) EC:DEC (ethylene carbonate, Sigma-Aldrich, $\geq 99\%$ and diethyl carbonate, Sigma-Aldrich, $\geq 99\%$) 1:1 by volume as electrolyte. All tests were conducted on two pair cells (for reproducibility) using a VMP 3 multichannel system (BioLogic, France) in a 20°C temperature-controlled room.

Rate performance was evaluated using a standard galvanostatic cycling procedure as follow: between 2 and 0.01 V, 3 formation cycles (or 5 for the CMC/SBR study) at C/20, 5 cycles at C/10, C/5, C/2, C, 2C, 5C, 10C followed by 5 cycles at C/10 and C/20 to check for possible capacity loss. Importantly, for cycles performed between C/2 and 10C, potassiation was kept at C/5 to mitigate the impact of the K metal polarization (Fig. S1). In addition, an alternative test was used to evaluate only the depotassiation rate capability as follow: between 2 and 0.01 V, 4 formation cycles at C/20, potassiation at C/20 followed by successive depotassiation (at xC from $x = 5, 1, 0.5, 0.2, 0.1, 0.05$, i.e. from 5C to C/20) and 30 min relaxation steps.

A similar procedure was used to evaluate the potassiation rate capability, using 3-electrodes Swagelok T-cells as follow: between 2 and 0.01 V, 4 formation cycles at C/20, followed by successive potassiation (at xC from $x = 5, 2, 1, 0.2, 0.1, 0.05$, i.e. from 5C to C/20) and 30 min relaxation steps. In this experiment, the cells were in PFA material, K metal was used as reference and counter electrodes, the electrolyte was 0.8 M KPF₆ EC:DEC and GF/D membrane was used as separator in contact with K metal while and additional PP/PE/PP membrane was added in contact with the graphite electrode.

Capacity retention was evaluated as follow: between 2 and 0.01 V, 3 formation cycles (or 5 for the CMC/SBR study) at C/20 followed by about 50 cycles at C/5 during potassiation and C during depotassiation.

Galvanostatic intermittent titration technique (GITT) was also used to discriminate the graphite polarization from the K metal one in the case of the CMC/SBR study as follow: during the first potassiation down to 0.01 V, successive 30 min constant current (-20 mA/g , i.e. 0.025 K^+ intercalation) and 8 h relaxation steps were applied.

3. Results and discussion

3.1. Impact of carbon black amount and electrode calendaring

The aim of this part is to find optimal conductive carbon black (CB) amount and calendaring pressure, i.e. to reach the best balance between electronic and ionic properties of graphite electrode in KIBs. The impact of the electrode loading was also evaluated. Fig. 2 shows galvanostatic

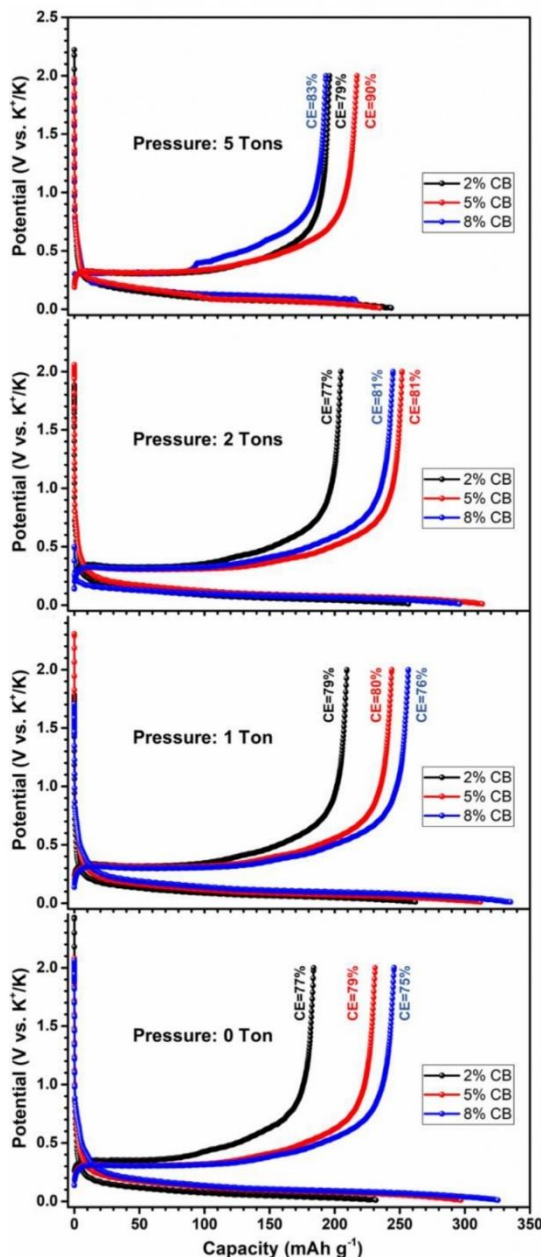


Fig. 2. 1st cycle galvanostatic discharge/charge profiles between 2 and 0.01 V at C/20 for graphite electrodes (4 mg cm^{-2}), densified at 0, 1, 2 and 5 tons, as function of the Gr/CB amounts.

profiles during the 1st cycle at C/20 for 4 mg cm^{-2} Gr electrodes densified at 0, 1, 2, and 5 tons as function of the Gr/CB amounts. For clarity, Fig. S2 shows the obtained porosity and pores volume for the different electrode formulations while Table S2 gathers the first cycle reversible capacity and coulombic efficiency (CE). Increasing the calendaring pressure up to 1 or 2 tons enhances the delivered capacity whatever the Gr/CB amounts are. This is more likely due to an improvement of the electronic contacts between Gr particles and the CB network (i.e. contacts quality and numbers). However, very low capacities were obtained at 5 tons and despite the C/20 rate, which is

explained by the concomitant low porosities (<20%, Fig. S2), i.e. high ionic limitations. In addition, as the pressure increased, the delivered capacity of the electrode containing 8 wt.% of CB decreased compared to electrodes with lower CB amounts. For such high carbon content, the CMC amount (10 wt.%) is probably not enough to completely coat both the graphite and carbon particles, leading to electrodes with poor mechanical properties. Thus, when the calendaring pressure increased, the high volume expansion induced by the graphite potassiation more likely lead to partial pulverization/disconnection of the electrode while lower calendaring pressure (i.e. higher electrode porosity) may help to buffer the volume expansion. Regarding the CE, improvements were obtained as the pressure (except for 5 tons) and CB amount increased. Overall, the favorable CB amount in term of both capacity and CE is 5 wt.%. The optimal calendaring pressure is between 1 and 2 tons, which corresponds to electrode porosity between 43 and 36%, respectively.

To discriminate further the impact of the 1 and 2 tons calendaring pressures as function of the Gr/CB amounts, rate performance was then evaluated (Fig. 3). For information, without and with 5 tons densification, very poor performance was observed due to bad electronic and ionic percolations, respectively (Fig. S3). However, with 5 wt.% of CB and a calendaring pressure of 2 tons, significant rate performance improvement was observed due to optimal electronic and ionic percolating networks. Also note that with this electrode formulation, nearly no capacity loss (<5%) was induced by the rate test, which means that the graphitic structure remains more likely undamaged. Capacity fading as the cycles number increased is more likely due to passivation of the K metal, associated to an increase of the K metal polarization and despite the use of C/5 potassiation (for C/5 to 10C depotassiation) to limit it (Fig. S1). Thus graphite capacities decreased as the cycling rate increased. Based on these results, both this carbon content (5 wt.%) and calendaring pressure (2 tons corresponding to a 36% electrode porosity, Fig. S2) were selected for the rest of the study.

Capacity retention was then evaluated for the 4 mg cm^{-2} Gr electrodes (5 wt.% CB, 36% porosity and $40 \mu\text{m}$ thickness) and compared to 2.4 mg cm^{-2} Gr electrodes (5 wt.% CB, 35% porosity and $29 \mu\text{m}$ thickness), Fig. 4. As expected, lowering the graphite loading led to a better capacity retention after 41 cycles with 210 mAh g^{-1} (only 5% loss) compared to 188 mAh g^{-1} (28% loss) for the higher loading. Note that when the 2.4 mg cm^{-2} electrodes were densified at 2 tons (corresponding to 29% porosity), a rapid capacity fading was observed (Fig. S4), demonstrating that lowering the porosity leads to ionic limitations. At the opposite, the 4 mg cm^{-2} electrodes densified at 1 ton (43% porosity) showed higher capacity fading (Fig. S4) but due to electronic limitations, probably increased by the volume expansion issue upon cycling. Overall, for both loadings, the optimal electrode porosity is about 35%. For the rest of the study, the 2.4 mg cm^{-2} graphite loading was selected.

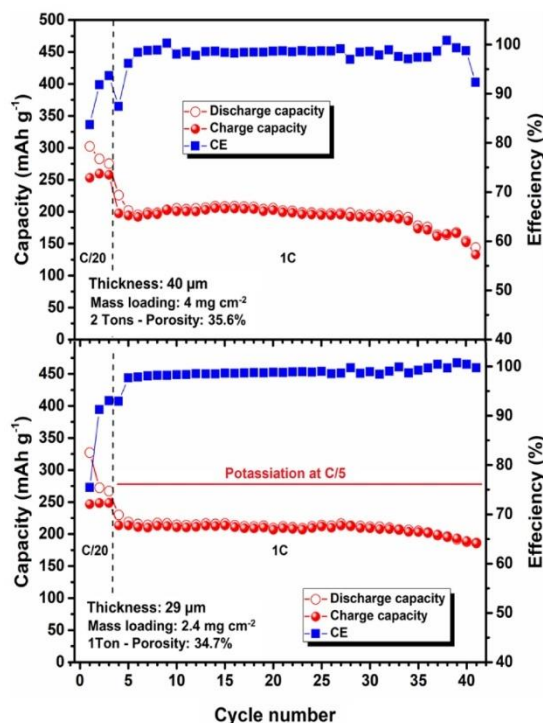


Fig. 4. Capacity retention and coulombic efficiency obtained between 2 and 0.01 V at C/5 potassiation and 1C depotassiation rates after 3 formations cycles at C/20 for 4 and 2.4 mg cm^{-2} graphite electrodes (5 wt.% CB and ~35% porosity).

3.2. Impact of SBR as co-binder

The aim of this part is to evaluate the effect of carboxylated SBR as co-binder with CMC regarding the volume expansion issue of graphite electrodes, i.e. the impact on high depotassiation rates and capacity retention. Fig. 5 shows galvanostatic profiles during the 1st and 5th cycles at C/20 for graphite electrodes (2.4 mg cm^{-2} , 5 wt.% CB and 35% porosity) as function of SBR/CMC amounts (0/10, 2/8 and 4/6 in wt.%). Compared with CMC only, using 2 wt.% SBR significantly increased the delivered capacities, more likely due to a better electrode structure. However, increasing the SBR amount to 4 wt.% decreased the reversible capacities, which can be explained by the poor swelling properties of SBR (i.e. non-polar material) in carbonate-based electrolytes [30,31]. In

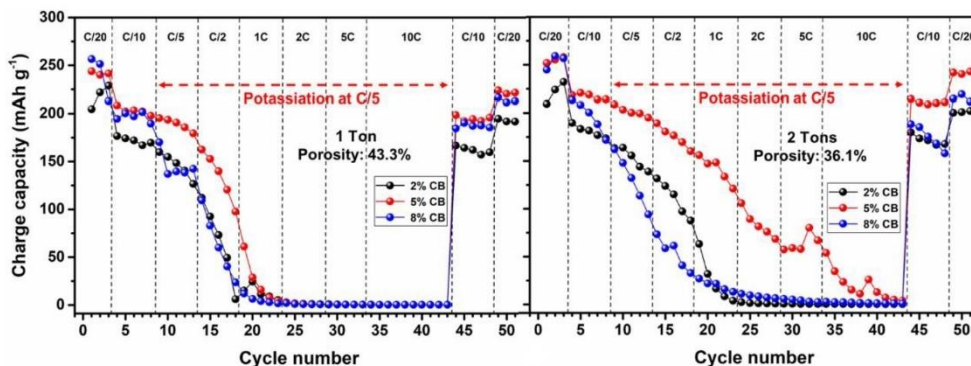


Fig. 3. Rate performance obtained between 2 and 0.01 V for graphite electrodes (4 mg cm^{-2}), densified at 1 and 2 tons, as function of the Gr/CB amounts.

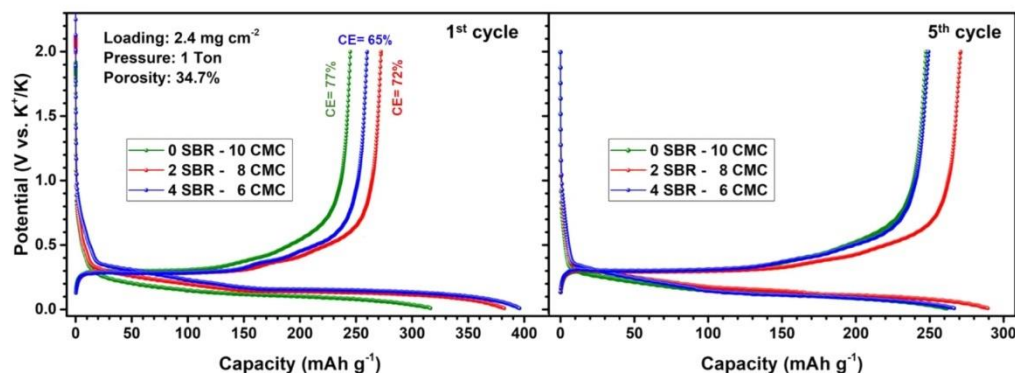


Fig. 5. Galvanostatic profiles between 2 and 0.01 V of the 1st and 5th cycle at C/20 for graphite electrodes (2.4 mg cm^{-2} , 5 wt.% CB and 35% porosity) as function of SBR/CMC amounts (0/10, 2/8 and 4/6 in wt.%).

other words, in a high content SBR matrix, the K^+ diffusion resistance would become a limiting parameter. In addition, at high content, SBR could isolate the graphite particles from the electrolyte. Regarding the CE, the higher the SBR amount was, the lower the CE was, probably due to the formation of thicker SEI with this SBR. At this point, a dedicated study will be necessary to confirm this phenomenon.

To discriminate further the impact of carboxylated SBR, rate performance was then evaluated, Fig. 5a. As expected, 2 wt.% SBR led to higher capacities from low ($\sim 270 \text{ mAh g}^{-1}$ at C/20) to high rate ($\sim 165 \text{ mAh g}^{-1}$ at C), which indicates an improvement of the electrode structure. This is confirmed by the lower polarization observed with 2 wt.% SBR during this rate test (Fig. S5). At the opposite, 4 wt.% SBR led to worst rate performance (Fig. 6a) and polarization (Fig. S5). This confirms that at high content, SBR limits the K^+ diffusion in the electrolyte (due to its poor swelling properties in carbonates) and/or isolate graphite particles from the electrolyte. Galvanostatic intermittent titration technique (GITT) further confirmed that using 2 wt.% SBR led to a rather small polarization (0.15 V) compared to the other compositions (about 0.2 V) (Fig. S6). Interestingly, such polarization is lower than the polarization observed for conventional carbonaceous electrodes in sodium and lithium ions batteries, as also reported elsewhere [3].

In addition, as K metal passivation upon cycling (i.e. K metal polarization increase) is more likely at the origin of the capacity decay observed during the conventional rate test (Fig. 6a), an alternative test (see the experimental section) was performed to evaluate only the depotassiation rate capability (Fig. 6b). For clarity, galvanostatic profiles are reported in Fig. S7. Overall, much higher depotassiation capacities were obtained compared to the standard rate test. For instance, the best electrodes (with 2 wt.% SBR) delivered 243 mAh g^{-1} during depotassiation at 5C using the alternative test (Fig. 6b) compared to $< 20 \text{ mAh g}^{-1}$ with the conventional test (Fig. 6a). These results thus confirm that graphite can deliver high capacities at high depotassiation rate when the graphite potassiation is not limited by the K metal polarization. Finally, such alternative rate test is relevant when half-cells are used.

The effect of the SBR type (i.e. the functional groups content) was then evaluated, as reported in Fig. 7. With the second SBR (SBR(2) from Synthomer), much higher CE were obtained during the formation cycles (Fig. 7c), more likely due a better pre-formed SEI. Note that the exact effect of SBR (as CMC co-binder and depending of its type) on the SEI formation needs to be evaluated in a dedicated study in the future. Interestingly, during depotassiation at 5C, the polarization was significantly decreased using SBR(2) to 0.32 V compared to 0.78 V for the previous SBR (Fig. 7a). As a result, during depotassiation at 5C, 94% of the previous potassiation capacity (at C/20) was delivered using SBR(2) compared to only 81% with the previous SBR. Finally, with SBR(2),

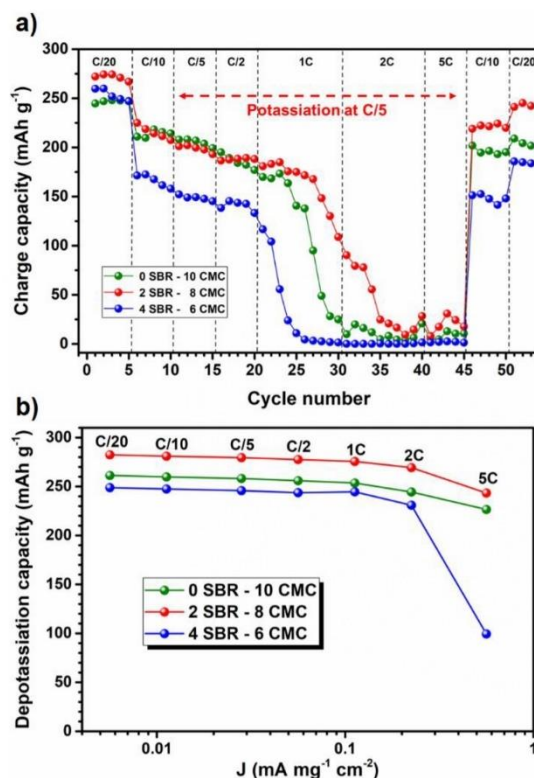


Fig. 6. (a) Galvanostatic rate performance between 2 and 0.01 V from C/20 to 5C and (b) depotassiation capacities obtained using the alternative rate performance during the 5th cycle (successive depotassiation / 30 min relaxation steps) for graphite electrodes (2.4 mg cm^{-2} , 5 wt.% CB and 35% porosity) as function of SBR/CMC amounts (0/10, 2/8 and 4/6 in wt.%).

nearly no capacity loss was observed after 55 cycles compared to a 45% capacity loss with the previous SBR (Fig. 7c). This is related to a lower volume expansion of the electrode with SBR(2), 11%, compared to 14% with SBR (Table S3). Interestingly, previous results without SBR (Fig. 4) led to a much higher volume expansion (24%) after only 35 cycles (Table S3). Overall, these results thus highlight that appropriate carboxylated SBR significantly improves the electrode cohesion/elasticity (i.e. the volume expansion management) and thus the resulting

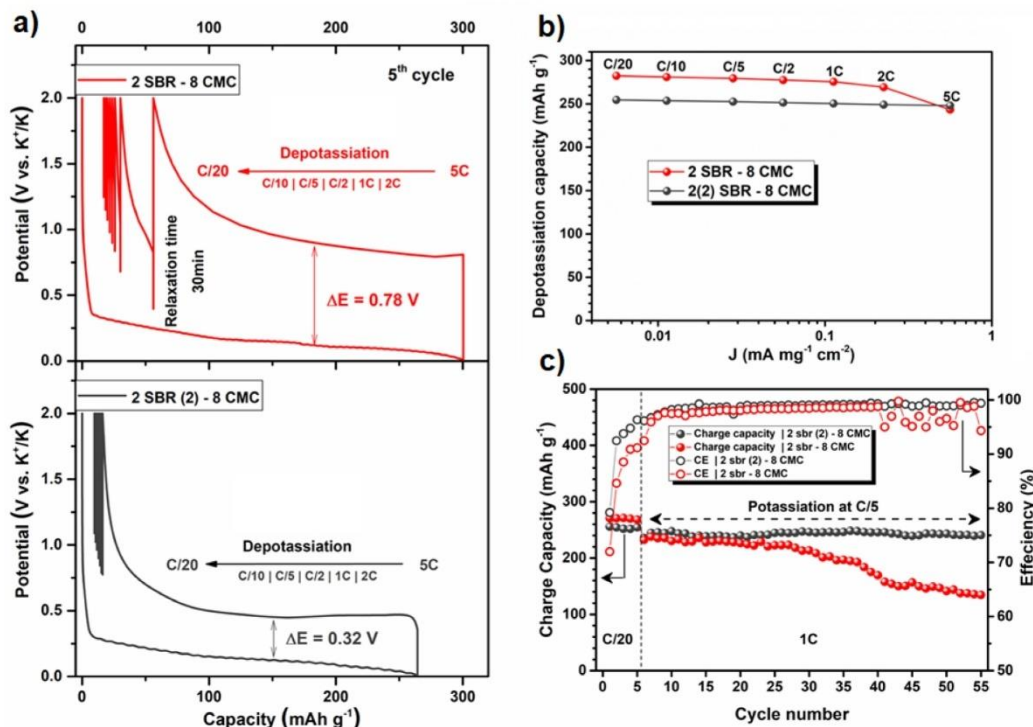


Fig. 7. a) Galvanostatic rate performance during the 5th cycle between 2 and 0.01 V (successive depotassiation / 30 min relaxation steps) and b) corresponding depotassiation capacities for graphite electrodes (2.4 mg cm^{-2} , 5 wt.% CB, 8/2 wt.% CMC/SBR and 35% porosity). c) Capacity retention and coulombic efficiency obtained between 2 and 0.01 V at C/5 potassiation/1C depotassiation for graphite electrodes (2.4 mg cm^{-2} , 5 wt.% CB, 8/2 wt.% CMC/SBR and 35% porosity) with 2 SBR types.

power performance and capacity retention of graphite electrodes for KIBs. It is believed that the COO^- groups of the SBR binder may bond with the graphite/CB surfaces so that SBR(2) having an higher COO^- content, it will further increase the electrode cohesion/elasticity.

Finally, the potassiation rate was also evaluated using a similar alternative rate test in 3-electrodes configuration (Fig. 8). The use of SBR (2) led to 205 mAh g^{-1} during potassiation at 1C compared to only 55 mAh g^{-1} with CMC only. This result further highlights the interest of SBR(2) to significantly improve the potassiation rate capability of graphite electrode in KIBs. However, in this 3-electrodes configuration, the low K stripping kinetics (Fig. S1) may still limit the high rate graphite potassiation so that better performance could be obtained in full-cells.

4. Conclusion

This work dealt with the optimization of the graphite electrodes formulation to enable high performance K-ion batteries. In a first step, optimal ionic (porosity) and electronic percolation networks were obtained by adjusting CB/graphite amounts as well as the electrode calendering pressure. Interestingly, 5 wt.% of CB led to better coulombic efficiency and power performance whatever the calendering pressure was, which points out the beneficial role of optimizing the electronic network. In addition, the optimal balance between electronic and ionic properties was obtained for a 35% electrode porosity, while lowering the graphite loading from 4 to 2.4 mg cm^{-2} led to slight improvement. In second/third steps, optimal electrode structure/mechanical properties were then obtained by using carboxylated SBR with appropriate amount/functional groups contents as co-binder with the CMC. The best electrochemical performance were thus obtained by electrodes constituted of 95/5/8/2 wt.% of graphite(SLP30)/CB(G65)/CMC—Na/SBR

(Synthomer) with 2.4 mg cm^{-2} loading and 35% porosity (pressed at 1 ton). Indeed, such graphite electrodes could delivered 92% ($\sim 250 \text{ mAh g}^{-1}$) of their capacity during depotassiation at 5C with a very low polarization (~ 0.3 V). These electrodes also delivered 205 mAh g^{-1} during potassiation at 1C (in 3-electrodes configuration) compared to only 55 mAh g^{-1} with CMC only. In addition, no capacity loss was observed after 50 cycles at C/5 potassiation/1C depotassiation due to a relatively low electrode volume expansion (11%) compared to 24% without SBR showed after 35 cycles at C/5 potassiation/1C depotassiation. Therefore, the use of carboxylated SBR (Synthomer) significantly improved the electrode structure/cohesion/elasticity, which led to much better rate performance, capacity retention as well as volume expansion management of graphite electrodes for KIBs. Finally, while further improvements could be obtained by tuning the electrolyte formulation (including the SEI formation), this work will benefit to the development of high energy KIBs.

CRediT authorship contribution statement

Badre Larhrib: Investigation, Formal analysis, Visualization, Writing – original draft. **Lénaïc Madec:** Conceptualization, Validation, Writing – review & editing, Supervision. **Laure Monconduit:** Validation, Writing – review & editing, Supervision. **Hervé Martinez:** Resources, Validation, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

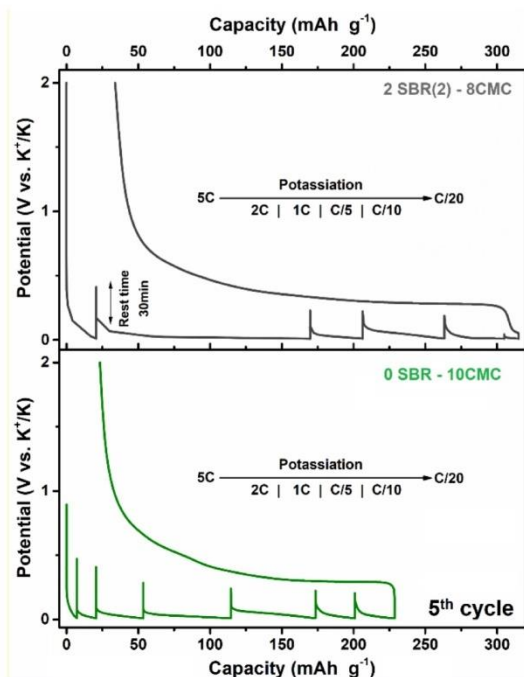


Fig. 8. (a) Alternative galvanostatic rate performance during the 5th cycle between 2 and 0.01 V using successive potassiation (from 5C to C/20) and 30 min relaxation steps for graphite electrodes (2.4 mg cm^{-2} , 5 wt.% CB and 35% porosity) using either 10 wt.% CMC or 8/2 wt.% CMC/SBR(2).

Data availability

Data will be made available on request.

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Supplementary materials

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Supporting Information

Optimized electrode formulation for enhanced performance of graphite in K-ion batteries.

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Table S1. Physical and chemical properties of the two SBR binders as provided by the supplier. *For the SBR from Synthomer, despite that no detail was provided about the styrene, butadiene and carboxyl contents, the manufacturer describes it as having a high acid (carboxyl groups) content and a Tg of 11   C.

	Nanografi SBR (called SBR)	Synthomer SBR (LITEX LB-420)* (called SBR(2))
Appearance	Milky white liquid emulsion	Milky white liquid emulsion
Total solid (%wt)	51.3	46
Styrene (%wt)	24-26	-
Butadiene (%wt)	71-73	-
Carboxyl (%wt)	5	-
PH	6-7	7
Viscosity (mPa s⁻¹)	159	<300
Relative density (water=1)	1.52	1.36 (calculated)
Storage temperature (��C)	0 - 38	5 - 35

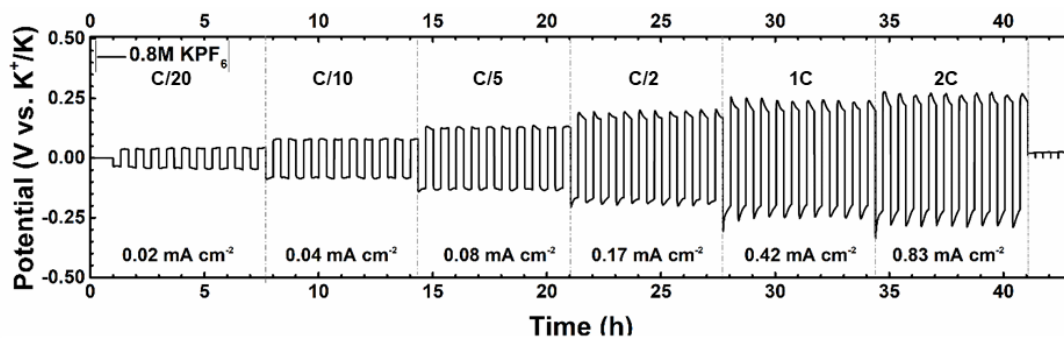


Figure S1. Voltage profiles of K plating/stripping (K//K cells filled with 0.8 M KPF_6 EC:DEC) at different current densities. Corresponding C rates for graphite electrodes are also indicated.

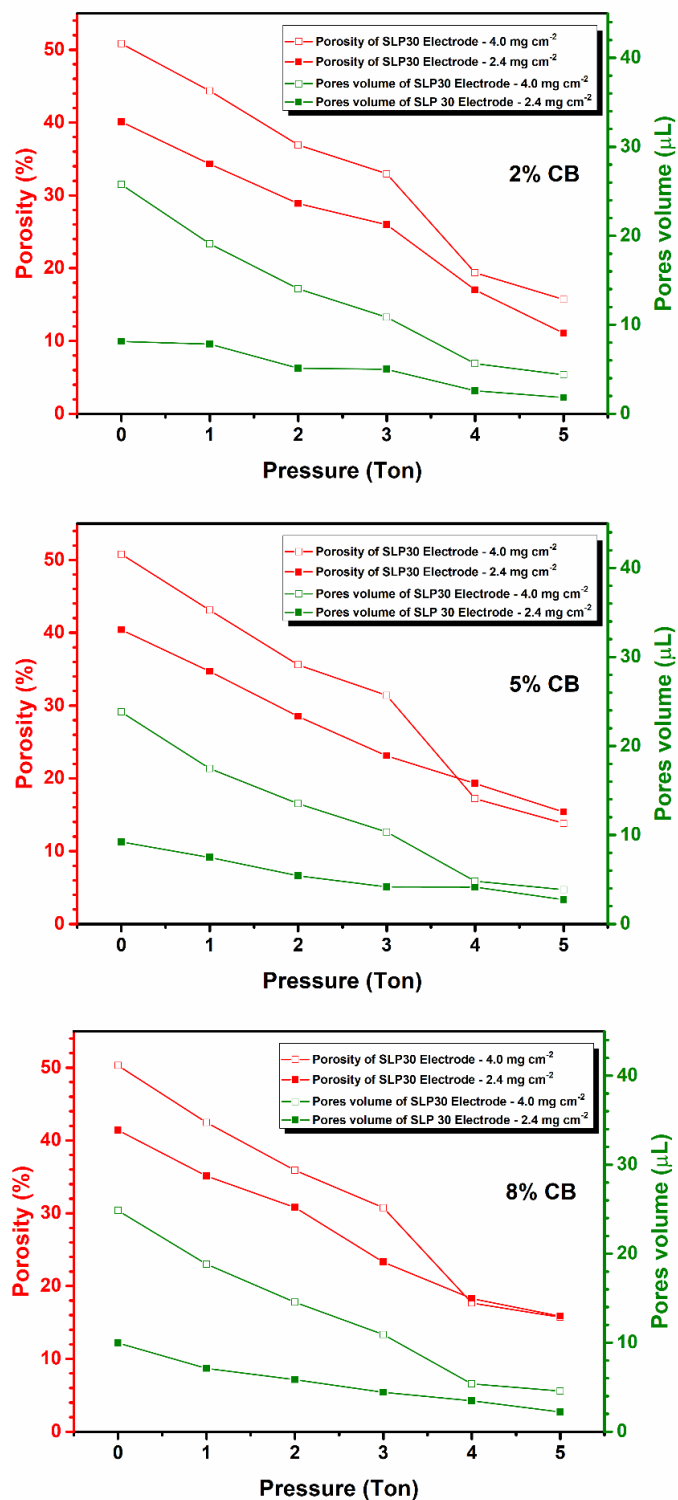


Figure S2. Variation of the porosity and pores volume as function of the calendering pressure for the graphite electrodes made of 90-x wt.% graphite SLP30, 10 wt.% CMC-Na and x wt.% carbon black C65 (x= 2, 5 and 8) and for two loadings (2.4 and 4 mg_{graphite} cm⁻²).

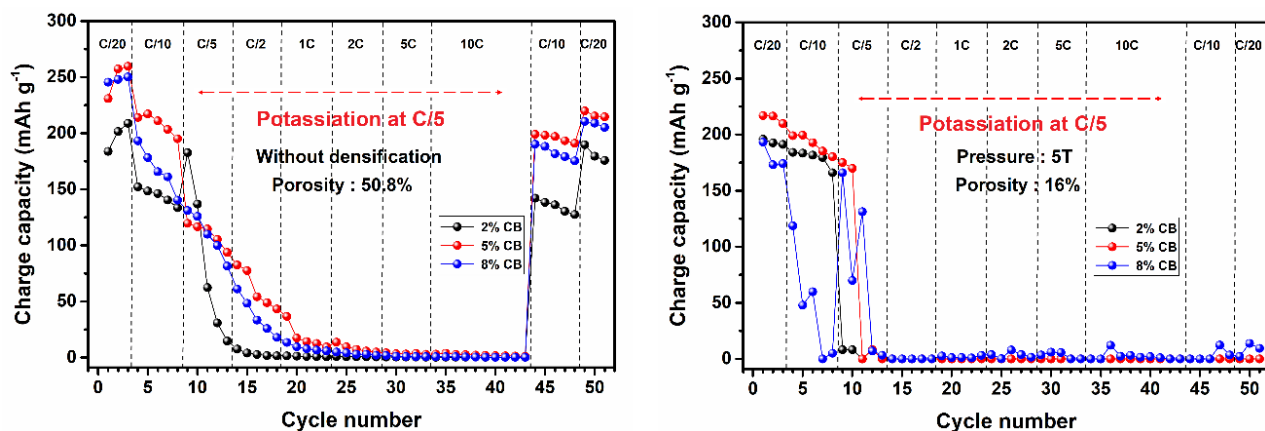


Figure S3. Rate performance obtained between 2-0.01 V for graphite electrodes (4 mg cm^{-2}), undensified and densified at 5 tons, as function of the Gr/CB amounts.

Table S2. Comparison of the electrochemical performance (1st cycle coulombic efficiency and reversible capacity obtained between 2-0.01V at C/20) for 4 mg cm^{-2} graphite electrodes as function of the Gr/CB amounts (88/2, 85/5 and 82/8 in wt.%) and calendering pressures (0, 1, 2 and 5 tons).

	Calendering pressure in Ton Ton cm ⁻²							
	0 0		1 1.05		2 2.10		5 5.26	
	1st cycle CE (%)	1 st cycle reversible capacity [mAh g ⁻¹]	1st cycle CE (%)	1 st cycle reversible capacity [mAh g ⁻¹]	1st cycle CE (%)	1 st cycle reversible capacity [mAh g ⁻¹]	1st cycle CE (%)	1 st cycle reversible capacity [mAh g ⁻¹]
COMPOSITION 1 88% Gr 10% CMC 2% CB	77	186	79	211	77	208	83	198
COMPOSITION 2 : 85% Gr 10% CMC 5% CB	79	232	80	248	81	254	90	220
COMPOSITION 3 : 82% Gr 10% CMC 8% CB	75	248	76	259	81	249	79	194

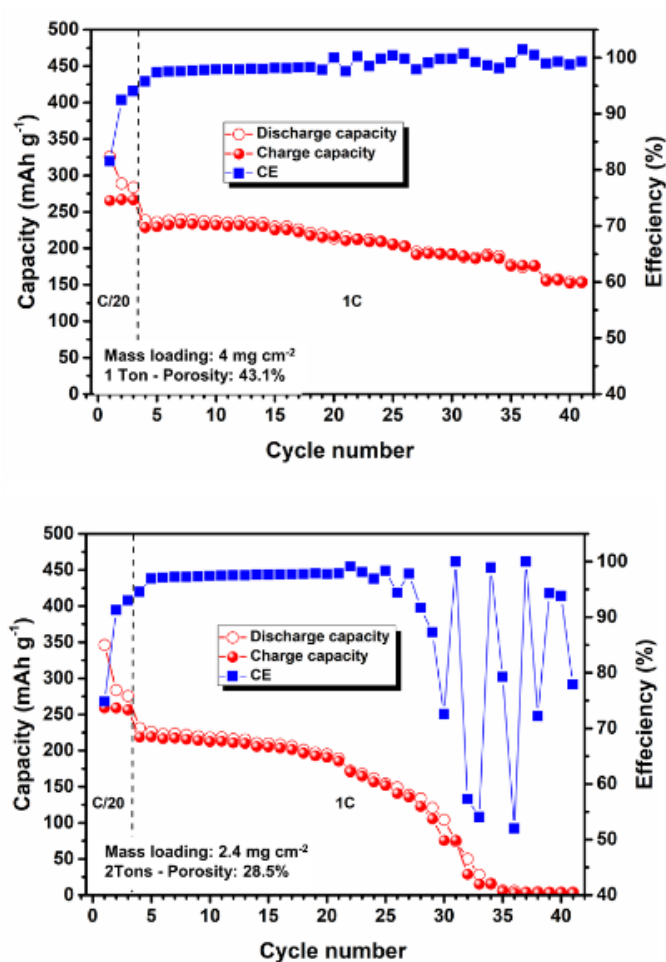


Figure S4. Capacity retention and coulombic efficiency obtained between 2-0.01 V at C/5 potassiation and 1C depotassiation rates after 3 formations cycles at C/20 for 4 mg cm⁻² graphite electrodes (5wt.% CB and 29% porosity) and 2.4 mg cm⁻² graphite electrodes (5wt.% CB and 43% porosity).

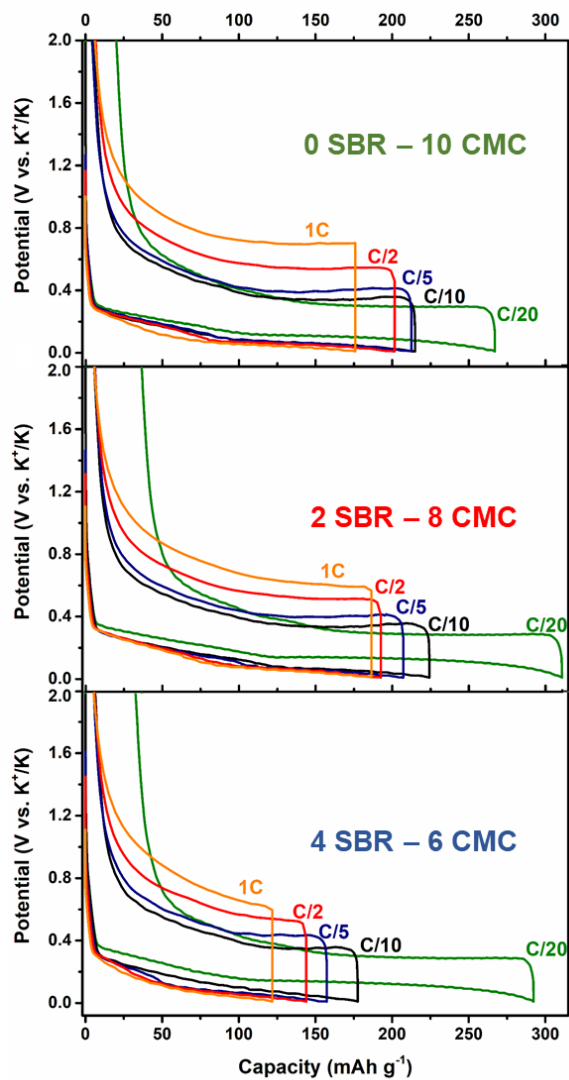


Figure S5. Galvanostatic discharge and charge profiles between 2-0.01 V from C/20 to 5C during the first cycle for each rate for graphite electrodes (2.4 mg cm^{-2} , 5 wt.% CB and 35% porosity) as function of SBR/CMC amounts (0/10, 2/8 and 4/6 in wt.%). These data correspond to the Figure 6a.

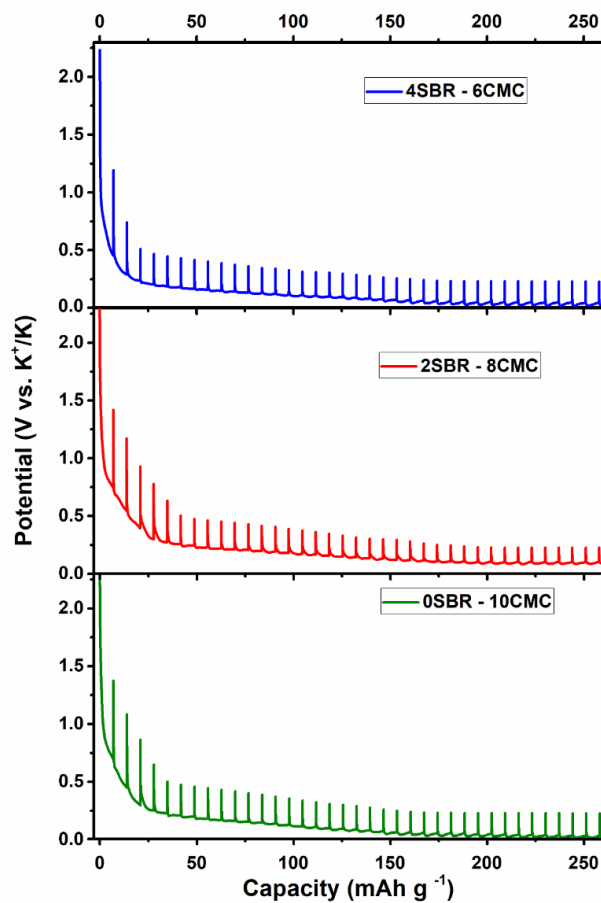


Figure S6. Galvanostatic intermittent titration technique (GITT) of graphite electrodes electrodes (2.4 mg cm^{-2} , 5 wt.% CB and 35% porosity) as function of SBR/CMC amounts (0/10, 2/8 and 4/6 in wt.%).

GITT was done as follow: during the first potassiation down to 0.01 V, successive 30 min constant current (-20 mA/g , i.e. 0.025 K^+ intercalation) and 8h relaxation steps.

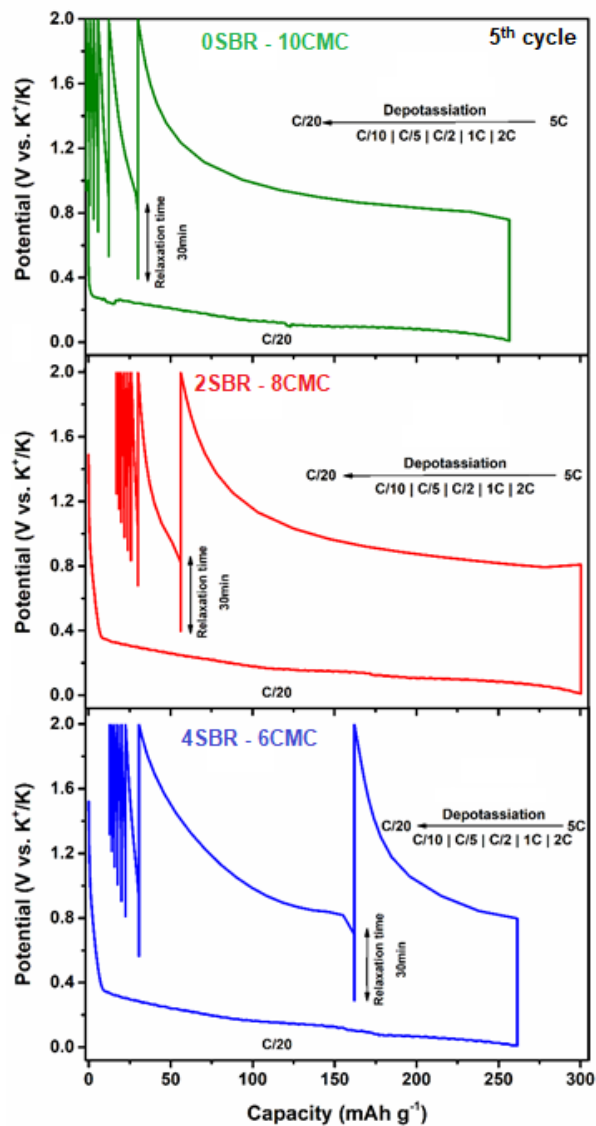


Figure S7. Alternative galvanostatic rate performance during the 5th cycle between 2-0.01 V using successive depotassiation (from 5C to C/20) and 30 min relaxation steps for graphite electrodes (2.4 mg cm⁻², 5 wt.% CB and 35% porosity) as function of SBR/CMC amounts (0/10, 2/8 and 4/6 in wt.%).

Table S3. Comparison of the electrode thickness increase (average obtained for two electrodes) after cycling for graphite electrodes (2.4 mg cm^{-2} , 5 wt.% CB and 35% porosity) without (10 wt.% CMC) and with SBR (8/2 CMC/SBR in wt.%) for two SBR types.

	10/0 CMC/SBR (After 35 cycles at C/5 potassiation and 1C depotassiation)	8:2 CMC:SBR (After 50 cycles at C/5 potassiation and 1C depotassiation)	8:2 CMC:SBR(2) (After 50 cycles at C/5 potassiation and 1C depotassiation)
Thickness of fresh electrodes (μm)	29	28	28
Thickness of cycled electrodes (μm)	36	32	31
Volume expansion (%)	24	14	11

II. Hard carbon electrodes: Physical, chemical, and electrochemical properties

II.1 Introduction

Hard carbons (HCs) are a promising choice for anode materials in KIBs, and researchers have invested significant effort in studying their properties and underlying mechanisms [2,3]. K ions can be both intercalated into the graphene layers and adsorbed onto the micropores, surface defects, and functional groups in HC anodes, resulting in significant improvements in K-ion power performance. Besides their excellent electrochemical performance, HC anodes also offer advantages such as the availability of abundant precursors, low cost, environmentally friendly characteristics, simple synthesis, large interlayer distance, lower working voltage, low volume expansion compared to graphite, and so on [4].

In this section, we will discuss hard carbon spheres that were synthesized by Louiza Larbi (PhD student in IS2M, CNRS) using a friendly approach (polymerization-precipitation process) in water at room temperature, followed by a pyrolysis step (1500, 1700, and 1900 °C corresponding respectively to three types of hard carbon spheres HCS1500, HCS1700, and HCS1900), under argon atmosphere. Different characterizations were carried out to determine the impact of the pyrolysis temperature on both the physical and chemical properties of the HCS and their electrochemical performance as anode materials for KIBs. Finally, electrochemical performance was compared with a commercial graphite (Gr-SLP30).

The same graphite composition was tested for hard carbons, but due to the high hydrophobicity of the synthesized HCs, attributed to the hydrophobic surface groups, we were unable to obtain a homogeneous slurry. Hence, the choice of the alternative solvent-based composition. The results were published in ACS Applied Energy Materials journal (Paper in appendix II) and some figures and tables in this chapter are extracted from it [5].



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Article

Impact of Hard Carbon Properties on Their Performance in Potassium-Ion Batteries

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and Camelia Matei Ghimbeu*



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II.2 Physical and chemical properties

Table 1 presents various characteristics of the analyzed materials. The crystallite height (L_c) and width (L_a) were calculated for each sample using the Scherrer formula from the (002) and (100) peaks. The average number of graphene layers was also estimated by dividing L_c by d_{002} . Gr-SLP30 had the highest L_c , L_a , and L_c/d_{002} values due to its well-organized structure, while HCS1900 had the highest L_c and L_a values, indicating an increase in graphene layer stacking with increasing pyrolysis temperature.

The I_D/I_G ratio, a measure of graphitization degree, was calculated and found to increase with pyrolysis temperature for the HCS samples. Gr-SLP30 had a low I_D/I_G ratio due to its high ordered structure. All samples had low Brunauer-Emmett-Teller (BET) specific surface areas, which is valuable for potassium ion storage by limiting electrolyte decomposition and excessive SEI growth [6].

Furthermore, CO_2 adsorption was performed to understand the texture of HCS samples, revealing the presence of some ultra-micropores. The helium density of the materials decreased with increasing pyrolysis temperature, likely due to the formation of a close porosity. The close and open porosity ratio of HCSs was calculated using the helium density values and the total pore

volume obtained by nitrogen adsorption. Close porosity increased with increasing pyrolysis temperature, while open porosity decreased. Gr-SLP30 had a very low close porosity ratio compared to HCSs.

Moreover, the amount of oxygen detected by X-ray photoelectron spectroscopy (XPS) decreased with increasing pyrolysis temperature, which can be advantageous for K-ion storage. However, a small amount of oxygen can ensure good wettability of the carbon active material by electrolyte. The total released amount of CO₂ and CO (CO_x) decreased for HCSs with increasing temperature. Active surface area (ASA) was measured to quantify the edge defects, and the values were found to decrease with increasing pyrolysis temperature. HCS samples presents different characteristics than Gr-SLP30 due to differences in carbon precursor and preparation conditions [7].

Table 2. Hard carbon spheres and graphite physical and chemical characteristics: particle size, graphite interlayer distance (d_{002}), crystallite height (L_c), crystallite width (L_a), number of graphene layers (L_c/d_{002}), I_D/I_G ratio, specific surface area (SSA), active surface area (ASA), oxygen (O%) and carbon (C%) surface amount, oxygen-based functional groups (CO_x) amount, Helium density and close porosity ratio, adapted from the reference [5].

Material properties	HCS1500	HCS1700	HCS1900	Gr-SLP30
Particle size (μm)	4.1	6.3	6.4	32
d_{002}^a (Å)	3.69	3.64	3.59	3.35
L_c^a (Å)	10.7	11.8	13.8	284
L_a^a (Å)	17.1	19.2	20.3	707
L_c/d_{002}^a	3	3	4	84
I_D/I_G^b	1.46	1.32	1.27	0.31
N ₂ SSA (m ² g ⁻¹)	3.6	1.4	1.0	6.5
CO ₂ SSA (m ² g ⁻¹)	18	14	8	n.a
ASA (m ² g ⁻¹)	1.6	0.1	0.1	0.4
O (at %)	5.35	1.59	1.46	3.3
C (at %)	92.4	98.2	98.2	96.7
CO _x (mmol g ⁻¹)	0.04	0.005	0.003	0.04
He density (g cm ⁻³)	1.8	1.5	1.4	2.3
Close porosity ratio (%)	19.6	35.1	38.6	0.8

^a determined from XRD, ^b from Raman spectroscopy

II.3 Electrochemical performance

The electrochemical performance of HCS and Gr-SLP30 materials as negative electrodes in KIBs, in terms of CE, capacity retention, and rate performance, were investigated and further correlated to the physical and chemical carbon properties.

Figure 1a and b illustrate the galvanostatic charge/discharge profiles for HCS1500, HCS1700, HCS1900, and Gr-SLP30 electrodes during the 1st cycle at C/20 and 50th cycle at C/10 rate.

The curves have two distinct regions: a sloping region from 2.0 to 0.35V and a plateau-like region from 0.35 to 0.01 V. Comparing the first plateau region between HCS materials, we noticed that HCS1700, HCS1900, and Gr-SLP30 have longer lengths than HCS1500, which has a higher slope region (i.e., capacitive behavior). After 50 cycles, the slope region becomes less pronounced for all materials, leading to a decrease in both irreversible and reversible capacity. The high irreversible capacity is mainly due to the formation of SEI involving the reduction of the electrolyte on the electrode particles and the K⁺ trapping in porosity or/and structure [8,9]. While there is no complete agreement on the association of these regions with a precise mechanism, several studies suggest that K-ions are adsorbed to defective sites or pores in the sloping region, while insertion of K ions between graphene layers or filling in close pores occurs in the plateau region [10–12]. Capacity retention over 50 cycles (**figure 1c**) shows that HCS1500 has the highest retention at 88% compared to HCS1700, HCS1900, and Gr-SLP30, which have 83%, 79%, and 87%, respectively. CE evolution (**figure 1d**) shows that HCS1700 reaches 98% after 10 cycles, while HCS1500 and HCS1900 reach 98% after 18 cycles. Gr-SLP30 does not reach 98% even after 50 cycles. However, the low initial coulombic efficiency (iCE) in the whole HCS series can also be explained by the PVDF strong swelling characteristics [13]. Based on these results, HCS1500 presents the best tradeoff based on reversible capacity, capacity retention, and CE evolution.

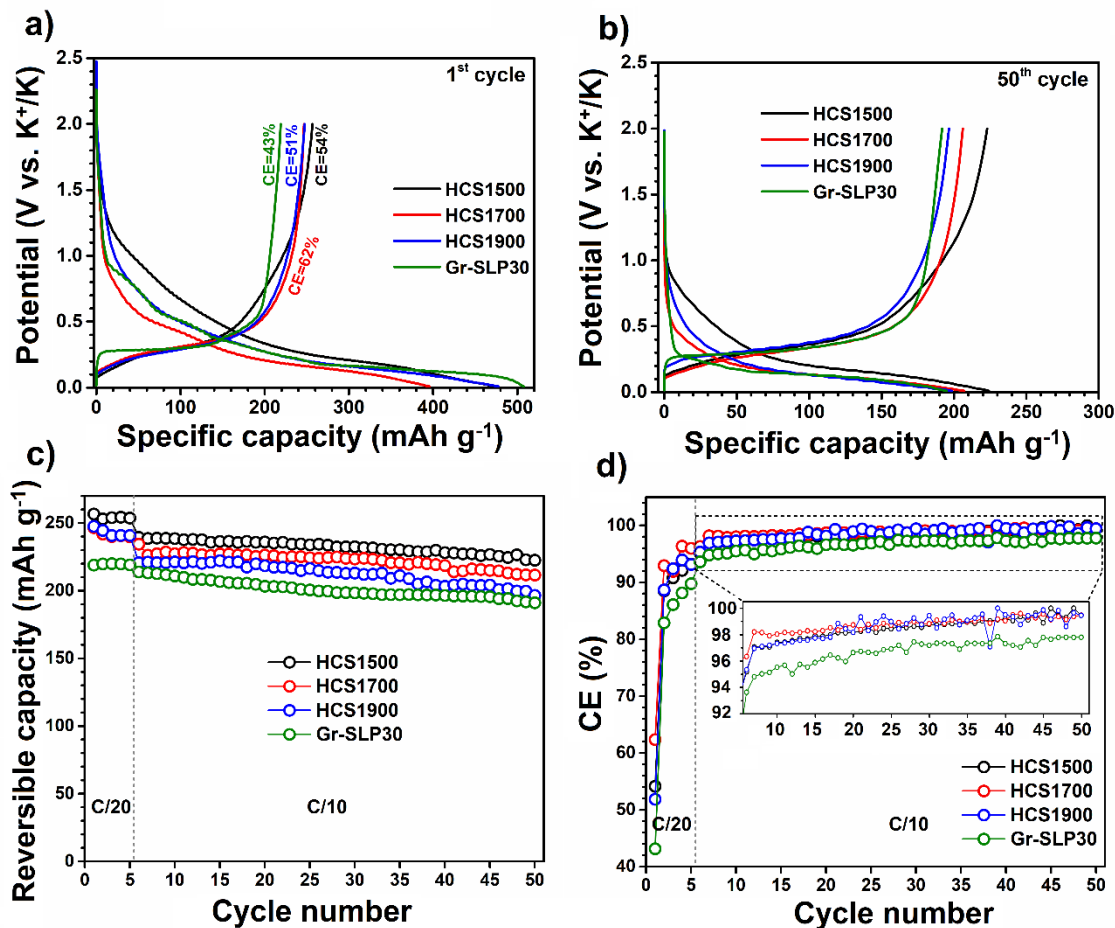


Figure 11. Discharge/charge profiles of the (a) 1st at C/20 and (b) 50th cycle at C/10 (c) capacity retention; (d) Coulombic efficiency at C/10 after 5 formation cycles at C/20 obtained between 2.0-0.01 V for HCS1500, HCS1700, HCS1900, and Gr-SLP30 electrodes, adapted from the reference [5].

To gain a better understanding of the mechanisms that occur in these materials, Cyclic voltammetry (CV) were performed (**figure 2a**). HCS1500, HCS1700, and HCS1900 exhibited similar CV profiles with two redox peaks (O1/R1) indicating the potassiation and depotassiation of K ions (diffusive behavior). The hysteresis between the two redox peaks (anodic and cathodic peaks) increased as the pyrolysis temperature increased, implying a decrease in polarization and an expected improvement in rate capability. As the scan rate was increased, the peaks became more intense for all materials, indicating the raise of capacitive phenomena. By analysing the capacitive (adsorption) and diffusive (insertion) contributions based on the CV curves and Dunn method [14], it was clear that the increase in capacitive phenomena came at the expense of the diffusive process (**figure 2b**). The diffusion contribution was predominant (~70 to 90%) compared to the capacitive

one (~10 to 30%) between 0.02-0.2 mV s^{-1} scan rate, with HCS1500 and HCS1900 exhibiting similar behavior, while HCS1700 showed more pronounced diffusive behavior. Additionally, the capacitive contribution shown in **figure 2b** was supported by the capacitive contribution (slope region in the galvanostatic curves), which was larger for HCS1500 and HCS1900 but only a small slope region was observed for HCS1700 (**Figure 1a**).

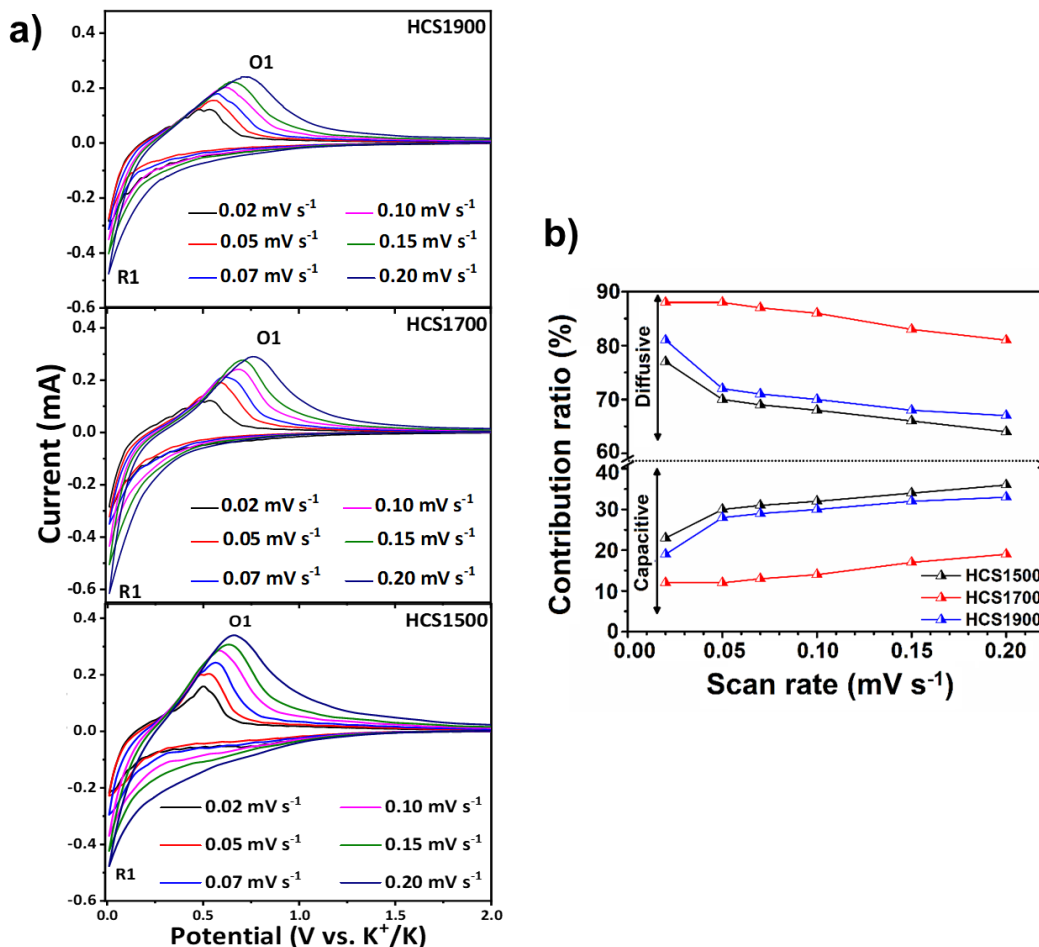


Figure 12. a) Cyclic voltammetry at different scan rates, b) Diffusive and capacitive contribution at different scan rates of HCS1500, HCS1700, and HCS1900 (extracted from cyclic voltammetry using the Dunn method), adapted from the reference [5].

As previously mentioned, in terms of capacity, the HCS1500 exhibits the highest initial charge capacity at 254 mAh g^{-1} , followed by HCS1700 (247 mAh g^{-1}) and HCS1900 (247 mAh g^{-1}), while the graphite material has the lowest capacity at 219 mAh g^{-1} . The values obtained for capacity decrease with increasing pyrolysis temperature, which is consistent with the decrease in interlayer

space, open porosity, and defects, as well as an increase in close porosity. These properties can impact the insertion/adsorption sites of K ions. Indeed, larger interlayer gaps allow for better accommodation of K ions, considering their size, which is larger than that of Li ions [7]. Defects also play a role in K-ion adsorption and close porosity does not seem to contribute to K-ion storage [15]. Furthermore, the HCS1700 has the highest initial coulombic efficiency of 62%, followed by HCS1500 (54%), HCS1900 (51%), and Gr-SLP30 (43%). The higher iCE of HCS1700 can be related to its low specific surface area, active surface area, and optimal interlayer space compared to its analogues prepared at 1500 and 1900 °C, as shown in **figure 3**. The higher SSA, ASA, and CO_x functional groups of HCS1500 could favor solid electrolyte interphase formation and more capacitive behavior (**table 1** and **figure 3**). For HCS1900, although it presents SSA and ASA like HCS1700, it has a smaller interlayer space, which can lead to irreversible trapping of K ions and lower iCE. Gr-SLP30 has the lowest initial ICE of 43%, which can be attributed to its higher active surface area and oxygen functionality amount, contributing to higher electrolyte degradation and more SEI formation.

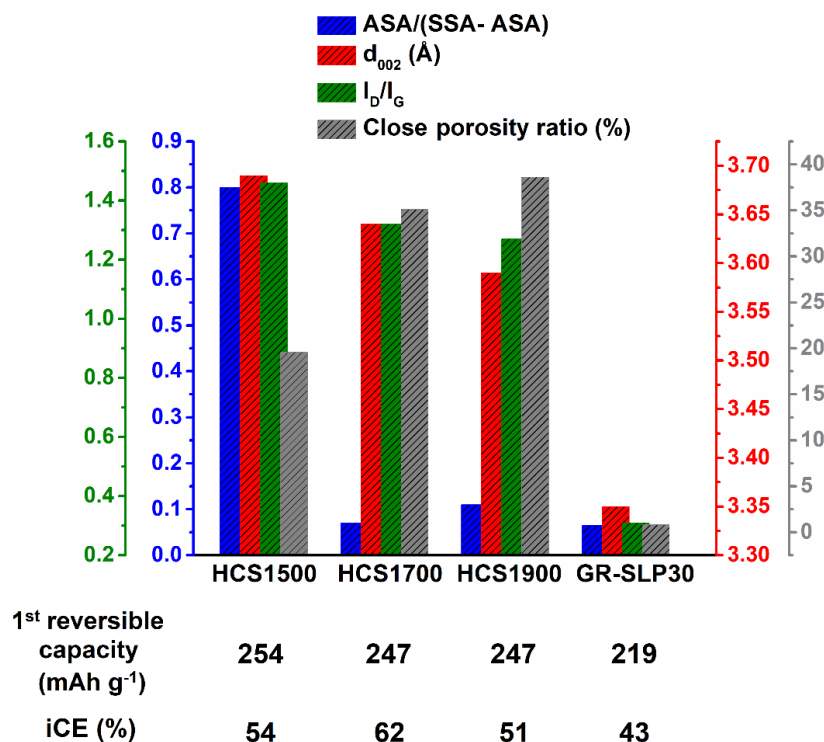


Figure 13. Correlation between the N₂ specific surface area, d_{002} , I_D/I_G , close porosity ratio and electrochemical performance; initial Coulombic efficiency (iCE) and first reversible capacity, adapted from the reference [5].

To further differentiate between disordered carbon materials (HCS) and well-organized carbon materials (Gr-SLP30), the performance at different rates was studied after 50 cycles (see **figure 4**). All carbons exhibited a significant decrease in capacity as the rate increased. HCS1500 was more resistant at high C rates, although its capacity decreased from about 235 mAh g⁻¹ at a C/10 rate to approximately 125 mAh g⁻¹ at a C/2 (115 mA g⁻¹) rate.

The maximum current limit that results in zero delivered capacity was found to be 2C, C/2, and C/5 for HCS1500, HCS1700, and HCS1900, respectively. The enhanced performance of HCS1500 can be attributed to its larger d_{002} , which allows for faster potassiation/depotassiation of K-ions, leading to better rate capability. Additionally, the presence of oxygen-functional groups, porosity, and defects may promote K-ion adsorption on HCS1500, particularly at high rates, where capacitive behavior is enhanced. This is consistent with the results of Kubota et al.[7], who suggested that the presence of hydrogen-terminated edges at lower pyrolysis temperatures (i.e., 1300°C) allows for better adsorption compared to higher temperatures (i.e., 1800 or 2000°C).

Additionally, at C/2, Gr-SLP30 exhibited a lower capacity than HCS1500 but a higher capacity than HCS1700 and HCS1900. This may be attributed to the higher active surface area and concentration of oxygen-based functional groups in Gr-SLP30, which may enhance adsorption and contribute to the capacity increase.

In addition, the great reactivity of K metal during cycling (i.e. an increase in K metal stripping polarization) is responsible for the capacity decay observed during the conventional rate test in a half cell [16,17]. Consequently, the rate of potassiation is limited by the polarization of the K metal stripping.

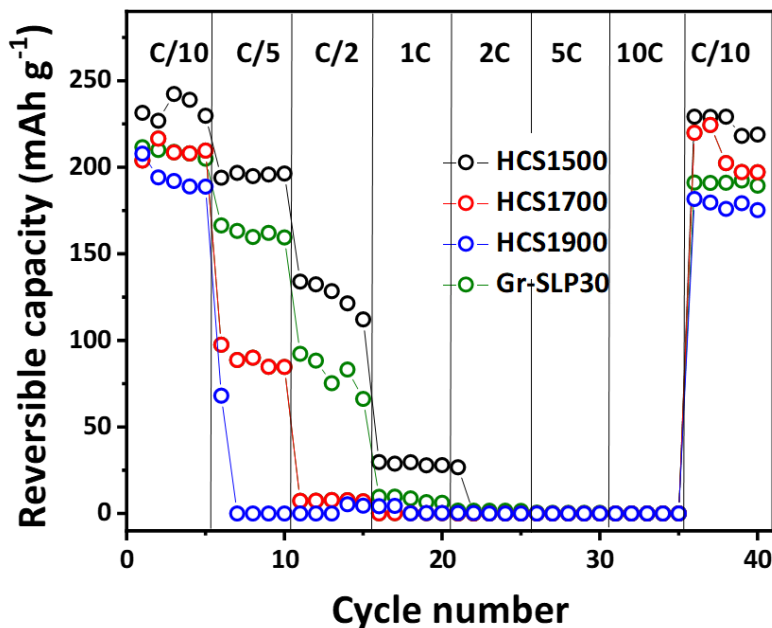


Figure 14. Rate performance after 50 cycles from C/10 to 10C obtained between 2-0.01V for HCS1500, HCS1700, HCS1900, and Gr-SLP30 electrodes, , adapted from the reference [5].

To address this issue, two alternative cycling tests were carried out at different C-rates. In the first test (**figure 5a**), the potassiation rate was kept at C/10, while the depotassiation rate varied from C/10 to 10C. Compared to the conventional rate test, substantially higher depotassiation capacities were obtained. The use of this rate capability test resulted in the delivery of 230 mAh g⁻¹ by HCS1500 after depotassiation at 10C, compared to 0 mAh g⁻¹ obtained from the conventional test, as shown in **figure 4**. These results demonstrate that HCS materials can offer high capacities at a high depotassiation rate when the potassiation of hard carbon is not limited by the stripping polarization of K metal. After 32 cycles at 10C depotassiation (**figure 5b**), HCS delivered high capacities of 230 mAh g⁻¹, 228 mAh g⁻¹, and 214 mAh g⁻¹ for HCS1500, HCS1700, and HCS1900, respectively, against 147 mAh g⁻¹ for Gr-SLP30.

High capacities for HCS are associated with a small potential hysteresis, or polarization, in the 32nd cycle, particularly at a high depotassiation rate of 10C, when the potassiation of HCS (C/10) is not limited by the stripping polarization of K metal (**figure 5b**). In addition, when the current drops back to lower values (C/10) after 35 cycles, HCSs recover nearly all their initial capacities, whereas Gr-SLP30 only recovers 83% of its initial capacity (**figure 5a**). This large difference in capacities between graphite and HCSs may be explained by the lower polarization of the latter, compared to

the high polarization of graphite, which exceeds 0.8V at 10C. The large volume expansion of graphite, which apply extra stress on the binder and protective SEI, explain the behavior of graphite using this composition (90:5:5 of Gr-SLP30:CB:PVDF).

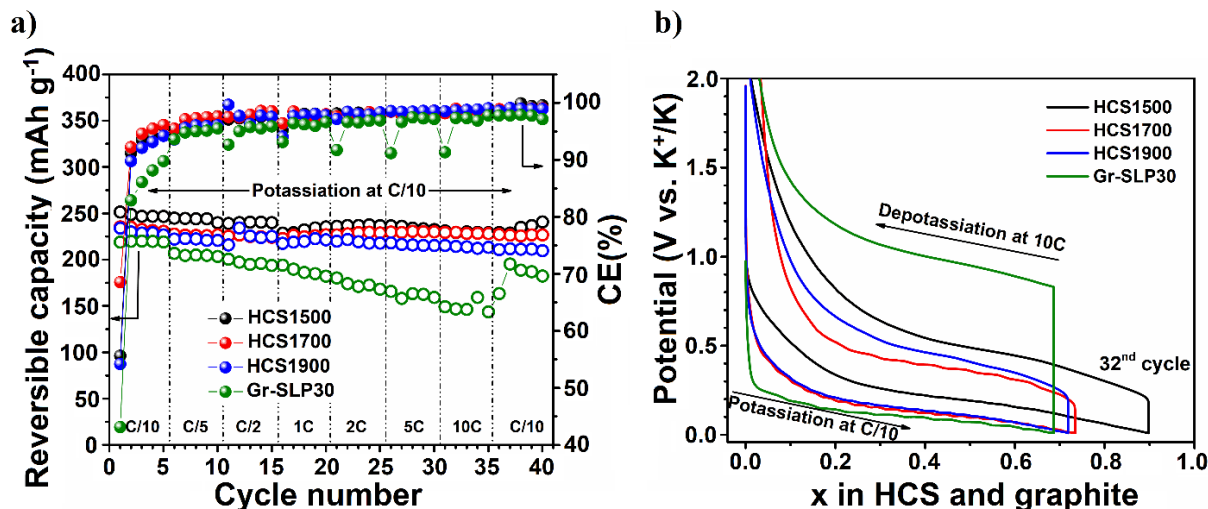


Figure 15. (a) Galvanostatic rate capability from C/10 to 10C depotassiation (C/10 potassiation) and CE evolution; (b) Galvanostatic profiles of the 32nd cycle at C/10 potassiation and 10C depotassiation obtained between 2.0-0.01 V for HCS1500, HCS1700, HCS1900, Gr-SLP30 electrodes, adapted from the reference [5].

As described in the experimental section (appendix II), we performed a second rapid alternative test to assess the depotassiation rate capability, overcoming potassium ageing and reactivity (refer to **figure 6a**). Generally, we obtained much higher depotassiation capacities compared to the conventional rate test mentioned earlier (**figure 4**). For example, during depotassiation at 10C (254 mAh g⁻¹ at C/10) using the rapid alternative test, HCS1500 delivered 245 mAh g⁻¹, whereas HCS1700, HCS1900, and Gr-SLP30 yielded 202, 214, and 195 mAh g⁻¹, respectively, at a 10C depotassiation rate (**figure 6b**). These results confirm that HCS1500 delivers high capacities due to its large interlayer space and higher number of defects. Thus, it allows for easy potassium adsorption/insertion without significant structural damage.

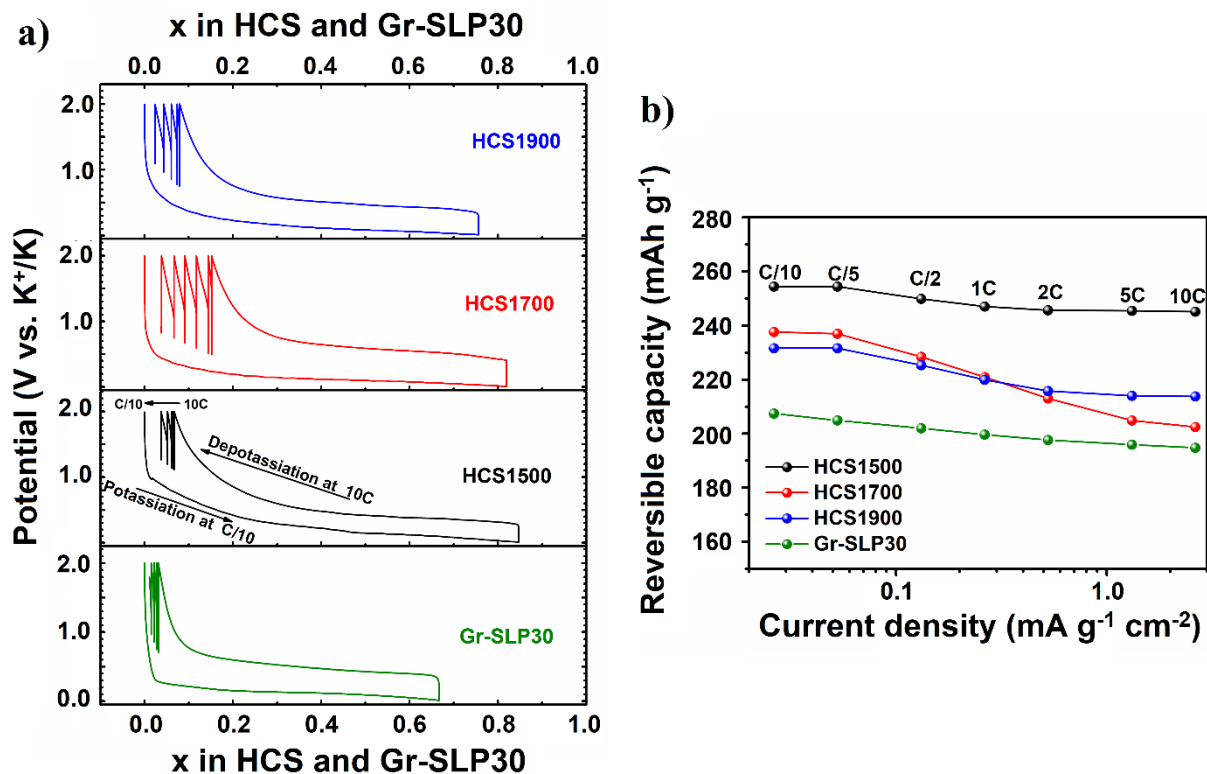


Figure 16. (a) Alternative rate performance, (b) depotassiation capacities obtained using the alternative rate performance during the 5th cycle (successive depotassiation / 2h relaxation steps) between 2.0-0.01V for HCS1500, HCS1700, HCS1900, and Gr-SLP30 electrodes, adapted from the reference [5].

III. Positive electrodes for KIBs

III.1 KVPO₄F_{0.5}O_{0.5} : Electrochemical properties

Within the realm of potassium-ion batteries, the pursuit of novel positive electrode materials with high energy density remains an ongoing challenge. In our dedicated efforts to tackle this challenge, we have boarded on a scientific exploration within the Fluorophosphate phases family, specifically focusing on KVPO₄F_{1-y}O_y (KVPFO). This exciting venture was carried out as part of the TROPIC project at ICMCB [18], underscoring the collaborative nature of our research.

Among the various compositions studied, one phase, KVPO₄F_{0.5}O_{0.5}, has emerged as a highly promising candidate. In this section, we will delve into the electrochemical characterization of this material, shedding light on its performance. These include a capacity of 93 mAh g⁻¹, a favorable operational potential of 4.2 V vs K⁺/K, and high-rate performance.

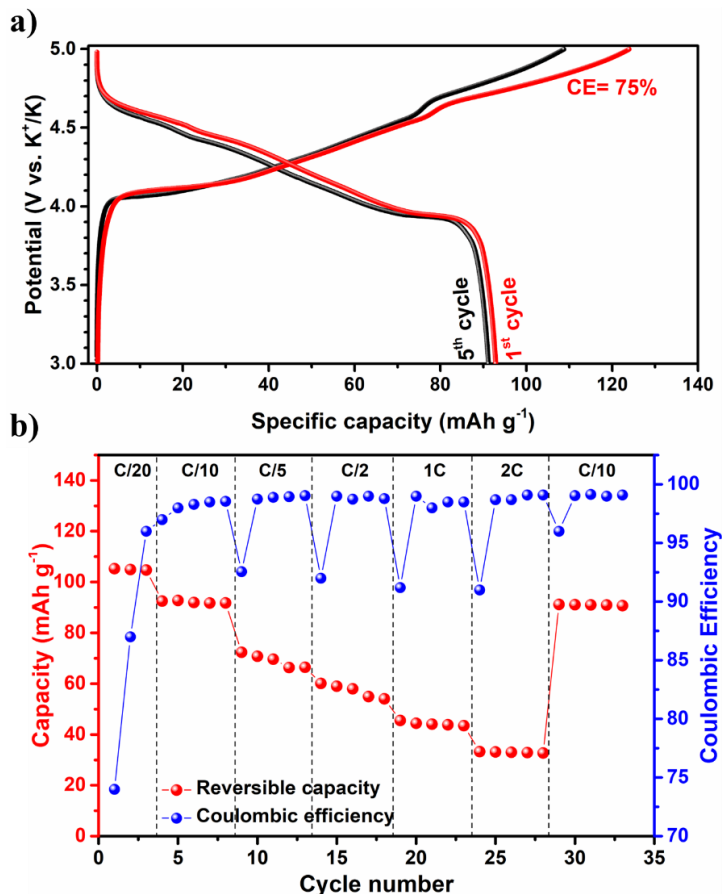


Figure 17. a) Charge/discharge profiles of the 1st and 5th cycle at C/10, and b) Rate performance from C/20 to 2C obtained between 3-5 V for KVPFO//0.8 M KPF₆ in EC:DE//K metal cell.

The crystallographic, physical, chemical, and morphological characterizations of the chosen KVPFO phase have already been validated in several studies in the context of TROPIC project [18,19]. The electrode composition used was 75% KVPFO, 15% CB (conductive carbon black), and 10% PVDF (polyvinylidene fluoride). The high carbon content in the composition is justified by the low electronic conductivity of phosphates. To address this issue, in-situ and/or ex-situ coating would need to be performed to better control the composition and achieve significant quantities of active material. This represents a challenge in our case, as KVPFO is not stable beyond 580°C.

As for the electrochemical characterizations, **figure 7a** shows the galvanostatic profile of the 1st and 5th cycle obtained between 3-5 V for KVPFO versus K metal in a 0.8 M KPF₆ EC:DEC (1:1 by volume) electrolyte. The electrochemical activity of KVPO₄F_{0.5}O_{0.5} presents one characteristic

sloping domains in the 4 to 4.5 V vs K^+/K voltage range and a very long plateau at 4.9 V with a total reversible capacity of 93 mAh g⁻¹ and an initial coulombic efficiency of 75%. After 5 cycles formation cycles at C/20, the capacity between 4.9 and 5V is still irreversible, indicating the electrolyte side reaction at high voltage. Moreover, the rate capability test was performed to get more insight about the power application of this material. **Figure 7b** demonstrate that KVPFO can offer high capacities at a high rate. At 1C, KVPFO delivered a capacity of 44 mAh g⁻¹. In addition, when the current drops back to C/10 after 28 cycles, KVPFO recovers nearly all its initial capacity, demonstrating the structural and electrochemical stability of this material. Regarding the coulombic efficiency evolution, it does not go above 99%, which confirms the permanent side reaction at high voltage.

III.2 Prussian Blue Analogue : Coating process and electrochemical properties

To address the low capacity of KVPFO, Prussian blue analogues (PBAs), characterized by a metal–ligand open framework [20], have been selected as excellent candidate for high energy density application. In particular, they offer a high capacity and average potential in commercial sodium-ion batteries (Novasis)[21], and recent research has explored their potential as positive electrodes for potassium-ion batteries, showcasing their versatility in energy storage applications[22–26].

Herein we will discuss the coating process (targeted loading: 8mg cm⁻²) and the impact of composition, as well as the electrolyte on the electrochemical performance of $K_{1.7}Mn_{0.65}Fe_{0.35}[Fe(CN)_6]_{0.92} \cdot 0.5H_2O$ (PBA). This phase was synthesized in ICGM by Phuong Nam LE PHAM as a part of TROPIC project using conventional precipitation [27].

III.2.1 Coating process

Electrode slurries were prepared by mixing 80:10:10 of PBA:CB:PVDF (**figure. 8**) in N-methylpyrrolidone (NMP) using mechanical planetary ball milling (PULVERISETTE 7) at 500 rpm for 1 h. Slurries were coated on an aluminum current collector foil with a 15 nm thickness using the doctor blade method with a blade thickness of 300 μm and total solid content of 32% for the 8 mg cm⁻² PBA loading. Films were then dried at 60°C for 1 night. Various PVDF types were tested to address the adhesion issue of the slurry to aluminum, but none of them improved adhesion. Similarly, several studies have shown that drying temperature affects the mechanical properties of coated films[28,29]. Notably, an enhancement was observed at 90°C, where the film exhibited reduced delamination compared to drying temperatures of 25°C and 60°C when using the same

PVDF binder, Solef 5130. Given the persistent challenge, We chose to modify the process by dissolving 6% PVDF by weight in NMP overnight, a common practice in industrial process [30]. We maintained the same process while changing the drying temperature to 90°C instead of 60°C and adding the pre-dissolved PVDF. With this new process, we achieved a homogeneous film with a loading of 8.1 mg cm⁻² (figure 8).



Figure 18. Image of the PBA formulated at 80:10:10 (PBA:CB:PVDF) using different PVDF types (Alfa Aesar, Solef 5130, Kynar HSV 900, and Kynar HSV 1810), employing different drying temperatures (25°C over 2 days and 90°C over 5 hours), and altering the process by diluting 6% PVDF by weight in NMP (Targeted Loading 8 mg cm⁻²).

To assess electrochemical performance, two compositions were selected, varying in carbon content, in order to ensure improved electronic percolation, given the low electronic conductivity of PBAs (i.e., 80:10:10 and 70:20:10 of PBA:CB:PVDF). **Figure 9a and b** depict the galvanostatic charge/discharge curve obtained at C/10 between 3-4.3V exhibited low capacity (91 mAh g^{-1}), coulombic efficiency (37%), and significant polarization for the 80:10:10 composition, in contrast to the 70:20:10 composition, which demonstrated a capacity of 105 mAh g^{-1} , a coulombic efficiency of 48%, and reduced polarization, all while employing a standard electrolyte (0.8M KPF_6 in EC: DEC). The composition 70:20:10 was selected for the electrolyte impact study.

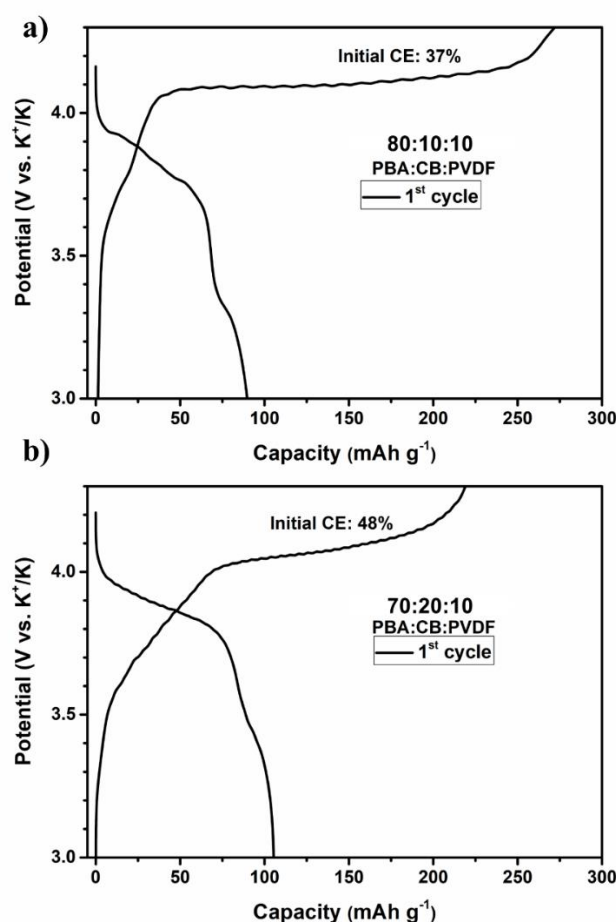


Figure 19. Charge/discharge profiles of the 1st cycle at C/10 (15 mA g^{-1}) obtained between 3-4.3V of PBA/0.8M KPF_6 in EC:DEC (1:1 by volume)//K metal using two electrode composition a) 80:10: 10 and b) 70:20:10 of PBA:CB:PVDF

III.2.2 Electrolyte impact on the electrochemical performance

For further optimization and to target potential energy applications, the investigation of electrolytes has proven to be of utmost importance in the case of PBAs, with the aim of achieving enhancements

in capacity, polarization, and initial coulombic efficiency. As mentioned in the first chapter, highly concentrated electrolytes have shown great promise, particularly since beyond a concentration of 5.3 M, aluminum corrosion can be effectively mitigated [31].

In our study, we selected various salts and solvents commonly employed in potassium-ion batteries for their high ionic conductivity and distinctive physical and chemical properties. We investigated three concentrated electrolytes: 6M Potassium(I) Bis(trifluoromethanesulfonyl)imide (KTFSI) in dimethoxyethane (DME), 6M Potassium(I) Bis(fluoromethanesulfonyl)imide (KFSI) in DME, and 6M KFSI in EC:PC (1:1 by volume). These electrolytes delivered capacities of 111, 106, and 115 mAh g⁻¹, along with Coulombic efficiencies of 86, 75, and 79%, respectively (**figure 10a**). The 6M KFSI in DME was excluded due to its lower capacity and Coulombic efficiency, as well as substantial polarization effects. Following 5 formation cycles at C/10, the 6M KTFSI with DME stabilized, exhibiting a coulombic efficiency of approximately 98% and a capacity of 109 mAh g⁻¹, in contrast to 6M KFSI in EC:PC, which yielded a coulombic efficiency of 75% (**figure 10b**). This disparity can be attributed to the ongoing solvent oxidation during cycling. The 6M KTFSI in DME can be regarded as a promising electrolyte candidate for full cell applications, notwithstanding the high cost and low cell energy density associated with concentrated electrolytes.

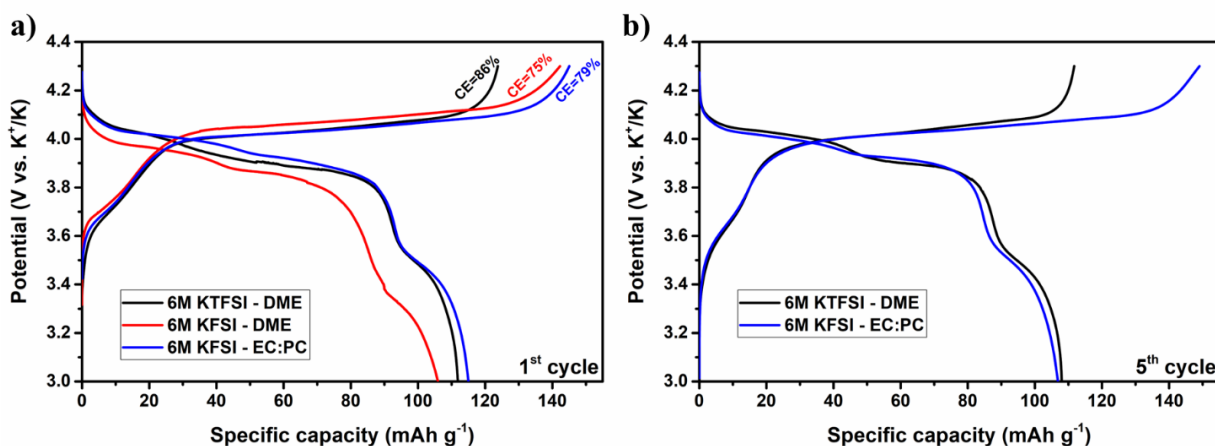


Figure 20. Charge/discharge profiles of a) the 1st cycle using 6M KTFSI in DME, 6M KFSI in DME, and 6M KFSI in EC:PC vs. K metal and b) 5th cycle using 6M KTFSI in DME and 6M KFSI in EC:PC vs. K metal at C/10 (15 mA g⁻¹) obtained between 3-4.3V (Composition 70:20:10 of PBA:CB:PVDF)

Conclusions

In this chapter, we have optimized the composition of the graphite electrode to achieve the best compromise between electronic and ionic percolating network, while maintaining a 35% porosity. We observed a significant improvement in the electrochemical performance and volumetric expansion of the graphite electrode with the composition of 85:5:2:8 for Graphite:CB:SBR(2):CMC. Additionally, we investigated hard carbons synthesized at different temperatures using a composition of 90:5:5 for active material:CB:PVDF. Given that the optimized composition for graphite did not yield satisfactory results for hard carbons (HCs), we found that the HC synthesized at 1500°C exhibited favorable electrochemical performance due to the presence of oxygen-functional groups, porosity, low close porosity, and edge defects that can enhance adsorption. This Hard carbon spheres based-material holds promise for power applications.

To complete the puzzle and move toward reliable full cells, the study of positive electrodes is of paramount importance. To achieve this, we have chosen two families of electrodes, namely, fluorophosphates ($\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$) and PBAs ($\text{K}_{1.7}\text{Mn}_{0.65}\text{Fe}_{0.35}[\text{Fe}(\text{CN})_6]_{0.92} \cdot 0.5\text{H}_2\text{O}$). These have been investigated and exhibit capacities of 93 and 111 mAh g^{-1} , with average potentials of 4.2 and 4 V, respectively.

Thus, this chapter serves as a critical step toward full cells and addresses the issue of cross-talk between working electrode and potassium metal. The significance of our findings extends beyond the laboratory, holding great potential for advancing the landscape of potassium-ion technology and its contributions to the broader domain of energy storage solutions.

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CHAPTER 3

Toward practical K-ion full cells

Introduction

Following the second chapter, which delved into the negative and positive electrodes for K-ion batteries in a half cell configuration, the current challenge lies in transitioning to a full cell setup to mitigate the impact of potassium metal reactivity as a counter electrode and to obtain results and characterizations on a reliable system.

To address this, the first section of this chapter presents a published review paper in “Journal of Energy Chemistry” periodical journal, focusing on non-aqueous full cells explored in the K-ion literature. This review aims to analyze results and acquire insights into the requirement for the practical use of this technology.

Hence, in the second section of this chapter, we presents our published paper “Toward Highly Reliable Potassium-Ion Half and Full Coin Cells” in “Batteries and Supercaps” periodical journal, offering procedures for the development of reliable full cells. This paper investigates the impact of electrolyte amount, capacity ratio, and electrode diameter ratio using both three-electrode cells and coin-cells.

Despite the optimizations outlined in this guideline, numerous pathways for further exploration remain. Thus, This chapter will pave the way for the practical application of K-ion batteries.

I. Review paper: Nonaqueous Potassium-ion Full Cells: Mapping the Progress and Identifying Missing Puzzle Pieces.

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Review

Nonaqueous potassium-ion full-cells: Mapping the progress and identifying missing puzzle pieces

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Nonaqueous potassium-ion full-cells: mapping the progress and identifying missing puzzle pieces

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Abstract

This review addresses the growing interest for potassium-ion full-cells (KIFCs) in view of the transition from potassium-ion half-cells (KIHs) toward commercial K-ion batteries (KIBs). It focuses on the key parameters of KIFCs such as the electrode/electrolyte interfaces challenge, major barriers, and recent advancements in KIFCs. The strategies for enhancing KIFC performance, including interfaces control, electrolyte optimization, electrodes capacity ratio, electrode material screening and electrode design, are discussed. The review highlights the need to evaluate KIBs in full-cell configurations as half-cell results are strongly impacted by the K metal reactivity. It also emphasizes the importance of understanding solid electrolyte interphase (SEI) formation in KIFCs and explores promising nonaqueous as well as quasi- and all-solid-state electrolytes options. This review thus paves the way for practical, cost-effective, and scalable KIBs as energy storage systems by offering insights and guidance for future research.



Dr. Badre Larhrib was born in Marrakesh (Morocco) in 1995. He obtained his Ph.D. in Material Chemistry and Physics from the “Université de Pau et des Pays de l’Adour” (IPREM-CNRS), France, collaborating with various CNRS Laboratories (ICGM, ICMCB, and IS2M) in 2023. His doctoral research primarily revolved around electrode design, full-cell optimization, and interface investigations via XPS toward high performance potassium-ion batteries. Throughout his academic occupation, he delved into synthesizing layered oxides and phosphate materials for Li-ion and Na-ion batteries, alongside designing electrolytes for high-voltage Li-ion batteries. Presently, he serves as an R&D researcher at Tiamat Energy, directing his efforts toward the development of sodium-ion batteries.



Dr. Louiza LARBI received her Ph.D. degree in 2023 in material chemistry from the University of Haute Alsace (IS2M-CNRS) with a co-direction from the University of Montpellier (ICGM-CNRS), France. During her Ph.D, She was supervised by Dr. Camelia GHIMBEU and Dr. Laure MONCONDUIT, her work was focused on the development of carbon anodes for the new generation of potassium-ion batteries. She is currently a post doctoral researcher at Sorbonne University (LCMCP-CNRS) working on the development of hybrid solid electrolyte for all-solid-state-batteries.



Dr. Lénaïc Madec was born in Mayenne (France) in 1986. After a master in chemistry of materials in Paris, he obtained a Ph.D in electrochemistry (2012) at the University of Nantes then continued as a postdoctoral fellow on redox flow battery. In 2013, he joined the University of Halifax, Canada, as a postdoctoral fellow with Prof. J. Dahn to study aging of Li-ion cells through XPS analysis. In 2015, he pursued XPS analysis on Li-ion anodes as a postdoctoral fellow in the French RS2E network (IGCM-IPREM labs). In 2016, he obtained a CNRS researcher position at the Institute of Analytical Sciences and Physico-Chemistry for Environment and Materials, Pau, where he developed researches on K-ion and solid-state batteries as well as supercapacitors with a focus on electrochemical/aging mechanisms through surface analysis (XPS, Auger) combined with

cross-section samples preparation. Recently, he proposed *operando* methods for XPS / SEM-Augur analysis to study Li plating and interphase formation in solid-state batteries. Since 2023, he joined the Institut des Matériaux Jean Rouxel, Nantes to pursue his work as a CNRS researcher.

1. Introduction

Potassium-ion batteries are being explored as a potential alternative to lithium-ion batteries (LIBs) and sodium-ion batteries (NIBs) for large-scale renewable energy storage systems. These systems require affordable and abundant precursors and materials. In that direction, potassium (K), which is highly abundant (2.1 wt.% of the Earth's crust), can be used with graphite as negative active material and aluminium as current collector [1–3]. KIBs are also expected to have high power performance due to the low desolvation energy of K^+ ($\sim 119 \text{ kJ mol}^{-1}$) vs. Na^+ ($\sim 158 \text{ kJ mol}^{-1}$) and Li^+ ($\sim 216 \text{ kJ mol}^{-1}$) in propylene carbonate based-electrolytes as well as the small solvated shell radius of K^+ ($\sim 3.6 \text{ \AA}$) vs. Na^+ ($\sim 4.6 \text{ \AA}$) and Li^+ ($\sim 4.8 \text{ \AA}$) in the same electrolyte [1,4]. However, there are still some challenges to overcome: the high atomic mass of potassium (39.1 g mol^{-1}) and the larger Shannon's ionic radius of K^+ ($1.38 \text{ \AA}$) compared to Na^+ ($1.02 \text{ \AA}$) and Li^+ ($0.76 \text{ \AA}$), as well as potential safety issues such as potassium plating[5–7]. Moreover, K-ion half-cells are strongly dependant of the K metal electrode (i.e. plating/stripping, coulombic efficiency, polarization, aging, cross-electrodes contamination due to the K metal reactivity with electrolytes) and thus cannot provide a complete performance assessment. Thus it appears mandatory to evaluate KIBs performance and perform solid electrolyte interphase studies in K-ion full-cells. Finally, mastering the procedure for transitioning from KIHCS to KIFCs becomes of high importance considering these factors. Overall, critical parameters, boosting strategies and progress map of potassium-ion full-cells are currently lacking in the KIBs literature.

This review thus summarizes the state-of-art of KIFCs. Indeed, an examination of the papers published between 2012 and the end of 2023 (**Fig. 1**) reveals that researchers have displayed increasing interest and focus on the development of K-ion full-cells in parallel to the research on K-ion half-cells toward the practical use of K-ion batteries. To the best of our knowledge, this is the first comprehensive report that reviews nonaqueous. To this end, this review first focus on key parameters that govern half-cells, i.e. the role and impact of K metal to show why full-cells should be preferred regarding both electrochemical and interfaces properties difference. Comparing these two cell configurations is crucial for gaining a comprehensive understanding of KIFCs. Moreover, interface properties play a significant role in KIFCs, and studying their features is essential for

addressing key challenges. Second, a map of the latest achievements in KIFCs is presented. Especially for nonaqueous electrolytes, which have shown promising results in terms of improved performance and stability. Additionally, the exploration of quasi- and all-solid-state electrolytes based-K-ion full-cells is also discussed as it has provided alternative pathways for advancing K-ion technology. Third, various improvement strategies are discussed to further enhance KIFCs performance, including the optimization of electrolytes to achieve stable passivation layers, screening of electrodes materials for power and energy applications and a guideline (i.e. Optimization of balancing ratio, diameter ratio, and electrolyte amount) toward optimized KIFC parameters for reliable cells. These strategies, along with other innovative approaches, aim to drive the development of efficient and reliable KIFCs. Thus, the integration of these aforementioned parameters should lead to a novel phase in the development of KIBs as energy storage systems that are practical, affordable, and scalable.

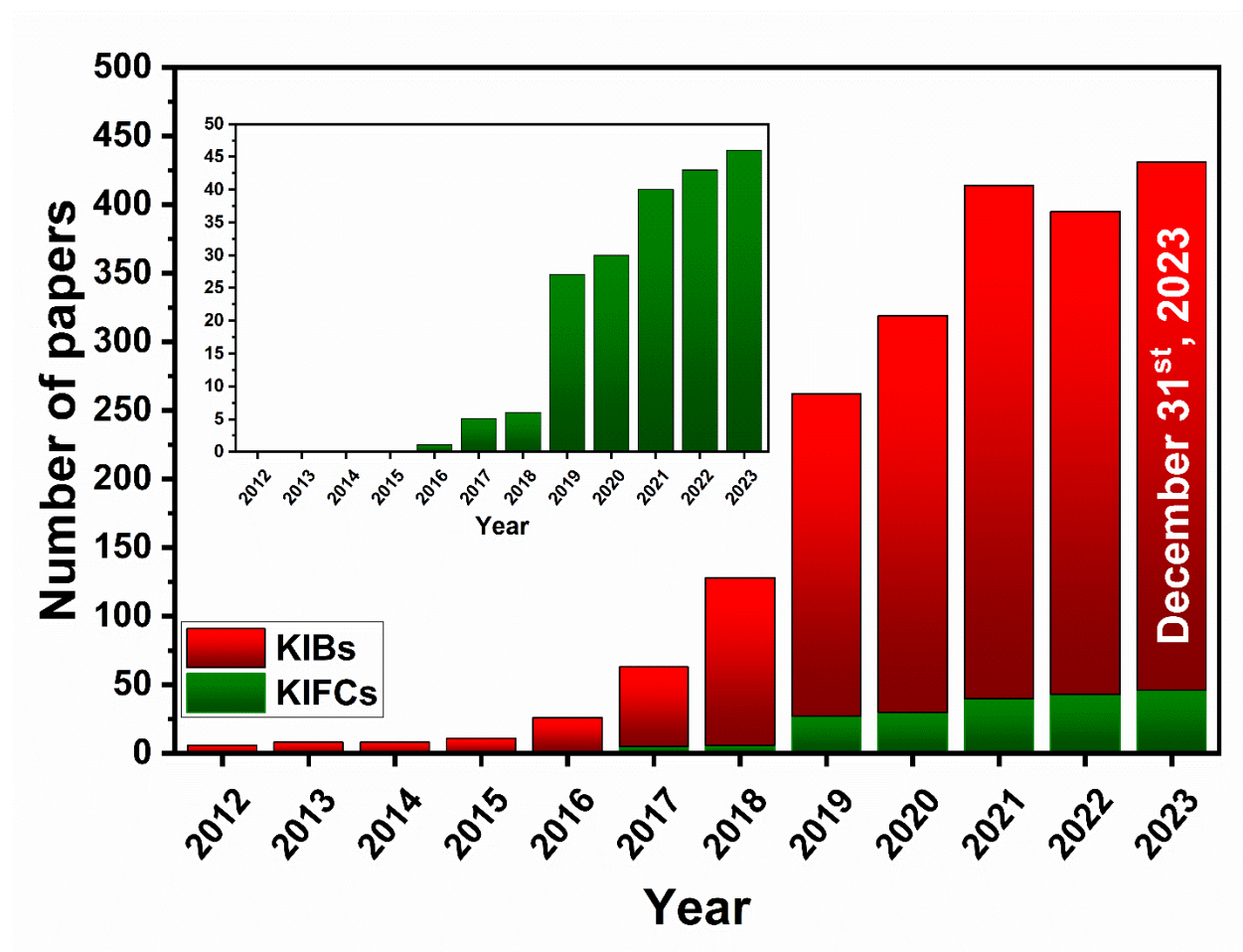


Fig. 1. Number of articles related to KIBs and specifically to KIFCs published from 2012 to December 31st, 2023 (obtained from Web of Science)

2. Why going from Half- to Full-cells?

Understanding the SEI growth, aging, and degradation mechanisms is essential to ensure the KIBs development and to obtain reliable studies, particularly in regards to the high reactivity of the potassium metal. To achieve this target, we will thoroughly investigate the difference between half- and full-cells from the electrochemical point of view then the interfaces one.

2.1. Electrochemical difference and issues

The practical application of half-cells using potassium metal as an anode in K-ion batteries is hindered by K metal passivation, high polarization, ageing and possible dendritic growth, which can lead to potential safety hazards caused by the high reactivity and low melting point of potassium metal [8]. In particular, the plating and stripping process of K metal exhibits a relatively low coulombic efficiency (CE) of less than 70% and high polarization, even at low rates, when using KPF₆ (hexafluorophosphate)-based carbonate electrolytes [9]. This thus significantly impact the rate performance and capacity retention evaluation in half-cells [10]. Substituting KFSI (i.e. Potassium Bis(FluoroSulfonyl)Imide) in carbonate electrolytes generally increases polarization by at least 0.1 V (**Fig. 2a and b**) [11].

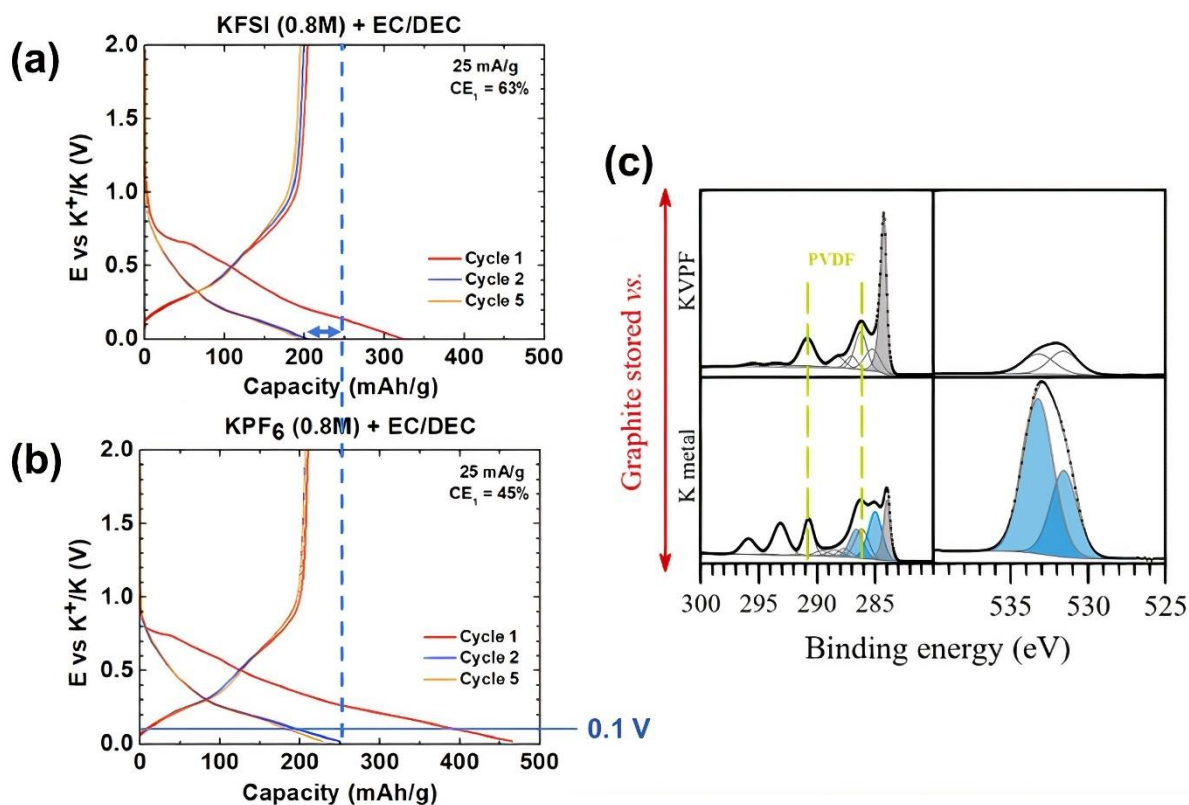


Fig. 2. Electrochemical performance of carbon nanofibers (CNF) vs K. Galvanostatic charge/discharge at 25 mA g⁻¹, (a) 0.8M KPF₆ and (b) KFSI in EC:DEC. Reproduced with permission from Ref. [11] Copyright 2020, Elsevier. (c) Comparison of K 2p – C 1s and O 1s X-ray Photoelectron Spectroscopy (XPS) Core-Level Spectra of Graphite Electrodes following 24 Hours of Storage with either a KVPO₄F or Potassium Metal Electrode, Utilizing a 0.8 M KPF₆ in EC:DEC Electrolyte: Normalized Intensities for Comparative Analysis. Highlighted in Blue are Peaks Indicating Electrolyte Degradation Products. Reproduced with permission from Ref. [12] Copyright 2022, American Chemical Society.

This is due to the improved passivation of K metal through the formation of a more inorganic solid electrolyte interphase based on degradation products of the FSI⁻ anion [8]. Interestingly, in half-cells, it is better to use highly concentrated KFSI DME (Dimethoxyethane) electrolytes as a substitute from carbonate electrolytes as these electrolytes offer the highest K plating/stripping CE, over 95% [9] and exhibit stable polarization across low, moderate, and high current densities [13]. Moreover, in half-cells, the aging of K metal, which involves passivation and impedance increase during cycling, also alters the performance evaluation [14] but is almost always neglected so far in the existing literature. Moreover, in half-cells, the irreversible consumption of active potassium

derived from SEI formation at the cathode is overcompensated by the unlimited source of K at the anode while in full-cells; this phenomenon becomes evident and will negatively impact the cell-lifetime due to the limited K content. In contrast, in full-cells, the irreversible consumption of active K will significantly impact the capacity loss and thus the overall performance, which can then be minimized using electrolyte optimization for instance.

2.2. Interfaces properties, difference, and issues

Because almost all electrochemical reaction sites are located at the different interfaces throughout KIBs cells, the feature of these interfaces is important. **Fig. 3** depicts the different interfaces for half- and full-cells and their main properties for typical nonaqueous liquid electrolyte.

2.2.1. Electrode/Electrolyte Interface

During electrochemical cycling, different side reactions can occur at the electrode particles surface that consume electrons and M^+ (M^+ : metal, K^+ in our case) cations. These reactions can cause the electrolyte degradation (salt and/or solvent), which is evident from the electrochemical curves that generally show significant irreversible capacity upon the first few cycles. As a result, electrolyte degradation products lead to the formation of passivation layers at the electrode particles surface called SEI for the negative electrodes, and CEI (cathode electrolyte interphase) or SPI (solid permeable interface) for the positive electrodes [15,16]. For clarity, note that despite that these interphases are all SEI, the naming difference for negative and positive electrodes originates from the different properties of these passivation layers as observed and proposed in Li-ion literature.

In half-cells, Caracciolo et al. [8] elucidated the complete electrolyte degradation pathways at the K surface of the commonly used 0.8 M KPF_6 or KFSI EC:DEC (Ethylene Carbonate:Diethyl Carbonate) electrolytes by combining X-ray photoelectron spectroscopy (solid products analysis) with gas chromatography (GC)–mass spectrometry and GC/Fourier transform infrared spectroscopy (gas product analysis). Note first that by comparison with Li metal in $LiPF_6$ EC:DEC, they pointed out an higher electrolyte reactivity at the K metal surface compared to the Li metal surface due to the salt cation effect. Indeed, without salt, the K and Li metal showed the same EC:DEC reactivity while with the addition of MPF_6 salt ($M = Li$ or K), the SEI was mostly based on LiF from the PF_6^- degradation and on solvent degradation products for Li and K, respectively. It is worth noting that this recent experimental study is in perfect agreement with theoretical calculations showing that for the Li^+ -solvent complex is much more stable than the K^+ -solvent

complex for MPF_6 ($M = \text{Li}$ or K) in carbonates [17,18]. More importantly, the study by Caracciolo et al. [8] also pointed out an anion effect as the K surface, the SEI was mostly organic with KPF_6 (from the solvent degradation) while it was mostly inorganic (from the FSI^- degradation) with KFSI , in agreement with theoretical calculation showing that in the K^+ -solvent-anion complex (with carbonates), the FSI^- is much closer to K^+ than PF_6^- , which stabilize the solvent reduction [17,18].

Another important consideration for half-cells, is the reactivity of the electrolyte at the K surface that forms electrolyte degradation products (i.e. KF , K_2CO_3 , ROK , and so on) [8], which migrate to the working electrode, i.e. causing cross-talk between electrodes, and more importantly regardless of the electrolyte or electrode used and even at open circuit voltage (i.e. Graphite electrode) [12,19,20] (**Fig. 2c**). At this point it is very important to note that most of the anode SEI analyzed in K-ion half-cells using KPF_6 and KFSI EC:DEC electrolytes [20–22] showed similar composition to the K metal SEI analyzed by Caracciolo et al. [8] so that considering the cross-talk phenomenon, it is impossible to assess that the anode SEI is formed only at its surface and does not originate mostly from the K metal side.

As an alternative, the use of potassium metal is possible in the case of quasi- and all-solid-state electrolytes for which the interface between the electrode and electrolyte may lead to nearly no irreversible consumption of active K as long as an appropriate electrochemical window is maintained, which depends on the specific electrolyte used [23]. However, the large interface impedance (R_{in}) and incompatibility resulting from the solid electrode/solid electrolyte contact significantly hinder the movement of K ions, which results in a low cycle stability and limited rate capability. In other words, while the electrode/electrolyte interface is more stable with quasi- and all-solid-state electrolytes compared to liquid electrolytes, the poor compatibility and large interface impedance do present significant challenges to the efficient operation of these devices.

2.2.2. Separator/Electrolyte Interface

Glass fiber (GF) is the most widely used separator among the reported studies on KIBs, due to its good wettability and ability to uptake a large amount of electrolyte. This is also due to the need of a glass fiber separator in contact with K metal in half-cells, which may be explained by a much better electrolyte wettability of the K surface thanks to the GF separator affinity with the K metal compared to a PP/PE/PP trilayer separator (so-called Celgard) [24]. However, traditional Celgard

membranes show poor compatibility and wettability with many electrolyte systems (such as PC and EC-PC), resulting in large impedance or battery failure [25,26]. Finally, the use of Celgard or Solupor separators that have low thicknesses of $\sim 25\mu\text{m}$ and high porosities ($\sim 53\%$, and $\sim 78\%$, respectively) should be preferred for full-cells and in any case, their use is crucial to meet the needed specifications for full-cells assembly [27,28].

2.2.3. Inter-particles Interface

In all systems, the interface between particles is critical for efficient ion migration and electron transfer. Various engineering strategies such as coating, composite, and morphology design (1D-3D) have been proposed to address this issue so far [2,29–31]. Furthermore, the electrode materials/carbon (i.e. conductive additive) interfaces should ensure a good electronic percolating network [32]. At this point, further studies are needed to develop KIFCs.

Finally, for quasi- and all-solid-state electrolyte, the electrolyte interparticle interface also requires a rapid transfer of K^+ ions while minimizing electronic transmission. Also, for such electrolytes, the interface with the electrodes materials often presents a challenge due to the large interface and/or grain boundary impedances. Overcoming this challenge will be one of the key to the development of solid-state batteries.

2.2.3. Electrode/Current collector Interface

The existence of this interface requires the binder to meet various requirements such as adhesion between the active material and conductive additive (carbon) particles together with the current collector surface and an electrochemical stability of this binder. If the adhesion is weak, the electrode may delaminate from the current collector or even separate completely, which can lead to battery failure. It have been demonstrated that an improvement on the electrode/current collector interface reduce the charge-transfer resistance, which is attributed to the removal of the native insulating oxide surface layer of the collector and to the enhanced adhesion at the active material/current collector interface [33]. Thus, in-depth interface studies are needed for further development of K-ion full-cells as this interface have been barely studied so far [34].

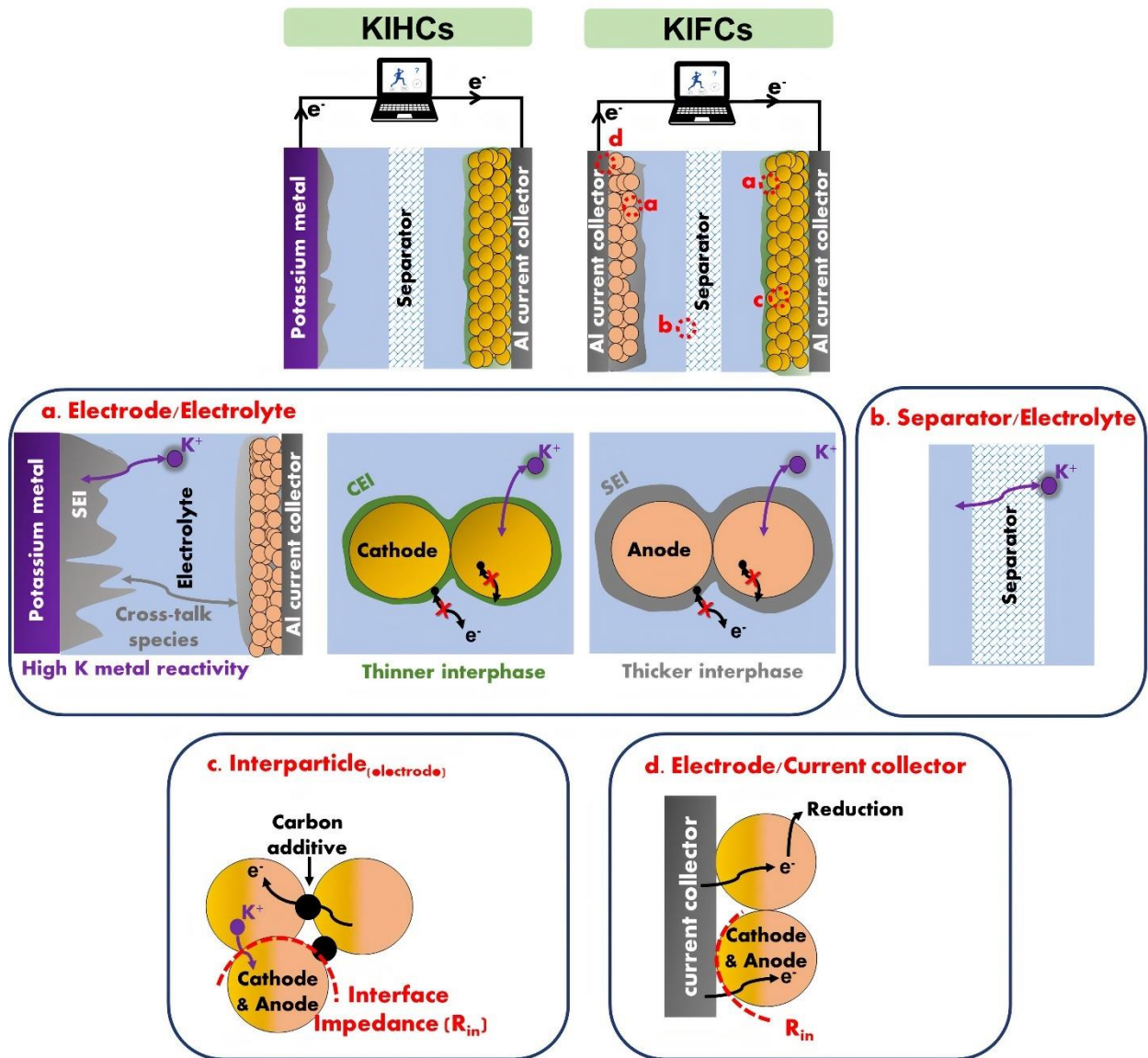


Fig. 3. Schematic illustration of half- and full-cells and their respective interfaces features.

To conclude, KIFCs with anodes other than K metal (i.e. graphite [35], carbon composite [36], MXene [37], red phosphorus [38] and other designed materials [39–42]) are recommended to overcome the above-discussed K metal issues. In other words, half-cells with K metal present to many issues to deal with so that full-cells, i.e. KIFCs are mandatory to evaluate KIBs performance, SEI analysis and aging mechanisms. Likewise, full-cells, when compared to half-cells, provide more reliable performance evaluation of KIBs. Furthermore, interfaces within KIFCs, including the electrode/electrolyte, separator/electrolyte, inter-particles, and electrode/current collector interfaces, play a crucial role in KIFC performance and require comprehensive study for the

industrialization of KIBs so that it is important to address challenges like SEI growth, interface impedance, and electrode material compatibility to achieve efficient and stable KIFCs. Overall, a detailed investigation of these interfaces is vital for advancing KIFCs.

3. Latest achievements on K-ion Full-Cells

Due to the intense study of KIBs, there is an increasing interest among researchers in KIFCs, which is expected to lead to their practical application. Literature statistics indicate that while KIFCs focus on a variety of research objects, such as electrode materials and electrolytes. On the other hand, for quasi- and all-solid-state based KIFCs, the first focus is on electrolytes development. This section will provide a summary of the recent progress made in researching various KIFCs and delve into the strategies employed to tackle the issues.

3. 1 Nonaqueous liquid based-electrolytes

In 2017, several research groups presented their findings pioneer works on KIFCs. The group of S. Komaba [43] presented a PB//graphite full-cell (PB stands for Prussian Blue, here $K_{1.75}Mn[Fe(CN)_6]_{0.93}$, i.e. K-MnHCFE) that delivered a reversible capacity of 110 mAh g^{-1} with a mean operating voltage of 3.5 V, as shown in **Fig. 4(b₁)**. Note that the corresponding electrochemical behaviour of graphite//K and K-MnHCFE//K half-cells were also presented as references (**Fig. 4a₁**). Also, **Fig. 4(c₁)** represents that the full-cell also demonstrated acceptable capacity retention of 75% over 60 cycles. Regarding the rate capability, the full-cell shows good rate performance even at a current density of 2000 mA g^{-1} (i.e. equivalent to $15 C_{\text{discharge-rate}}$) with a capacity of 60 mAh g^{-1} , as shown in **Fig. 4(d₁)**. However, the electrode loading was not specified in this study. Table S1 illustrates consistently low loading across the majority of the referenced papers. X. Wang et al. [44] presented a KIFC based on interconnected $K_{0.7}Fe_{0.5}Mn_{0.5}O_2$ nanowires and soft carbon, which achieved a high initial coulombic efficiency (ICE) of $\sim 92\%$ in the first cycle. Although the cell delivered a discharge capacity of 82 mAh g^{-1} at 40 mA g^{-1} , the capacity retention was $\sim 90\%$ after 50 cycles, and a low operating voltage of 2.0 V was observed. However, the cell showed considerable long-term cycling stability even when tested at 100 mA g^{-1} . In the same year, a $K_{0.6}CoO_2$ //graphite full-cell was tested, which delivered a specific discharge capacity of $\sim 53 \text{ mA h g}_{\text{cathode}}^{-1}$ at a rate of 3 mA g^{-1} , with a capacity retention of 50% over 5 cycles [45]. Note that in this work, the graphite anode was cycled between 0.01 and 1.5 V before the full-cell assembly due to the large irreversible capacity in the first discharge process so that the capacity

retention of the full is more likely overestimated. Note also that no coin-cell assembling optimization was done. Moreover, a 3,4,9,10-perylene tetracarboxylic acid dianhydride (PTCDA)/pyridinic N-doped porous carbon monolith (PNCM) full-cell was assembled by pairing the as-obtained PNCM anode with PTCDA cathode [46]. The obtained KIFC exhibited discharge capacities of 245, 168, 143, 114, 99, and 85 mAh g⁻¹ (calculated based on the mass of the PNCM anode) at increasing current densities of 50, 100, 200, 500, 1000, and 2000 mA g⁻¹, respectively. After 70 cycles, the full-cell delivered a capacity retention of 37% at 100 mA g⁻¹. However, the capacity fades at long term cycling is probably due to PTCDA dissolution in carbonate-based electrolytes, which limits its practical use.

In 2019, various KIFC systems were investigated for their capacity and long-term cycling performance. One system was the K₃V₂(PO₄)₃/C//K₃V₂(PO₄)₃/C (KVP/C) symmetric full-cell, which exhibited an initial CE of 91.7% with charging and discharging capacities of 88 and 80.9 mA g⁻¹ during the first cycle [47]. The cell maintained a reversible capacity of 88.6% over 500 cycles, with an average voltage of 2.3V but with cathode and anode mass loadings of only 1 mg cm⁻². Another K-ion full-coin cell system was investigated in the same year, which developed reduced graphite (KC₈) as the anode and oxidized potassium 9,10-anthraquinone-2,6-disulfonate (KQ26DS) as the cathode [48]. This system delivered a capacity of 82 mAh g⁻¹ at 50 mA g⁻¹ with a capacity retention of 33% over 2500 cycles and an average voltage of 1.3V. The KQ26DS//KC₈ system exhibited a rate performance of 46 mAh g⁻¹ at 1000 mA g⁻¹. Another group investigated the performance of a PTCDA//KC₈, where the positive and negative electrodes were precycled vs K metal [49] to preform the SEI in half-cells and then limit the electrolyte degradation in the full-cell. This system exhibited an average voltage of 1.9 V and delivered a capacity of 140 mAh g⁻¹ at 50 mA g⁻¹ with 73% of capacity maintained over 30 cycles. The rate performance for this system was similar to the KQ26DS//KC₈ system, exhibiting 46 mAh g⁻¹ at 1000 mA g⁻¹. Still in 2019, another group proposed a KIFC system based on P2-K_{0.75}MNFO₂ and hard carbon as cathode and anode electrode materials, respectively [50]. The full-cell exhibited an initial discharge capacity of 60 mAh g⁻¹ and stable long-term cycling, with approximately 60% capacity retention over 1000 cycles at 0.2C and an average voltage of 2.1V. The diffusion pathways of K ions and the activation barrier energy for K⁺ diffusion in the P2-K_{0.75}MNFO₂ structure were calculated using the nudged elastic band method, supporting the experimental observation of the excellent power capability of the P2-K_{0.75}MNFO₂ active material. Another study used a P2-K_{0.83}[Ni_{0.05}Mn_{0.95}]O₂//hard carbon full-cell

system, which demonstrated a high capacity of 135 mAh g^{-1} (2.1V average voltage) and exceptional long-term cyclability, with a capacity retention of approximately 80% over 300 cycles [51]. However, the active material loading was only 3 and 2.3 mg/cm^2 for cathode and anode materials, respectively. Ex situ XRD and TEM analysis of electrodes before and after extensive cycling confirmed the structural stability of the $\text{P2-K}_{0.83}[\text{Ni}_{0.05}\text{Mn}_{0.95}]\text{O}_2$. The post-cycled electrode maintained its high crystallinity, sharp features of (002) and (004) peaks for the P2 phase, and slight variation in lattice parameters. TEM analysis of electrodes before and after extensive cycling further confirmed that the post-cycled electrode maintained the original morphology of the pre-cycled electrode without morphological degradation after 500 cycles. However, this finding was reached after the cathode and anode were precycled vs K metal so that electrolyte degradation was reduced in the full-cell, which more likely led to an overestimation of the long term capacity retention. Still in 2019, Komaba's group [52–54] conducted three studies on $\text{K}_2\text{MnFe}(\text{CN})_6$ //graphite full-cells. In the first study, the group investigated the impact of electrolytes on the cell's performance [52]. They found that using a $1\text{M K}[\text{FSA}]/[\text{C}_3\text{C}_1\text{pyrr}][\text{FSA}]$ electrolyte resulted in a capacity retention of 76% after 200 cycles with an initial discharge capacity of 91 mAh g^{-1} . Between the 2nd and 200th cycles, the average voltage and CE were 3.2 V and 99.5%, respectively, which was better than anything previously reported for KIFCs. The use of FSA-based ionic liquid improved stability and passivation ability, preventing undesired side reactions at both the graphite anode and Prussian blue analogue cathode interfaces. Note, however, that the active mass loading was still limited to 4.0 and 2.0 mg/cm^2 for the cathode and anode, respectively. In the second study, the group evaluated the use of different KFSI-KPF₆-binary based electrolytes and selected PTFE (Polytetrafluoroethylene) and CMC (carboxymethylcellulose) binders for the positive and negative electrodes, respectively [53]. They found that the KICF with 0.75KPF_6 - 0.25M KFSI EC/PC electrolyte demonstrated the highest initial coulombic efficiency, ICE of 72.5% and the smallest polarization, delivering a reasonably high reversible capacity of 105 mAh g^{-1} with an average voltage of 3.6 V (**Fig. 4a2 and b2**). The capacity retentions of 0.75M KPF_6 - 0.25M KFSI EC:DEC and 0.75M KPF_6 - 0.25M KFSI EC:PC cells after 500 cycles were 72 and 75%, respectively. Such capacity retention were far superior to the full-cell using the commonly used $0.75\text{M KPF}_6 \text{ EC:DEC}$ based electrolyte (37%), as shown in **Fig. 4(c2)**. An increase in the average voltage was noticed from 3.2 to 3.6 V compared to the previously mentioned study with ionic liquid-based electrolyte. It is also significant that the full-cells maintained more than

85% of reversible capacity at a 5C discharge rate compared to that of 0.1C regardless of the electrolyte, which demonstrates good rate capability for the full-cells [53]. Note, however, that such high rate capacity were achieved for cathode and anode active material loading of 4.0 and 2.0 mg/cm², respectively. In the third study, the group investigated the electrochemical performance of KIFCs using two different glyme-based highly concentrated electrolyte solutions: 5.5 mol kg⁻¹ KFSI G1 + 0.5 wt% vinylene carbonate (VC) and 5.6 mol kg⁻¹ KFSI G3 + 0.5 wt% VC. The addition of 0.5 wt% VC into the electrolyte solution was effective in suppressing the initial irreversible capacity of the full-cells [54]. The G1 and G3 cells delivered reasonable initial discharge capacities of 86 and 79 mAh g⁻¹, respectively (**Fig. 4a3 and b3**). The cell with G1 showed a significant decrease in discharge capacity after 100 cycles, while the cell with G3 exhibited considerably higher cycle performance, maintaining high CE over 100 cycles (**Fig. 4c3**). The study suggests that KFSI G3 electrolytes are more suitable for high voltage (3.95 V) than KFSI G1 electrolytes. The high oxidation stability of KFSI G3 electrolytes was explained by the strong interaction of K ions with long glymes (Solution structures were investigated using Raman spectroscopy).

In 2021, an investigation was conducted on a natural graphite vs Prussian blue/polyvinylpyrrolidone/reduced graphene oxide (PB/PVP-rGO) as full-cell [55]. The intercalated graphite (KC₈) was employed as the anode for the full-cell electrochemical testing, prepared through pre-potassiation vs. K metal. The rate performance of the composite-based full-cell was evaluated with a current density range of 0.5-10 C. PB/PVP-rGO displayed excellent rate performance, achieving capacities of 127.9, 115.5, 104.7, 89.0, and 77.0 mA h g⁻¹ at 0.5, 1, 2, 5, and 10 C, respectively. Furthermore, PB/PVP-rGO//KC₈ cells exhibited 88.1% of capacity retention over 150 cycles at 1C with an average voltage of 3.3 V.

In 2022, A. Li et al. [56] studied a new type of Pitch-derived soft carbon vs. K_{1.69}Mn_{0.779}Ni_{0.221}[Fe(CN)]_{0.93}·0.392H₂O as full-cell. The assembled full-cell also exhibited high-rate capability, maintaining a discharge capacity of 62.5 mAh g⁻¹ at a current density of 500 mA g⁻¹. When the current density was brought back to 50 mA g⁻¹, a reversible capacity of 87.2 mAh g⁻¹ was recovered. As well, the cycling performance was evaluated at 100 mA g⁻¹, and 89.6% of the initial capacity (71.8 mAh g⁻¹) was maintained after 100 cycles, with an average potential of 3.83 V.

In 2023, research was conducted on a $\text{K}_{0.95}\text{Cs}_{0.05}\text{VPO}_4\text{F}/\text{graphite}$ full-cell that used Cs^+ doping to lower the energy barrier for ion diffusion and volume change during the potassiation/depotassiation process of the cathode active material [57]. This resulted in an important improvement in the K^+ diffusion coefficient and provided stability to the positive electrode framework. The full-cell had a high average voltage of 3.93 V and provided a capacity of 103 mAh g^{-1} at 100 mA g^{-1} . The capacity retention was high, with 90% of the capacity being maintained over 1000 cycles. Additionally, the full-cell could reach a capacity of 62.7 mAh g^{-1} when cycled at 2000 mA g^{-1} . The Cs^+ doping approach used in this study could have a significant impact on the development of high-performance cathode material for KIBs.

In the field of KIFC, **Table S1** provides a comprehensive summary of the full-cell system evaluated so far, highlighting its tremendous potential. However, upon thorough analysis, we notice that most studies involve a pre-cycling of the electrodes versus K-metal before assembling the full-cells, which first is not practical and second more likely leads to overestimation of the full-cells capacity retention. Also importantly, the practical cathode active mass loading should be higher than 8 mg/cm^2 (ideally as high as possible) for an up-scaled application while it remains always between 0.5 and 6 mg/cm^2 in all studies so far [58]. Additionally, many investigations still utilize glass fiber (GF) as a separator, which is not optimal for practical use.

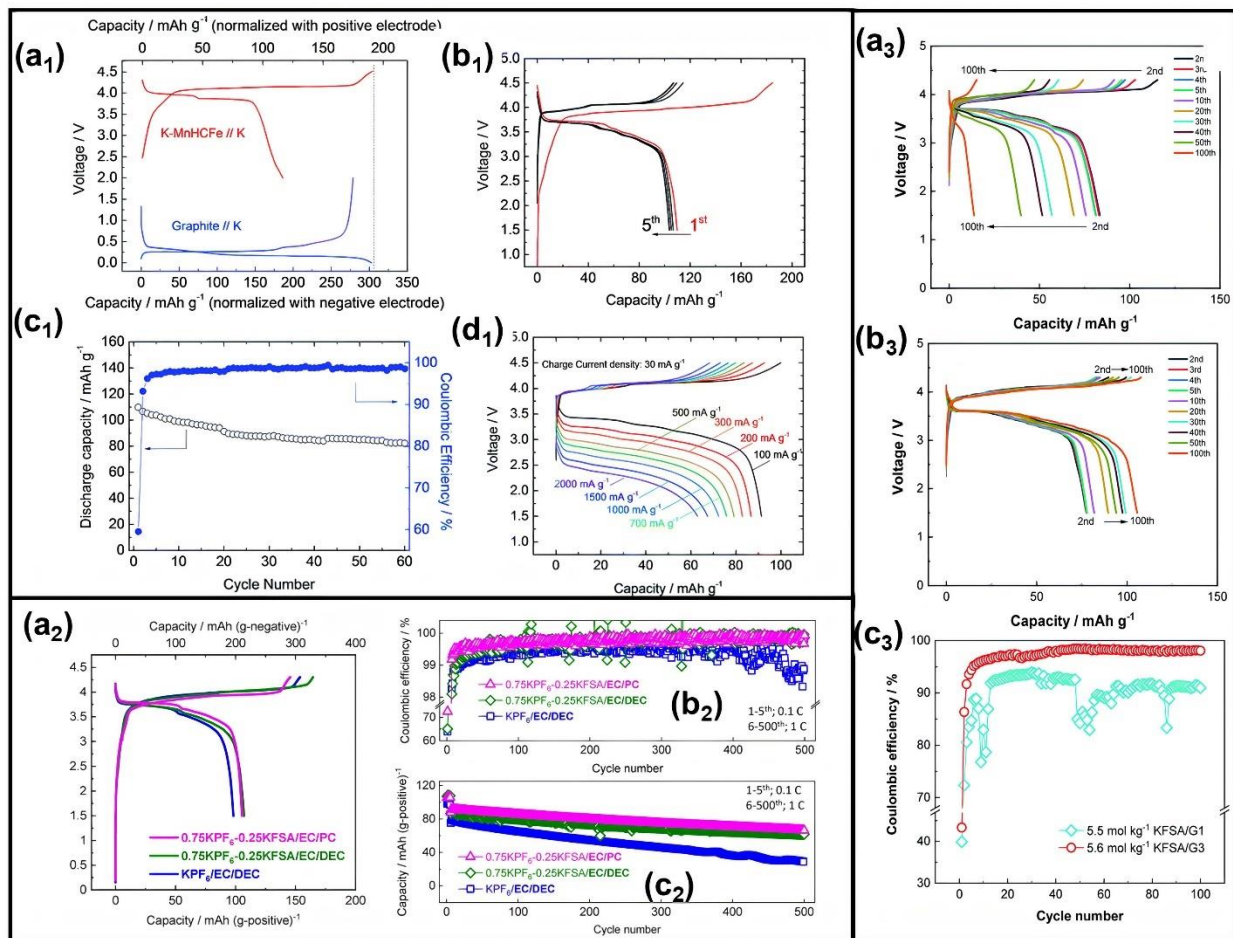


Fig. 4. (a₁) Initial charge–discharge profiles of K-MnHCFE//K and graphite//K in a half-cell configuration, (b₁) electrochemical cycling profiles of the K-ion cell, K-MnHCFE/graphite, cycled at a current rate of 30 mA g⁻¹ cathode in a voltage range of 1.5 – 4.5 V, c₁) long term cycling capacity and efficiency, and (d₁) rate performance of the K-ion full-cell, charge current density is 30 mA g⁻¹ and discharge current densities are from 100 to 2000 mA g⁻¹. Reproduced permission from Ref. [43] Copyright 2017, Royal Society of Chemistry. (a₂) Initial charge/discharge profiles of graphite//K₂Mn[Fe(CN)₆] full-cell filled with 0.75 mol kg⁻¹ KPF₆/EC/DEC, 1.0 mol kg⁻¹ K(PF₆)_{0.75}(FSA)_{0.25}/EC/DEC, and 1.0 mol kg⁻¹ K(PF₆)_{0.75}(FSA)_{0.25}/EC/PC, (b₂) evolution of their specific capacity, and (c₂) evolution of their CE. The current density was 15.5 mA g_{cathode}⁻¹ from 1st to 5th cycle and 155 mA g_{cathode}⁻¹ from 6th to 500th cycle. Reproduced with permission from Ref. [59] Copyright 2020, American Chemical Society. (a₃) Charge – discharge profiles of graphite//K₂Mn[Fe(CN)₆] full-cells filled with 5.5 mol kg⁻¹ KFSI/G1 + 0.5 wt% vinylene carbonate

(VC), and **(b3)** 5.6 mol kg⁻¹ KFSI/G3 +0.5 wt% VC, **(c3)** Evolution of their CE upon 100 cycles. Reproduced with permission from Ref. [54] Copyright 2020, Royal Society of Chemistry.

3. 2 Quasi- and All-Solid-State based-electrolytes

Despite significant progress in the development of KIBs since 2015, there are still several challenges that need to be addressed, particularly the issue of severe side reactions between the electrolyte and K metal due to its high reactivity [8]. These reactions can result in an unstable SEI and low CE. Therefore, the selection of an excellent electrolyte is crucial for the advancement of KIBs. Unfortunately, there has been a lack of systematic research on electrolytes and their role in performance, taking into consideration safety concerns [60].

To overcome this limitation, quasi and all-solid-state electrolytes have gained attention, as they are non-flammable and do not present risks of leakage or explosion. These electrolytes can be categorized into inorganic, organic, and hybrid-based types [61]. While inorganic-based solid-state electrolytes (SSE) have been studied for their high ionic conductivity, their synthesis typically requires high temperatures and they tend to have poor interface contact with electrodes, hindering further improvement [60]. On the other hand, organic-based electrolytes offer simple preparation, excellent chemical stability, and good interface contact with electrodes, and have garnered significant interest [23,62]. However, their low ionic conductivity at room temperature limits their application, especially for low-operating temperatures. Therefore, hybrid based SSE could be a promising alternative that combines the features of all the mentioned types.

The quasi and all-solid-state electrolytes application in KIBs gained momentum in 2018 when the synthesis of inorganic 3D open-framework potassium ferrite, $\text{K}_2\text{Fe}_4\text{O}_7$, was successfully achieved through an hydrothermal process [63]. The framework of $\text{K}_2\text{Fe}_4\text{O}_7$ comprises FeO_6 octahedral and FeO_4 tetrahedral units, allowing for high ionic conductivity through the channels. The polycrystalline sample exhibited an ionic conductivity of $5 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature, with an activation energy of 0.08 eV (7.7 KJ mol^{-1}). Notably, the all-solid-state potassium metal battery with a Prussian blue cathode demonstrated exceptional rate capability, delivering a reversible specific capacity of 13 mAh g^{-1} at a high charge/discharge rate of 250C (charge/discharge in 14 s), and a reversible specific capacity of 87 mAh g^{-1} for the cell cycled at 1C (charge/discharge in 1 h). These results go well beyond those reported for KIBs using liquid electrolytes vs K metal. In the same year, Huifang Fei et al. [64] presented a study on all-solid-state electrolytes based on 3,4,9,10-perylene-tetracarboxylic acid-dianhydride (PTCDA) as the positive electrode and solid polymer electrolyte (SPE) for the first time. The SPE employed was Poly(propylene carbonate)-KFSI with

cellulose nonwoven backbone (PPCB-SPE), which exhibited an ionic conductivity of $1.36 \times 10^{-5} \text{ S cm}^{-1}$ at 20°C . The PTCDA cathode in the all-solid-state battery demonstrated a working discharge voltage of 2.3 V, an initial high capacity of 118 mAh g^{-1} at 10 mA g^{-1} (**Fig. 5a1**), and over 40 cycles, the cell retained 84% of its initial capacity (**Fig. 5b1**). At the opposite, the cell with organic-liquid electrolyte (KFSI based-electrolyte) presented a significant capacity fading of 45.7%, likely due to the high solubility of PTCDA into the organic-liquid electrolyte. This highlights the crucial advantage of using all-solid-state electrolytes in the case of organic electrodes and underlines the potential for further investigations. In the subsequent year, the same group designed a $\text{Ni}_3\text{S}_2@\text{Ni}$ electrode for KIBs with a poly(ethylene oxide)-bis(fluorosulfonyl)imide (PEO-KFSI)-based hybrid electrolyte, which exhibited an ionic conductivity of up to $2.7 \times 10^{-4} \text{ S cm}^{-1}$ at 60°C [65]. The electrochemical performance of the solid-state KIBs revealed a high capacity of 312 mAh g^{-1} with a high CE of 97% during the first discharge process. The high CE can be attributed, in part, to the less solid electrolyte interphase growth. In 2021, Guangyuan Du et al.[60] introduced a novel approach to prepare polymer-based hybrid electrolyte membranes as quasi solid-state electrolytes using perfluorinated sulfonic resin powder (referred to as PFSA-K membrane). This method represents the first-ever development of such membranes for low-operating temperature of a KIB system. The PFSA-K membranes exhibit promising ionic conductivity across a wide temperature range from -15 to 85°C , as well as excellent electrochemical stability and high mechanical flexibility. The synthesized electrolyte demonstrates good mechanical flexibility, outstanding electrochemical stability, and high ionic conductivity of $9.31 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C . Commercial raw materials, namely PTCDA and graphite were used as the cathode and anode materials to assemble the first quasi solid-state KIB cell, which exhibits excellent performance at low temperatures, with a reversible capacity of 94.8 mAh g^{-1} even at -15°C . Upon returning to 25°C , the initial capacity was recovered (**Fig. 5a2**). The cycling performance at -15°C and 100 mA g^{-1} shows a capacity retention of 85% over 200 cycles (**Fig. 5b2**), with an average CE close to 100%, indicating the stability and practicality of the PFSA-K membrane as quasi-solid-state electrolyte for KIBs operating at low temperatures. These results confirm the great potential for further commercialization.

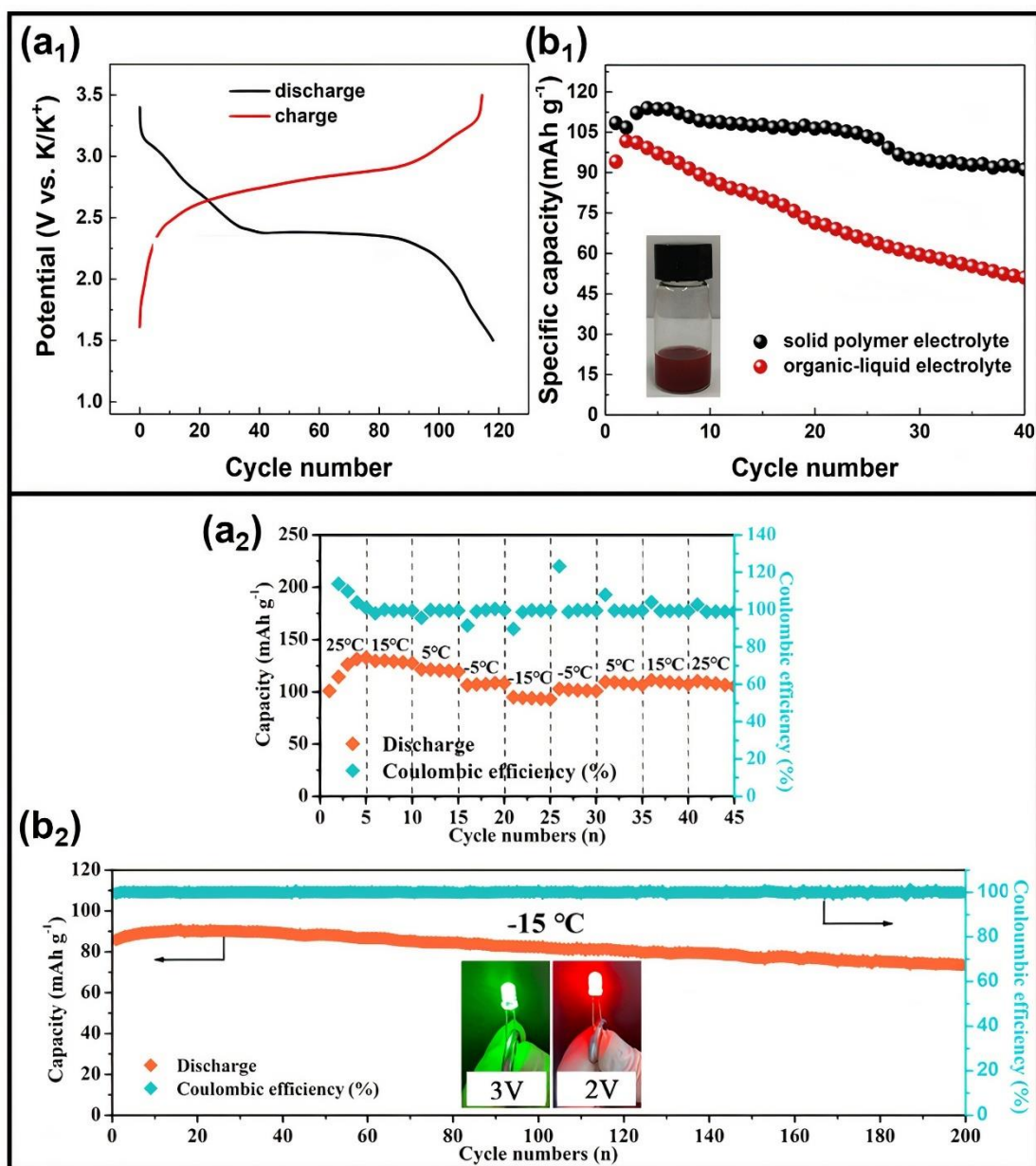


Fig. 5. (a1) Charge/discharge profiles of PTCDA with PPCB-SPE at a current density of 10 mA g⁻¹. (b1) Cycling performance of PTCDA with PPCB-SPE or organic-liquid electrolyte at a current density of 20 mA g⁻¹. The inserted digital image is the solubility test of PTCDA in 1M KFSI in EC/DEC (v/v, 1:1) electrolyte. Reproduced with permission from Ref. [64] Copyright 2018, Elsevier. (a2) Cycling performance at different temperature and (b2) capacity vs. cycle number of PCTDA || PFSA-K || Graphite full-cell at -15 °C. Reproduced with permission from Ref. [60] Copyright 2021, Elsevier.

4. Improvement strategies for innovative KIFCs

The previously mentioned achievements suggest that KIFCs have the potential to play a crucial role in the energy storage landscape, offering a sustainable and efficient solution for a range of applications, from portable electronic devices to grid energy storage. However, despite these remarkable advancements, several challenges still need to be overcome to fully achieve efficient and reliable KIBs as discussed thereafter. Thus, the following subsections will address the main strategies to improve further KIFCs with: (i) the optimization of electrolytes in regards to the SEI layers formation and thus the capacity retention (i.e. lifetime) improvement; (ii) the screening of electrodes materials in regards to the power and/or energy applications; (iii) a guideline regarding the assembly of liquid based KIFC so that highly reliable cells are obtained and (iv) others strategies to further unlock the full potential of KIBs.

4.1. Optimizing electrolytes to enable stable passivation layers.

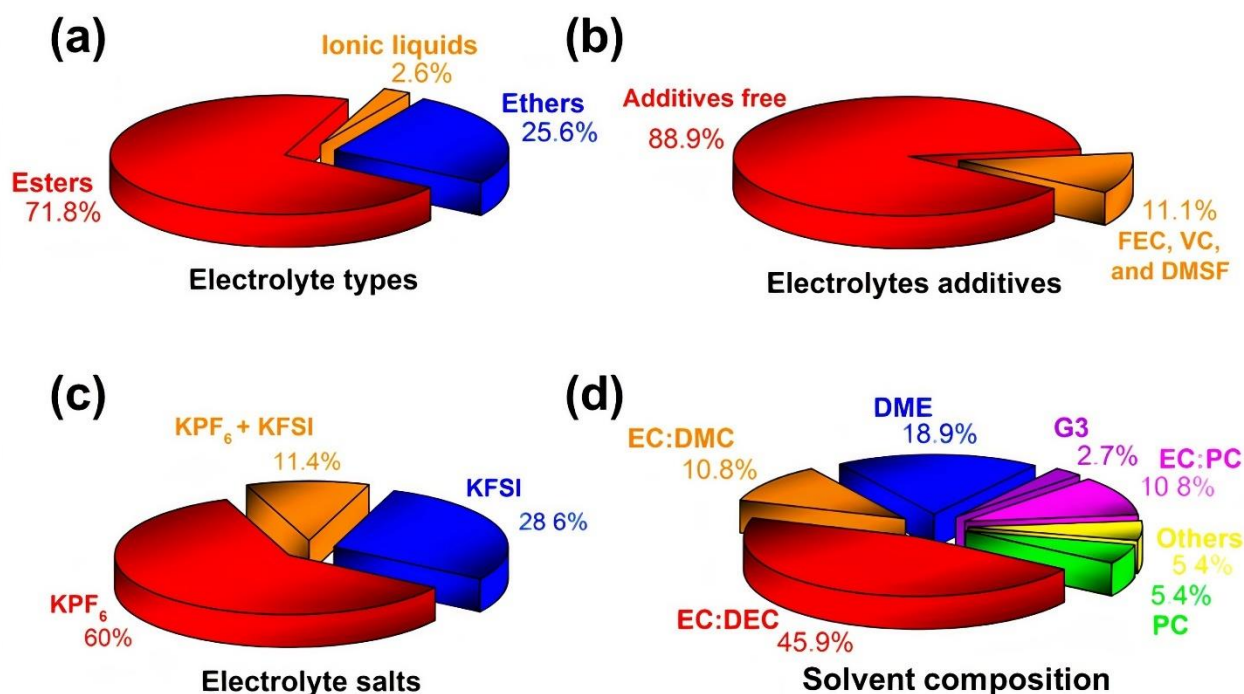


Fig. 6. Summary for the distribution of electrolyte (a) types, (b) additives, (c) salts, and (d) solvent composition in KIFCs.

Anodes and cathodes working at lower and higher voltages are commonly used to develop cells with higher energy. However, this often leads to higher electrolyte side reactions and the formation of thicker SEI films with higher impedance, thus lowering the overall cells performance. **Fig. 6(a)**

depicts that nonaqueous liquid electrolytes for KIFCs are classified into three categories: esters, ethers, and ionic liquids. It can be observed that ester-based electrolytes are the most used in KIFCs and are usually binary solvent systems. Although ethers exhibit good compatibility with most anodes, their susceptibility to oxidation at high voltages makes them rarely used in full-cells so far [66–68]. Ionic liquids offer higher safety and can operate over a wide temperature range, but their high viscosity, low ion mobility, and high cost limit their further application [69,70].

The ionic conductivity of the liquid electrolyte is closely related to the solvent's viscosity and dielectric constant. An ideal electrolyte should have high ionic conductivity, low viscosity, and sufficient high dielectric constant. Unfortunately, many solvents exhibit a mutual correlation between these parameters, so they are often used in combination with other solvents. The most commonly used solvents in current full-cells are EC, PC and DEC solvents (**Fig. 6d**), which often leads to poor cycle stability and should be used in combination with other solvents or additives. Linear carbonates exhibit lower viscosities and lower dielectric constants, but they usually involve poor electrochemical performance when used alone. Thus, they are often used as auxiliary solvents for the above two solvents (EC and PC) to enhance the overall performance of the electrolyte, and SEI stability [67]. Overall, the most commonly used solvents composition is EC:DEC.

The electrolyte salt type (**Fig. 6c**) is also an important factor to control the electrochemical performance (ionic conductivity, solvation/desolvation energy) and SEI formation. KPF_6 is the most commonly utilized electrolyte salt in KIFCs. It has moderate solubility in esters and the PF_6^- anions provide a passivation effect on the aluminium current collector. KPF_6 -based electrolytes have been extensively studied and used in K-ion batteries [13,71]. However, the drawback of KPF_6 -based electrolytes is that they tend to form an unstable SEI mostly based on organic solvent degradation products (in carbonates) on the anode surface as demonstrated so far in a half-cell using the highly reactive K metal [8,19,72]. Thus, most KPF_6 -based electrolytes have low CE due to insufficient SEI passivation. On the other hand, KFSI-based electrolytes have also been studied, owing to their stable SEI growth (based mostly on KFSI degradation products in carbonates as observed in half-cells studies so far), resulting in low irreversible capacity and stable CE evolution upon electrochemical cycling. In contrast, they suffer from several issues, especially corrosion of the aluminium (Al) current collector at moderate and high voltages [53]. So, one possible solution to the Al corrosion issue is to utilize highly concentrated KFSI electrolytes (as illustrated in **Fig.**

7) along with KFSI-containing ionic liquids [13,52,73]. Nonetheless, KPF₆-KFSI binary salt electrolyte with a suitable salts ratio can overcome this challenge, leading to both effective Al passivation and high CE (as depicted in **Fig. 7**) [53]. This approach resolves the dilemma and offers a promising way forward.

Regarding additives, it is evident that this is a barely explored aspect in K-ion batteries (i.e. 88.9% of studies do not address additives), as shown in **Fig. 6(d)**. To date, the majority of existing studies on additives in KIBs have been conducted in half-cell configuration rather than in full-cell, impacting the potassium metal SEI [12,74]. The observed electrochemical improvements may come from stabilizing the SEI of the potassium metal rather than the interface of the studied material. Consequently, electrolyte studies need to be conducted in a full-cell configuration for a comprehensive understanding.

In summary, the development of efficient and reliable nonaqueous electrolytes for K-ion batteries still faces numerous challenges. Future research should focus on the following aspects. Firstly, the formation mechanism and charge transfer of the SEI layer for full K-ion batteries are still not well explored, and more investigation is rapidly needed. Advanced in situ characterization methods, including in situ and operando analysis techniques, as well as theoretical simulations [75] can be used to explore further the reaction mechanism, crosstalk phenomenon [76], and microstructure of the electrode/electrolyte interface. Secondly, efforts should be made to reduce or control side reactions at high voltage. Although concentrated electrolytes can regulate polarization and reduce side reactions by solvation effects, their oxide-resistant properties at high potential should also be considered [54]. While KFSI-based electrolytes have been widely studied for their ability to make stable interfaces, their tendency to corrode the collector at high potential should be considered. Therefore, it is necessary to develop a more suitable new-type K-salt system, such as binary-salts, that can build a stable interface and avoid collector corrosion simultaneously. As the chemistry of electrolytes and their associated electrode/electrolyte interface continue to develop, we are confident that K-ion batteries with high energy density (and thus with relatively high voltage), low cost are possible.

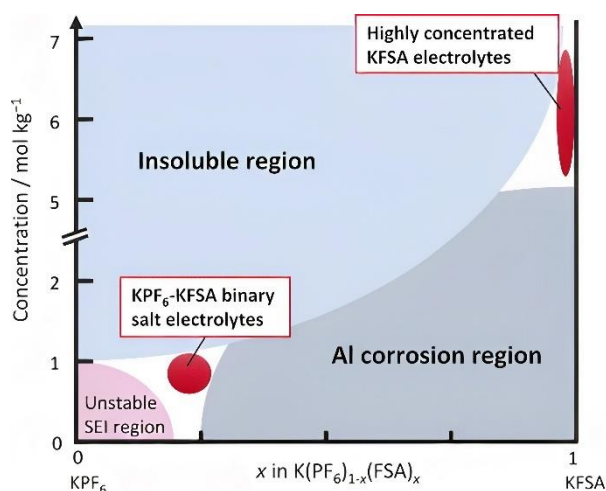


Fig. 7. Diagram of binary KPF_6 -KFSI (in the diagram, KFSA stands for KFSI) salts ratio and concentration as function of corrosion, solubility, and SEI stability region. Reproduced from Ref. [68] with permission from the Chemical Society of Japan.

4.2. Screening electrode materials for power and/or energy applications

At present, most of the work on KIFCs is based on nonaqueous liquid electrolytes. As illustrated in **Fig. 8**, among these reported KIFCs, the most prevalent positive electrode materials are PBAs (Prussian Blue Analogues) compounds followed by organics, while carbonaceous materials are the mainstream in negative electrodes materials [56,77–79].

Regarding anodes materials, graphite has demonstrated reasonable electrochemical performance when appropriate binders and electrolytes are used. Although other carbon forms have been shown to intercalate K ions, they are unlikely to be as effective as graphite in terms of energy (i.e. hard and soft carbons present a higher average potential and lower electrode density compared to graphite) [80]. Alloying anodes may not be a suitable choice for KIBs, as the same issues that affect them (i.e. huge volume expansion, and rapid capacity degradation) in LIBs and NIBs are worsened in KIBs, resulting in a significantly reduced energy density [81]. However, Gu et al. [82] explores enhancing the performance of the Alloy CoSe anode material by introducing a flexibly designed core-shell structure (CoSe-C@C) and promoting an SEI rich in inorganic compounds. The CoSe-C@C electrode shows remarkable stability, maintaining a high capacity of 432 mA h g^{-1} at 200 mA g^{-1} over 1000 cycles and demonstrating high rate capability (233 mA h g^{-1} at 10 A g^{-1}). On the other hand, intercalation oxide and phosphate materials have been shown to be stable for long-term cycling (i.e. $\text{K}_2\text{Ti}_4\text{O}_9$, $\text{K}_2\text{Ti}_8\text{O}_{17}$, and $\text{KTi}_2(\text{PO}_4)_3$), in contrast candidates with higher capacity

and low average voltage are still needed [83–85]. Finally, conversion and organic molecules as anode materials are still in the early stages of development and require further evaluation for practical application. Hence, to advance the practical application in KIFCs and achieve enhanced performance, there is a need for further research and investigation into carbonaceous negative electrodes (i.e. composition, doping, and optimization of the electrode formulation process).

In the range of positive electrode materials for K-ion batteries, various types have been explored, each with its own set of advantages and drawbacks. Organic materials, such as small organic molecules, polymers, and organometallic complexes offer the benefits of low cost and reduced energy consumption during synthesis. However, they require an additional pre-potassiation step before use. Although organic cathode materials like Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and polyanthraquinone sulfide (PAQS) exhibit high capacity, they face challenges such as the need for annealing to improve electronic conductivity, slow ion migration, dissolution issues at high current densities, and low electronic conductivity [86,87]. Nonetheless, organic materials still hold potential for high capacity and good cycling performance for grid applications. Layered oxides, known for their high energy density, are commonly used as cathodes in Li-ion batteries and Na-ion batteries [88]. They have a 2D framework where transition metals and alkali ions are arranged in alternating blocks, facilitating rapid alkali ion migration. Various layered oxides have been developed for K-ion batteries, including $K_{0.3}MnO_2$ [89], P3-type $K_{0.5}MnO_2$ [90], and P2- and P3-type K_xCoO_2 [91]. However, layered K-compounds exhibit a low working potential, steeper voltage curves, and more voltage steps compared to Li and Na systems due to long-ranged repulsive interactions between alkali ions [92]. Additionally, the inherent structural instability of layered oxides limits their maximum allowable voltage, leading to capacity decay during overcharge [93]. Structural alteration upon depotassiation further restricts the range of K de/intercalation. Overcoming these limitations requires further investigation. PBAs have gained attention for K-ion batteries. While their use is not based on the performance of their Li counterparts, they offer stability, high ionic diffusion coefficient, and working potentials that exceed those of LIBs [94]. The electrochemical performance of PBA depends on chemical composition, morphology, particle size, and interstitial water content [30]. They display good performance at high current densities and have the potential for high capacity. However, their low-rate performance compared to polyanionic materials has limited their use from the power application point of view.

Polyanionic compounds, represented by $M_xT_y(XO_4)_z$ structures, exhibit good thermal and structural stability, operate at high potentials, and allow for rapid ion diffusion. However, they generally have low practical capacity, poor CE, and low electronic conductivity due to insulating groups between transition metals [95]. Notably, polyanionic compounds based on vanadium and phosphates or fluorophosphates have shown promising electrochemical properties for K-ion batteries. Various structures, including Tavorite compounds based on fluorophosphate and vanadium exhibit high operating potentials and theoretical energy densities comparable to $LiFePO_4$ [96]. For practical use, fluorophosphates (power applications) and PBAs (energy applications) demonstrate promising electrochemical performance with high working voltage, high-rate performance, and high structural stability. However, despite their potential, both fluorophosphates and PBAs require further improvement to address challenges such as capacity limitations, and low electronic conductivity. Continued research and development efforts are necessary to optimize their electrochemical properties and enable their practical application in full K-ion batteries.

To summarize, numerous studies have employed lamellar oxides as positive electrodes in K-ion batteries. However, these materials require enhancements due to their limited capacity and average voltage (i.e. new phases with more Manganese and Nickel). On the other hand, Prussian blue and its analogues have shown promise with their high capacity and average voltage. Yet, their water content remains a challenge that must be addressed to prevent catalytic reactions and safety concerns, especially at high voltage. Organic molecules used as cathode materials exhibit a combination of high capacity and low operating voltage. Nonetheless, there is route for improvement, particularly in mitigating the dissolution in organic electrolyte of these molecules and enhancing their density. Polyanionic frameworks as cathode materials offer advantages such as high power density and high average potential. However, their high anodic voltage limit, typically in the range of 4.5 to 5 volts, presents a challenge for conventional carbonate-based electrolytes, which struggle to resist such high potentials. In this context, the way of progress focuses on the electrolyte design, involving the strategic combination of additives (i.e. succinonitrile [97], vinylene carbonate [98], propene sulfone [99], and so on) and materials design, which involves the doping [100], coating [95,101], and substitution [102]. Turning to the negative electrode side, graphite emerges as a promising candidate for KIFCs, but the volume expansion issue (approximately 60%) needs to be carefully addressed. Furthermore, a significant gap remains in the systematic research on electrolytes and their effects on KIFC performance, especially in

terms of safety considerations. Additionally, the low ionic conductivity of organic-based electrolytes at room temperature presents a limitation that could be addressed using solid-state based electrolytes.

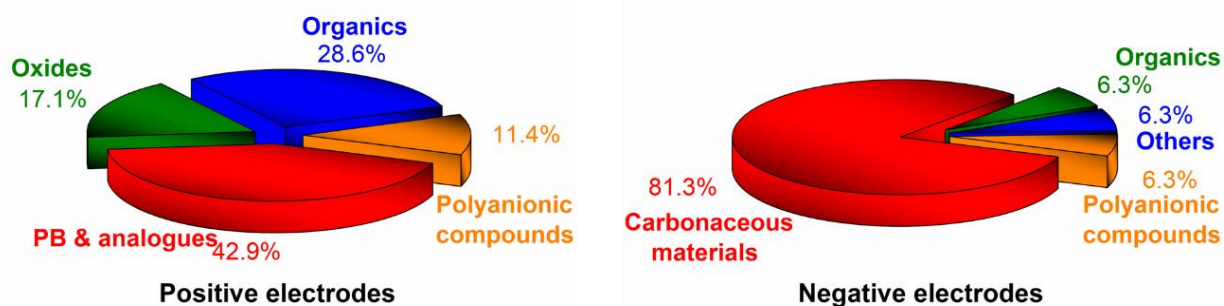


Fig. 8. Distribution summary of different electrodes materials in KIFCs (PB stands for Prussian blue).

4.3 Improving liquid KIFCs parameters: Guideline toward reliable cells.

This subsection aims to eliminate the need for electrochemical pre-cycling of electrodes prior to full-cell assembly, paving the way for the development of reliable KIFC configurations.

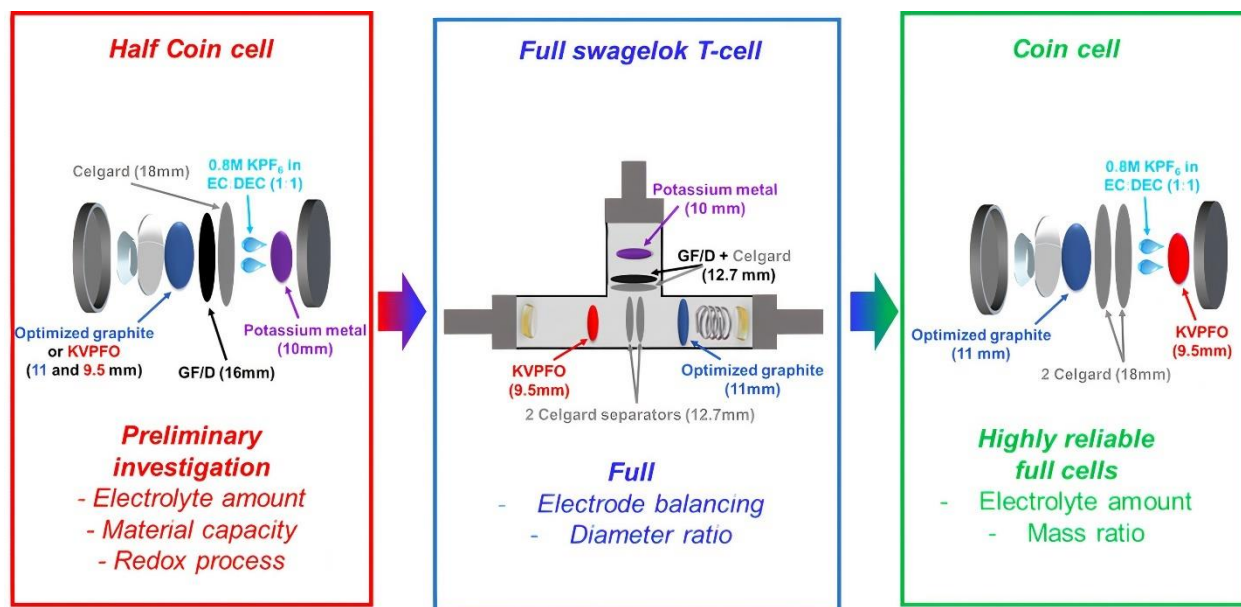


Fig. 9. Schematic representation of the method followed to optimize the assembly of highly reliable K-ion full coin cells. Reproduced with permission from Ref. [24] Copyright 2023, Wiley-VCH.

A full-cell optimization guideline was recently published, focusing on evaluation of different parameters for practical K-ion batteries assembly, as illustrated in **Fig. 9** [24]. Due to their promising electrochemical performance, graphite and KVPO₄F_xO_{1-x} were chosen as active materials for the negative and positive electrodes, respectively. Note that another study have also previously addressed the challenge of graphite volume expansion by optimizing the electrode formulation (i.e. carbon additive content, binders choice and amount...), enhancing its potential as an electrode material [103]. Among the KVPO₄F_xO_{1-x} family, KVPO₄F_{0.5}O_{0.5} (KVPFO) exhibits the most favourable galvanostatic profile, showing lower polarization, smoother redox plateaus, improved reversible capacity, and CE [96]. The full-cell optimization guideline study aimed at assessing the parameters impacting the performance of half-cells before assembling full-cells. To ensure accurate evaluation, precautions were taken during the preparation of K metal electrodes. The investigation highlights the importance of using a glass fiber separator on the K metal electrode side, due to its electrochemical instability when using Celgard or Solupor separators [24]. The choice of electrolyte also plays a crucial role, with 0.8M KPF₆ EC: DEC exhibiting lower polarization versus K metal compared to other electrolytes tested. Interestingly, the volume of electrolyte, while often overlooked in literature, was found to significantly impact half-cells and full-cells performance. An optimal electrolyte volume of 70 μ L was determined for both KVPFO and graphite half-cells, four times the total porosity of electrodes and separators. The impact of electrolyte volume on full-

cell performance was also investigated. Increasing the electrolyte volume from 15 to 50 μL enhances capacity and CE while reducing polarization. However, further increasing the volume to 70 μL and 100 μL decreases capacity and CE, likely due to excessive electrolyte degradation and passivation of electrode surfaces by SEI. The optimal electrolyte volume for KVPFO//graphite cells was found to be 50 μL , four times the total porosity of electrodes and separators as for half-cells.

This study also examined the influence of the negative//positive (N/P) electrode diameter ratio on full-cell performance. Larger diameter ratios lead to increased irreversible capacity and polarization associated with electrolyte degradation. A N/P diameter ratio of 1.16 was found to provide optimal performance. Further investigation into the graphite//KVPFO capacity ratio reveals that a ratio of 1.16 provides the highest initial capacity, CE, capacity retention, and lowest polarization. Lower and higher ratios result in limitations involved by KVPFO and graphite electrodes, respectively.

Furthermore, Pre-cycling the electrodes before battery assembly may offers an effective solution for the balancing challenges. However, this method encounters safety concerns and high expenses. Zhao et al. [104] presented a cost-effective and direct approach to compensate for potassium deficiencies by using a self-sacrificial additives (i.e. as $\text{K}_2\text{C}_4\text{O}_4$) within positive electrode to enhance potassium-ion battery performance. Their findings demonstrate that incorporating $\text{K}_2\text{C}_4\text{O}_4$ into a P3-type $\text{K}_{0.5}\text{MnO}_2$ cathode remarkably elevates the initial coulombic efficiency from 53.6% to an unprecedented high of 93.5%.

Finally, the optimized N/P diameter and capacity ratios were applied to assemble high-loading KVPFO//graphite coin cells (4 mg cm^{-2} for graphite and 10 mg cm^{-2} for KVPFO). The study achieves an energy density of approximately $47 \text{ Wh kg}^{-1}_{\text{device}}$ with 68% capacity retention after 20 cycles, representing probably the highest reported energy densities for KIBs, especially considering the high active material mass loadings. Thus, with optimized electrode formulation and practical electrolyte volume, pouch cells could potentially reach an energy density of around 80 Wh kg^{-1} . These findings thus highlight the importance of electrode material selection, electrolyte choice, electrolyte volume, electrode surface ratio, and electrode areal capacity ratio in optimizing the performance of KIFCs and also importantly their reliability, thus paving the way for their potential application as high-energy density storage systems.

Furthermore, the analysis of solid electrolyte interphase and cathode electrolyte interface in full-cell configurations requires more investigations due to the superior reliability of results and the circumvention of K metal cross-talk species compared to half-cell studies. Notably, the SEI and CEI layers in full-cell setups were found to be notably thinner, measuring less than 5 Å [105], as opposed to the substantially thicker layers exceeding 10 Angstroms observed in half-cell configurations [27]. This distinction underscores the heightened relevance of investigating these interfaces within full-cell configuration.

Moreover, Larhrib et al. showed an insightful exploration into the SEI and CEI growth and aging in KVPFO/graphite full-cells. As summarized in **Fig. 10**, their investigation shed light on critical findings: **(i)** Open circuit voltage (OCV) temperature Influence: Higher OCV temperatures, particularly at 40°C for 12 hours, resulted in a pronounced inorganic passivation layer. This enhancement potentially improves electrode wetting by electrolyte, correlating with better electrochemical performance compared to other temperatures. **(ii)** Upper cut-off voltage (UCV) Optimization: An optimal UCV of 4.8 demonstrated a balanced formation between organic and inorganic passivation layers, leading to improved capacity retention and coulombic efficiency evolution, unlike the UCVs of 4.5 and 5 V UCVs. **(iii)** Depth of discharge (DOD) Impact: SEI dissolution was observed to be higher at 1.2V DOD, resulting in a thinner SEI. An SEI inorganic/organic species ratio close to 1 at 2.0V DOD suggested a more stable passivation layer (more KF, K₂CO₃, and KPF₆ decomposition species), contributing to better electrochemical performance. **(iv)** Vanadium Dissolution: In the graphite/KVPFO full-cell, capacity loss was attributed partly to vanadium dissolution initiated from the first cycle. **(v)** Effect of DOD on Rate Performance: Higher DOD at 1.2V showed lower capacity at high rates, indicating increased impedance (i.e. Different SEI and CEI aging mechanisms). In contrast, 2 V DOD exhibited higher capacity at high rates.

Thus, the comprehensive exploration of SEI and CEI analysis within potassium-ion full-cells reveals a wealth of insights crucial for advancing this energy storage technology. However, to truly control the potential of KIBs and translate these insights into practical applications, the next pivotal step is the transition toward prototyping KIBs. Through prototyping efforts, we can bridge the gap between academic and industrial implementation, driving KIBs toward their full potential in the landscape of energy storage solutions.

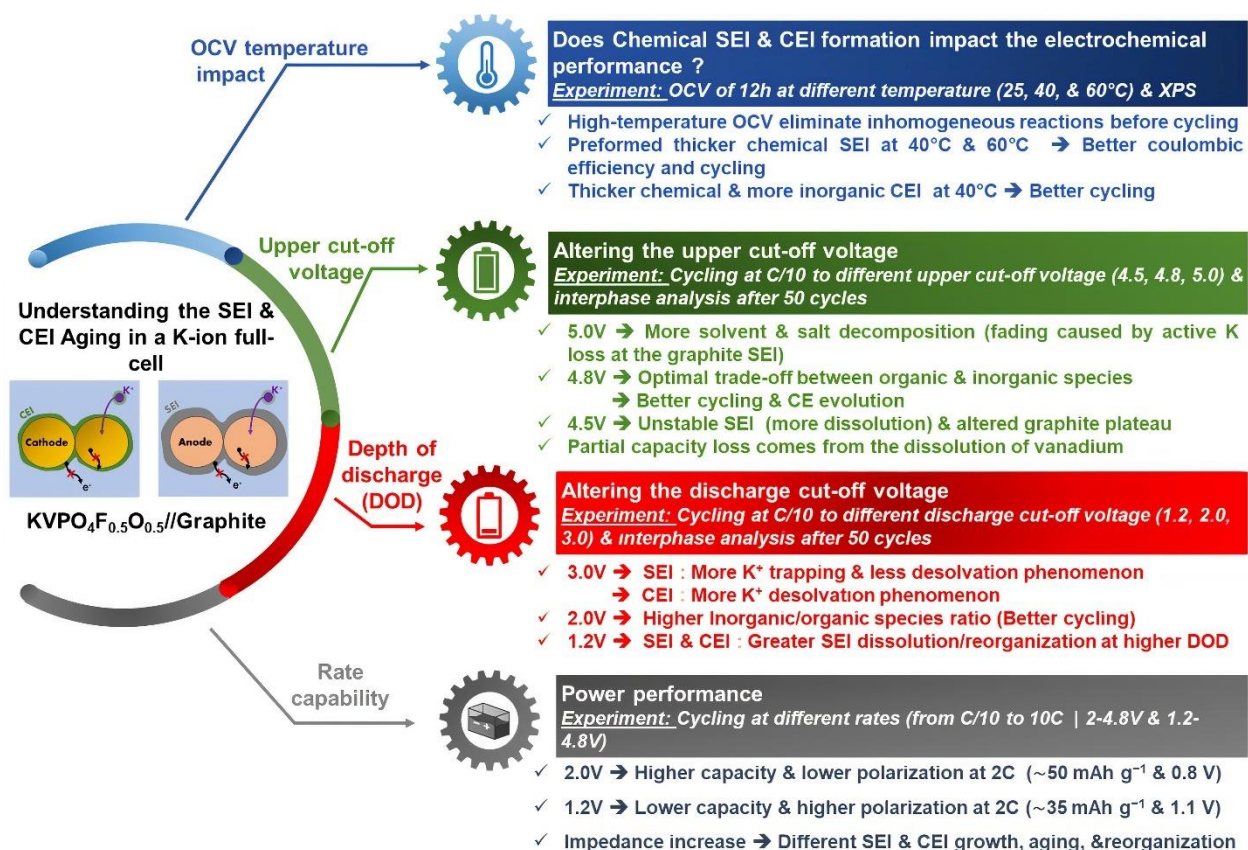


Fig. 10. Summary scheme illustrating the main results obtained from SEI and CEI growth/aging in the KVPO₄F_{0.5}O_{0.5}//Graphite full-cell configuration [105].

Likewise, as a proof of concept, the electrochemical performance of KIFCs should be investigated preferably in pouch and 18650 cells format to demonstrate their practical interest. **Fig. 11** presents a brief history of the pouch cell studied in K-ion technology so far with the surface area of the cells and their capacity when available. For instance, the design of a stackable PTCDA||KC₈ pouch cell provides the highest obtained capacity for KIBs [106] with 106 mAh g⁻¹_{cathode}. PTCDA||KC₈ pouch cells consisted in 3-layer PTCDA cathodes (7 cm × 11 cm) sandwiched by 2-layers KC₈ foils (7 cm × 11 cm). Moreover, the cell demonstrates a capacity retention of 84.1% even after 100 cycles, indicating its long-term performance. Moreover, it is worth noting that there have been no research articles published so far regarding cylindrical 18650 cells in KIBs, in contrast to the extensive research conducted on Na and Li technologies [107,108]. Exploring the potential of cylindrical 18650 cells is of utmost importance for the advancement of K-ion technology, as it would provide valuable insights into their applicability and practicality.

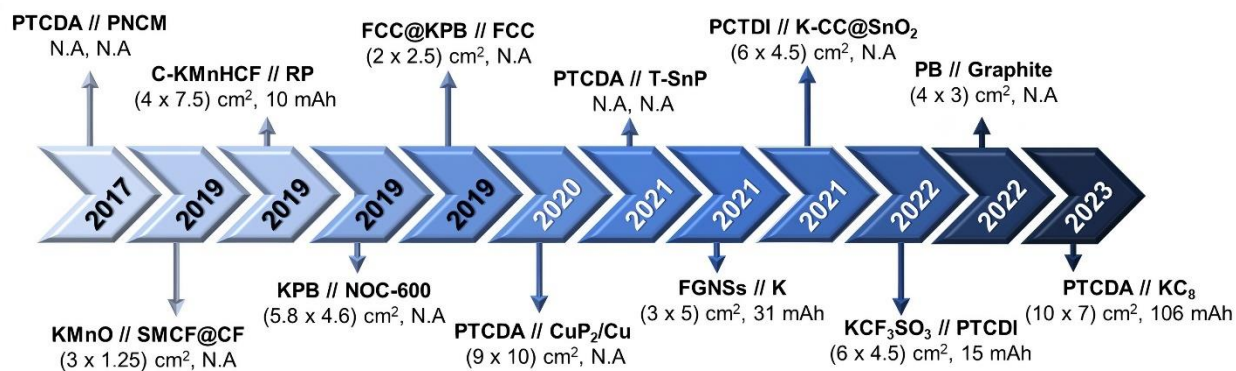


Fig. 11. A Brief History of K-ion Pouch Cells (cathode//anode materials, (width × length) of the pouch cell, cell capacity, and N.A stands for Not Available). N-doped porous carbon monolith (PNCM) [46], K_{0.3}MnO₂ (KMnO) and self-supporting carbon nanotubes encapsulated in submicro carbon fiber (SMCF@CNTs) [109], potassium manganese hexacyanoferrate (KMnHCF) and red Phosphorus (RP) [110], potassium Prussian blue (KPB) and nitrogen/oxygen co-doped amorphous carbon (NOC-600) [111], flexible carbon cloth (FCC) and KPB [112], copper nanowires (CuP₂/Cu NWs) and PTCDA [113], SnP_{0.94} teardrop nanorods (T-SnP) and PTCDA [114], K metal and fluorinated graphite nanosheets (FGNSs) [115], PTCDI and K metal on SnO₂-modified commercial carbon cloth (K-CC@SnO₂) [116], KCF₃SO₃ and PTCDI [117], Graphite and Prussian blue (PB) [118], PTCDA and Potassiated graphite (KC₈) [106].

4.4 Other strategies

In the existing literature, only a limited number of papers have addressed the topic of electrode formulation and design, which was crucial in the advancement of Li- and Na-ion batteries [119–124]. Regarding KIBs, it has been observed that the use of polytetrafluoroethylene (PTFE) as a binder for PBA positive electrodes offers advantages due to the formation of a more stable solid electrolyte interphase compared to polyvinylidene fluoride (PVDF) [53] despite that for practical use PVDF is more suitable. For the negative electrode, it has been demonstrated that the use of CMC as a binder yields high ICE, low polarization, and stable SEI growth compared to sodium polyacrylate (PANa) and PVDF [53,125]. This outcome has been confirmed by a recently published study, which highlights the impact of the binder in terms of electrochemical performance of graphite electrode [103]. This study showcased that the use of a binary binder comprising CMC and styrene-butadiene rubber (SBR) enhances several aspects, including volume expansion management, cohesion between the active material (graphite), carbon black, and binders, along

with the overall electrochemical performance (i.e. rate performance, polarization, CE, and capacity). The electrode composition plays a crucial role in determining the energy density of a battery. Achieving a high loading of active materials in the electrodes while minimizing the use of carbon blacks and binders is essential to optimize the electrochemical performance. However, striking a balance between these parameters is necessary to achieve the best overall performance. Thus, the consideration of composition and formulation processes is crucial and needs increased focus. More importantly, as the electrode formulation plays a critical role in the overall materials performance, it should be a prerequisite for any new materials performance evaluation in the future. Similarly, increasing the active mass loading to a minimum range of 3-5 mg/cm² should also be a prerequisite to really investigate the practical performance of new materials. Overall, these aspects provide key factors in advancing the commercialization of KIBs.

5. Conclusions and outlook

Although potassium-ion batteries exhibit slow dynamics compared with Li-ion batteries and Na-ion batteries, the abundant resource and low cost endow KIBs to be the ideal candidate for large-scale energy storage systems. Research interest for K-ion full-cells has rapidly increased. Many novel KIFCs have been reported recently in the literature. This review summarizes the current status and prospects of potassium-ion full-cells. By studying and understanding the key issues including, K metal cross-talk issues, interfaces, the selection of appropriate electrode materials and proper electrolyte will remedy the K metal reactivity challenges and promote the use of KIFCs for large-scale energy storage applications. We have shown throughout this review that KIFCs are generally categorized into three main groups: liquid KIFCs, quasi-and all-solid-state KIFCs. Depending of the cell-type, it allow achieving high structural stability in a wide range of temperature and voltage. Giving more attention to the KIFCs will contribute to the advancement of KIBs industrialization because of the significant difference in electrochemical performance between half- and full-cells. As an advisory, more attention should be paid to KIFCs in the future research such as evaluating electrode materials, electrolytes, and so on. Furthermore, improving the initial coulombic efficiency is the key to enable the full electrochemical performance of KIFCs without pre-cycling the electrodes versus K metal. Moreover, KIFCs are the most widely studied and most promising KIB technology. Currently, its specific capacity can reach 104 mAh g⁻¹ based on the mass of cathode and an average voltage of 3.9V. However, its long-term cycle stability needs to be improved further by playing with the electrode material interface the electrolytes optimization

and electrode design, as well as material engineering (coating, doping, and so on) [126,127]. Thanks to more stable interface characteristics, the quasi and all-solid-state KIFCs can exhibit better cycle durability than liquid ones when organic cathodes are used. However, few reports are obviously not conducive to its rapid progress, so it is expected to receive more attention based on its own superiority. The all-solid-state KIFCs with high voltage stability and safety can enable the potential of higher voltage materials to be fully utilized and thus achieve significant increase in energy densities. Notably, in place of the irreversible consumption of potassium ions, the electrode/electrolyte and electrolyte/electrolyte interface impedance in all-solid-state cells are the key factors that restrict their dynamic behaviours, thus their cycle stability and capacity at room temperature are often unsatisfactory. Generally, among the three types of full-cells, the all-solid-state ones still have a long way to go. How to manipulate effectively the solid–solid interface is the tipping point to realize its practical use toward the high-energy density.

Energy density, as a key indicator to evaluate the overall KIFCs performance, is primarily affected by operating voltage, capacity, materials tap density, cell design, and coulombic efficiency. Therefore, to obtain the targeted energy density, KIFCs need to be further investigated while the capacity ratio of cathode/anode must be strictly controlled. Irreversible consumption of K^+ ions is inevitable in a cell due to the presence of SEI and CEI growths and cross-talk. To compensate for these losses, novel strategies should be studied, most importantly the electrolyte formulation that have been neglected so far. Constrained by the previously mentioned issues, the cost/performance compromise and safety issues faced by this technology will be the biggest barrier toward the first efficient KIFCs prototype. Indeed, there is a lack of research articles on the use of cylindrical 18650 cells in KIFCs compared to the extensive research on sodium and lithium technologies. However, it is crucial to investigate the potential of both pouch and cylindrical 18650 cells in KIBs as it would offer valuable insights into their feasibility and practical use. Overall, in the current research of KIFCs, comprehensively examining the performance of KIFCs from the perspective of various mentioned gaps is critical for accelerating its progress.

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Supporting Information

Nonaqueous Potassium-ion Full Cells: Mapping the Progress and Identifying Missing Puzzle Pieces

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Table 1. Summary of electrode materials, electrolytes, and electrochemical parameters of LKIFCs.

<i>Anode</i>	<i>Cathode</i>	<i>Average voltage (V)</i>	<i>Separator type</i>	<i>Electrolyte</i>	<i>Cell configuration</i>	<i>Initial capacity (mAh g⁻¹) @ current density (mA g⁻¹) iCE Capacity retention after n cycles</i>	<i>Rate performance: Capacity (mAh g⁻¹) @ n/C (current density)</i>	<i>Electrode loading (mg cm⁻²)</i>	<i>Electrode surface area (cm²)</i>	<i>Remark</i>	<i>Ref</i>
Graphite	K _{1.75} Mn[Fe(CN) ₆] _{0.93}	3.5	GF	0.7M KPF ₆ in EC:DEC (1:1)	Coin cell 2032	110 @ 30 59% 75 % over 60 cycles	60 @ 2000 mA g ⁻¹ (I _{charge} : 30 mA g ⁻¹)	N.A	N.A	-	[1]
Soft carbon	K _{0.7} Fe _{0.5} Mn _{0.5} O ₂	2.0	GF	0.8M KPF ₆ in EC:DMC	Coin cell 2016	82 @ 40 84% 90% over 50 cycles	50 @ 100 mA g ⁻¹	(-) 1.8-2.0 (+) 1.4-1.6	(+) and (-) : 0.49	Soft carbon precycling was performed	[2]
Graphite	K _{0.6} CoO ₂	2.8	GF	0.7M KPF ₆ in EC:DEC (1:1)	Coin cell 2032	53 @ 3 88% 50% over 5 cycles	N.A	(-) 3.38 (+) 6.76	N.A	Graphite precycling was performed	[3]
Soft carbon	K _{0.6} CoO ₂	2.2	GF	0.8M KPF ₆ in EC:DMC	Coin cell 2016	101 @ 10 86.7% 80% over 50 cycles	57 @ 100 mA g ⁻¹	(-) 1.2-1.5 (+) 1.7-2.1	(+) and (-) : 0.49	Soft carbon precycling was performed Capacities based on the anode mass	[4]
PNCM	PTCDA	2.1	GF	0.8M KPF ₆ in EC:DEC	Coin cell 2025	307 @ 100 23% 37% over 75 cycles	85 @ 2000 mA g ⁻¹	(-) 1.0 (+) N.A	N.A	Capacities calculated based on the mass of the PNCM anode	[5]

$K_3V_2(PO_4)_3/C$	$K_3V_2(PO_4)_3/C$	2.3	GF	1M KPF ₆ in EC:PC	Coin cell 2032	80.9 @ 25 91.7% 88.6% over 500 cycles	N.A	(-) 1.0 (+) 1.0	N.A	-	[6]
KC ₈	AQ26DS	1.3	GF	1M KPF ₆ in DME	Coin cell 2032	82 @ 50 92% 33% over 2500 cycles	46 @ 1000 mA g ⁻¹ (I charge : 50 mA g ⁻¹)	(-) 3.5 (+) 2.0	(+) and (-) : 1.13	Cathode and anode were precycled	[7]
KC ₈	PCTDI	1.9	GF	3M KFSI EC:DMC:DEC (1:1:1)	Coin cell 2032	140 @ 50 N.A 73% over 30 cycles	76 @ 500 mA g ⁻¹	(-) 2.0 (+) 2.0	(+) and (-) : 1.13	Cathode and anode were precycled	[8]
Hard carbon - Flexible carbon cloth (FCC)	FCC@KPB	2.9	GF	1M KPF ₆ in PC:FEC (9:1)	Pouch cell	0.11 mAh cm ⁻² @ 0.02 mA cm ⁻² N.A 95% over 200 cycles	0.027 mAh cm ⁻² @ 143 mA cm ⁻²	NA	N.A	Pre-potassiation for the FCC anode	[9]
Hard carbon	$K_{0.75}Mn_{0.8}Ni_{0.1}Fe_{0.1}O_2$	2.1	GF	0.5M KPF ₆ in EC:DEC	Coin cell 2032	60 @ 21 N.A 60% over 1000 cycles	N.A	(-) and (+): 3 - 4	N.A	Hard carbon was precycled	[10]
KC ₈	V ₂ O ₅	2.5	GF	0.8M KPF ₆ in EC:DEC	Coin cell 2025	94 @ 100 N.A 84% over 100 cycles	60 @ 2000 mA g ⁻¹	(-) and (+): 0.5	N.A	Graphite was pre-potassiated	[11]
Graphite	PB	3.3	GF	0.8M KPF ₆ in EC:DEC	Coin cell 2032	50 @ 200 75% 50% over 50 cycles	40 @ 400 mA g ⁻¹	(-) 2.0 (+) N.A	(+) and (-) : 1.13	Cathode and anode were precycled	[12]
VPO ₄	KVPO ₄ F	3.1	GF	1M KPF ₆ in PC	Coin cell 2032	101 @ 0.5C 65% 86% over 300 cycles	71 @ 50C	(-) 1.5 (+) 3.0	N.A	VPO ₄ was precycled	[13]

Hard carbon	$K_{0.83}[Ni_{0.05}Mn_{0.95}]O_2$	2.1	GF	0.5M KPF ₆ in EC:DEC	Coin cell 2032	135 @ 52 N.A 80% over 300 cycles	N.A	(-) 2.3 (+) 3.0	(+) 1.54 (-) 2.01	Cathode and anode were precycled	[14]
Graphite	$K_2MnFe(CN)_6$	3.2	N.A	1M KFSI in [C ₃ C ₁ pyrr][FSA]	Coin cell 2032	91 @ 27 58% 76% over 200 cycles	57 @ 1C (270 mA g ⁻¹)	N.A	N.A	-	[15]
Graphite	$K_2MnFe(CN)_6$	3.6	GF	0.75M KPF ₆ in EC:DEC	Coin cell 2032	92 @ 15.5 63% 72% over 500 cycles	N.A	(-) 2.0 (+) 4.0	N.A	-	[16]
				1M K(PF ₆) _{0.75} (FSA) _{0.2} in EC:DEC		106 @ 15.5 64% 37% over 500 cycles					
				1M K(PF ₆) _{0.75} (FSA) _{0.2} in EC:PC		105 @ 15.5 72.5% 75% over 500 cycles					
Graphite	$K_2Mn[Fe(CN)_6]$	3.9	GF	5.6 mol/kg KFSI in G3 + 0.5 wt% VC	Coin cell 2032	79 @ 47% 134% over 100 cycles	N.A	(-) 0.4 (+) 0.8	N.A	High polarization	[17]
K ₄ TP	PTCDI-DAQ	1.4	GF	1M KPF ₆ in DME	Coin cell 2032	200 @ 100 91% 62% over 300 cycles	94 @ 10 000 mA g ⁻¹	(-) 2.2 (+) 3.0	N.A	Anode was precycled insoluble organic cathode	[18]
K ₂ TP	PVK	3.2	GF	1M KPF ₆ in DME	Coin cell 2032	67 @ 200 65% 86% over 30 cycles	62 @ 2000 mA g ⁻¹	(-) 2.0 (+) 2.2	(+) and (-) : 1.13	Anode was precycled	[19]
Natural graphite	PB/PVP/rGo	3.3	Celgard	0.5M KPF ₆ in EC:DEC	Coin cell 2032	127.9 @ 0.5C 73% 85.5% over 100 cycles	77 @ 10C	(-) and (+): 0.7–1.0	N.A	Cathode and anode were precycled	[20]

TiNbO ₄ /C	PTCDA	2.4	GF	1M KFSI in EC:DMC	Coin cell 2032	200.6 @ 100 49.8% 28.5% over 100 cycles	N.A	(-) and (+): 1.0	(+) and (-) : 0.78	Cathode and anode were precycled	[21]
ZnSe/CoSe ₂ @N-CNTs/rGO	K _{0.72} Fe[Fe(CN) ₆]	2.5	Celgard	3M KFSI in EC:DEC	Coin cell 2032	105 @ 100 33% 112% over 50 cycles	N.A	N.A	N.A	Cathode was pre-potassiated vs K metal	[22]
Pitch derived soft carbon	K _{1.69} Mn _{0.78} Ni _{0.22} Fe _{0.93} (CN) ₆	3.8	GF	0.8M KPF ₆ in EC:DEC	Coin cell 2032	80 @ 100 86% 89.6% over 100 cycles	62.5 @ 500 mA g ⁻¹	(-) and (+): 2.0	N.A	-	[23]
B-doped porous carbons	PB	1.7	GF	3M KFSI in EC:DEC	Coin cell 2032	112 @ 500 N.A 98% over 750 cycles	112 @ 500 mA g ⁻¹	(-) 0.8-1.8 (+) 0.6-1.0	(+) and (-) : 1.13	Cathode was pre-potassiated vs K metal	[24]
Graphite	K ₂ Mn[Fe(CN) ₆]	3.4	GF	1M K(PF ₆) _{0.75} (FSA) _{0.25} in EC:PC	Coin cell 2032	121.4 @ 0.1C N.A 65.4% over 500 cycles	104 @ 1C	(-) and (+): 1.6-3.0	N.A	-	[25]
				1M K(PF ₆) _{0.75} (FSA) _{0.25} + 10% DMSF in EC:PC		119 @ 0.1C N.A 82.4% over 500 cycles	109.5 @ 1C				
				0.75M KPF ₆ in EC:DEC		109.5 @ 0.1 N.A 37.5% over 500 cycles	95.2 @ 1C				
MSTC900	PTCDA	1.8	GF	4M KFSI in DME	Coin cell 2032	89.1 @ 50 N.A N.A	N.A	(-) 1.0 (+) N.A	N.A	Cathode and anode were precycled	[26]
In ₂ S _{3-x} Se _x @C	PB	2.1	GF	4M KFSI in DME	Coin cell 2032	94 @ 20 57% 84.6 over 180 cycles	69 @ 200 mA g ⁻¹	(-) 1.5 (+) 4.5	(+) and (-) : 0.78	Anode was precycled	[27]

KC ₈	PTCDA	2.4	GF	3M KFSI in DME	Pouch cell	129 @ 100 N.A 86.8% over 300 cycles	97.9 @ 2000 mA g ⁻¹	(-) 3.67 (+) 6.42	(+) and (-) : 77	Anode was pre-potassiated	[28]
Graphite	K _{0.95} CS _{0.05} VPO ₄ F	3.9	GF	1M KPF ₆ + 2% FEC in EC:DEC	Coin cell 2025	103.7 @ 100 N.A 90.1% over 1000 cycles	62.7 @ 2000 mA g ⁻¹	N.A	N.A	Cathode and anode were precycled	[29]
KC ₈	NTCDI-DAQ@C	1.1	GF	1M KPF ₆ in DME	Coin cell 2032	236 @ 100 N.A 51% over 400 cycles	182 @ 2000 mA g ⁻¹	(-) 5.0 (+) 2.0	(+) and (-) : 1.13	Cathode and anode were precycled	[30]
FePSe ₃ /CNT	K ₂ CoFe(CN) ₆	2.3	GF	1M KFSI in DMC	Coin cell 2032	62.4 @ 50 73.8% 81.3% over 500 cycles	25.8 @ 1000 mA g ⁻¹	N.A	N.A	Anode was precycled	[31]
Hard carbon	PTCDA	2.2	GF	0.8M KPF ₆ in EC:DEC	Coin cell 2032	247.4 @ 30 N.A 71% over 90 cycles	228.8 @ 500 mA g ⁻¹	(-) and (+): 0.5-1.0	N.A	Cathode and anode were precycled	[32]
Graphite	KVPO ₄ F _{0.5} O _{0.5}	3.9	Celgard	0.8M KPF ₆ in EC:DEC	Coin cell 2032	71 @ C/10 60% 70% over 50 cycles	N.A	(-) 4.0 (+) 10.0	(+) 0.71 (-) 0.95	Guideline toward reliable K-ion full coin cells	[33]

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II. Published paper: Toward Highly Reliable Potassium-Ion Half and Full Coin Cells.

VIP Very Important Paper

Toward Highly Reliable Potassium-Ion Half and Full Coin Cells

Badre Larhrib^[a] and Lénaïc Madec^{*,[a, b]}

To develop high energy and high-power potassium-ion batteries (KIBs), performance need to be evaluated in full-cells instead of half-cells based on the highly reactive K metal that leads to misinterpretation of the results. However, assembling KIBs full-cells is not trivial as many parameters are critical to the obtained performance. This work demonstrates approaches to assemble reliable K-ion full-cells using graphite and $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ based electrodes. First, the optimal separators choice/number and electrolyte choice/volume are determined in half-cells then the optimal electrolyte volume is determined in full-cells. Importantly, the electrolyte volume should be fixed

to about 4 times the porosity volume for both half- and full-cells. Then, using 3-electrodes cells, the optimal negative/positive (N/P) diameter ratio then the optimal N/P capacity ratio are determined to be 1.16 ± 0.2 . Finally, these approaches allow assembling $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ /graphite coin-cells with an energy density of about $47 \text{ Wh kg}_{\text{device}}^{-1}$ using a high N/P loading ratio of 4/10 (in $\text{mg}_{\text{active-material}} \text{ cm}^{-2}$). Overall, this work can be used as a guide to assemble any KIBs full-cell system and thus paves the way to the determine the best negative/positive materials combination in order to develop efficient KIBs.

Introduction

Potassium-ion batteries (KIBs) are emerging as a possible alternative to Li- and Na-ion batteries in the context of renewable energy development requiring large-scale storage systems for which low cost and abundant materials are required. Indeed, potassium has a high abundance (2.1 wt.% of the Earth's crust) while graphite and Al can be used as negative active material and current collector, respectively. Also, high power batteries are expected due to the low desolvation energy of K^+ ($\sim 115 \text{ kJ/mol}$ vs. ~ 155 and $\sim 210 \text{ kJ/mol}$ for Na and Li) and small solvated radius of K^+ ($\sim 3.6 \text{ \AA}$ vs. ~ 4.6 and $\sim 4.8 \text{ \AA}$ for Na^+ and Li^+) in carbonate electrolytes. However, some drawbacks remain: the high atomic mass of K (39.1 g/mol vs. 23 and 6.9 g/mol for Na and Li), the high Shannon's ionic radius of K^+ ($1.38 \text{ \AA}$ vs. 1.02 and $0.76 \text{ \AA}$ for Na^+ and Li^+) and possible safety issue (i.e., K plating). Thus, high energy and high power KIBs will be obtained only if the benefits exceed these limitations. To address this challenge, KIBs performance needs to be evaluated in full cells. However, as half-cells results are partially driven by the K metal electrode, it is not trivial to assemble KIBs full-cells. In particular, the K plating/stripping has a relatively low coulombic efficiency ($< 70\%$) and high polarization ($\geq 0.1 \text{ V}$ even at low rate) in KPF_6 based carbonate electrolytes,^[1] which greatly alters the rate performance and capacity retention

evaluation.^[2,3] Using KFSI instead (in carbonate electrolytes) generally increases the polarization (at least $+0.1 \text{ V}$)^[3] due to a higher/better passivation of K metal by a more inorganic solid electrolyte interphase (SEI) based on FSI^- degradation products.^[4] Note that the full electrolyte degradation pathways at the K metal surface of the commonly used 0.8 M KPF_6 or KFSI EC:DEC was recently studied experimentally^[4] with a perfect agreement with recent theoretical calculation.^[5,6] As an alternative to carbonate electrolytes, highly concentrated KFSI DME electrolytes should be preferred in half-cells for its K plating/stripping $\text{CE} > 95\%$ ^[1] with a stable polarization at low/moderate/high rate.^[7,8] Also, K metal aging, i.e., K metal passivation and impedance increase over cycling further limit the performance evaluation,^[10] while it remains often neglected in the literature. Finally, the electrolyte reactivity at the K surface forms electrolyte degradation products that migrate to the working electrode where they are deposited (electrodes cross-talk or interaction between electrodes) whatever the electrolyte/electrode are,^[4,11,12] so that SEI study should be performed in full-cells. Based on these considerations, it is thus of great interest to master the procedure to go from KIBs half-cells to full-cells. Especially, the K metal preparation, electrolyte volume as well as negative/positive diameter and capacity ratios are critical parameters that are still missing in the KIBs literature but need to be evaluated.

To fill this gap, this work aims to assess the impact of electrolyte volume, negative/positive diameter and capacity ratios on the electrochemical performance (CE, polarization, active materials utilization and capacity retention) in order to assemble highly reliable K-ion full-cells. To do so, graphite and $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ based electrodes are selected while 2-electrodes half-cells, then 3-electrodes full-cells and finally 2-electrodes full-cells are used to evaluate the impact of these various parameters on the electrochemical performance. Finally, the approaches followed in this work are used to assembled

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KVPFO/graphite coin-cells with high negative/positive loading ratio, i.e., with relatively high energy density. Overall, this work can be used as a guide to assemble any KIBs full-cell system.

Experimental Section

Materials and electrodes preparation

K metal electrodes were prepared from K ingot (Alfa Aesar, 99.95%) as followed: using Teflon tweezers, pieces of K metal were placed then spread (using an 8 cm diameter Teflon roller) between 2 latex gloves (as it is very sticky otherwise). Then, 10 mm diameter K metal disks were punched out (on the latex gloves). The K metal disks were then removed from the latex gloves using Teflon tweezers, then placed on a stainless-steel spacer (1 mm thick, 16 mm diameter) and finally scratched with the back of the tweezers.

Graphite electrodes were prepared following a previously optimized electrode formulation:^[10] 425 mg of SLP30 (TIMCAL), 25 mg of C65 (MTI), 40 mg of CMC-Na (Sigma-Aldrich, Mw ~250000) and 10 mg of carboxylate SBR (LITEX LB-420, Synthomer) were mixed (85:5:8:2 weight ratio) in 1 mL distilled water using ball milling (PULVERISETTE 7) at 500 rpm for 1 h. Slurry was coated on aluminum foil (15 μ m thickness) by doctor blade (125 or 250 μ m corresponding to 2 or 4 mg_{graphite} cm⁻²). The film was then dried at room temperature for 1 night under air. Then, 11 or 12.7 mm diameter electrodes were cut out, pressed at 2 tons/cm² (leading to ~35% electrode porosity) and dried again under vacuum at 80 °C for 12 h.

KFPO₄F_{0.5}O_{0.5} (KVPFO) was synthesized following the procedure reported by Wernert et al.^[13] KVPFO electrodes were prepared by mixing 1 g of KVPFO, 0.2 g of C65 (MTI), 0.13 g PVDF (Sigma-Aldrich, M_w ~250000) (75:15:10 weight ratio) in 2.5 mL NMP (Sigma-Aldrich, anhydrous, 99.95%) using ball milling (PULVERISETTE 7) at 500 rpm for 1 h. Slurry was coated on aluminum foil (15 μ m thickness) by doctor blade (250, 265, 280, 300 or 350 μ m corresponding to 4.2, 4.5, 4.7, 5, and 5.6 mg_{KVPFO} cm⁻²). The film was then dried at 60 °C for 12 h under air. Then, 9.5 mm diameter electrodes were cut out, pressed at 3 tons cm⁻² (leading to ~36% electrode porosity) and dried again under vacuum at 80 °C for 12 h. At this point, no optimization of the KVPFO electrodes formulation was performed but it will be considered in the future.

Electrochemical experiments

Galvanostatic cycling was conducted using a VMP 3 multichannel system (BioLogic, France) in a 20 °C temperature-controlled room. Two pair cells were assembled for reproducibility while in the results section, data for only one cell is presented for clarity. The electrolyte was 0.8 M KPF₆ (Sigma-Aldrich, $\geq$ 99%) EC:DEC (ethylene carbonate, Sigma-Aldrich, $\geq$ 99% and diethyl carbonate, Sigma-Aldrich, $\geq$ 99%) 1:1 by volume. This electrolyte was selected based on our results of K plating/stripping (Figure S1), as discussed in the results section. For half-cells and 3-electrodes cells, i.e., for cells using K metal, a glass fiber membrane (GF/D, from Whatman) was added in contact with the K metal electrode in addition to the two microporous trilayer membranes (PP/PE/PP, from Celgard). The need for a GF/D separator in contact with K metal may be explained by a much better electrolyte wettability of the K surface thanks to the GF/D separator affinity with the K metal compared to a PP/PE/PP separator. This point is further discussed in the result part. In full cells, i.e., without K metal, only the two microporous trilayer membrane (PP/PE/PP, from Celgard) were used. Note that only one PP/PE/PP separator should be necessary but two were used instead as a precaution. For the full-cells assembly, the areal capacities used for both positive and negative electrodes corresponds to the practical capacities obtained experimentally in half-cells, i.e., $Q_{\text{graphite-practical}} \sim 264 \text{ mAh g}^{-1}$, and $Q_{\text{KVPFO-practical}} \sim 82 \text{ mAh g}^{-1}$. Note that in this work, the polarization (ΔV in Figures) was considered as the difference between the average potential in charge (depot-assiation) and discharge (potassiation). Thus, in order to assemble reliable K-ion half and full coin-cells (CR2032 316 L were used), different parameters were evaluated as presented in Figure 1.

Before assembling half-cells, the choice of the electrolyte, which is of high importance to control the K plating/stripping performance, was evaluated using K/K symmetric cells.

Then, the optimal electrolyte volume was determined for graphite and KVPFO electrodes in regard to the reversible capacity, coulombic efficiency (CE) and polarization using half-cells. To do so, after and OCV of 1 h, 5 cycles were performed at C/10 between 2–0.01 V and 3.5–5.0 V for graphite (2 mg_{graphite} cm⁻²) and KVPFO (5 mg_{KVPFO} cm⁻²) electrodes, respectively. The optimal electrolyte volume was then also determined for full KVPFO/graphite cells. To do so, after and OCV of 1 h, 5 cycles were performed at C/10 (vs. KVPFO) between 2–5 V while both negative/positive diameter and capacity ratios of 1.16 (2 mg_{graphite} cm⁻² and 5 mg_{KVPFO} cm⁻²) were used.

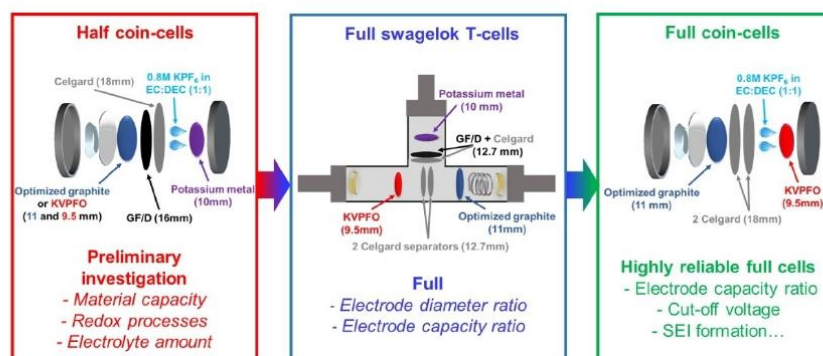


Figure 1. Schematic representation of the approach followed in this work to optimize the assembly of highly reliable K-ion full coin cells.

Second, the optimal graphite/KVPFO diameter ratio (12.7/9.5 and 11/9.5 in mm with $2 \text{ mg}_{\text{graphite}} \text{ cm}^{-2}$ and $5 \text{ mg}_{\text{KVPFO}} \text{ cm}^{-2}$ electrodes) was determined in regards to the reversible capacity and CE using 3-electrodes Swagelok T-cells (i.e., full-cells with K metal reference). Note that another 3-electrodes Swagelok cell type was first used in this step, but this cell type was not selected due to some electrolyte reactivity issue (Figure S3), as discussed in the results part. To do so, after an OCV of 1 h, 10 cycles were performed at C/10 (vs. KVPFO) with potential limitations of 3.0–5.0 V, 2–5.0 V and 0.01–2.0 V for E_{KVPFO} (E_{WE}), $E_{\text{KVPFO-graphite}}$ ($E_{\text{WE-CE}}$) and E_{graphite} (E_{CE}), respectively.

Second/third, the optimal graphite/KVPFO capacity ratio (0.98, 1.05, 1.09, 1.16, and 1.30) was determined in regard to the reversible capacity, CE and polarization using both 3-electrodes Swagelok T-cells and full coin-cells. To do so, the loading of the graphite electrode was fixed to $2 \text{ mg}_{\text{active-material}} \text{ cm}^{-2}$ while the loading of KVPFO electrode was varied from 4.2 to $5.6 \text{ mg}_{\text{active-material}} \text{ cm}^{-2}$ (i.e., 4.2, 4.5, 4.7, 5, and 5.6 corresponding to N/P capacity ratios of 0.98, 1.05, 1.09, 1.16, and 1.30, respectively). For the 3-electrodes Swagelok T-cells, after an OCV of 1 h, 5 cycles were performed at C/10 (vs. KVPFO) with potential limitations of 3.0–5.0 V, 1.2–5.0 V and 0.01–2.5 V for E_{KVPFO} (E_{WE}), $E_{\text{KVPFO-graphite}}$ ($E_{\text{WE-CE}}$) and E_{graphite} (E_{CE}), respectively. For the full coin-cells, after an OCV of 12 h at 40°C , 50 cycles were performed at C/10 (vs. KVPFO) between 1.2–4.8 V. Note that the reported capacities were calculated based on KVPFO weight. Here, the OCV at 40°C was found beneficial to the preformation of an SEI, which will be the subject of another study. Also, the 1.2–4.8 V voltage windows was selected based on the 3-electrodes results, especially, the 4.8 V upper cut off voltage allows limiting the electrolyte oxidation at high potential.

Finally, full coin-cells with high electrodes loadings (N/P loading ratio of 2/5 and $4/10 \text{ mg}_{\text{active-material}} \text{ cm}^{-2}$) were assembled to evaluate the practical energy density for the KVPFO/graphite system. To do so, after an OCV of 12 h at 40°C , 20 cycles were performed at C/10 (vs. KVPFO) between 2–4.8 V. Importantly, the energy density (in $\text{Wh kg}_{\text{device}}^{-1}$) reported in Figure 5 takes into account the mass of both electrodes (including the active materials, carbon additives and binders), the electrolyte and separators.

Results and Discussion

In this study, graphite and KVPFO were selected as active materials for negative and positive electrodes based on their promising electrochemical performance. Indeed, graphite can reversibly intercalate K^+ , leading to KC_6 , i.e., a theoretical capacity of 279 mAhg^{-1} .^[14] Moreover, some of us recently showed that optimized electrode formulation, i.e., optimized ionic/electronic networks and electrode cohesion/elasticity allows controlling the graphite volume expansion issue, which further increases its interest.^[10] Moreover, among the $\text{KVPO}_4\text{F}_{x-1-x}$ family, $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ (KVPFO) shows the best galvanostatic profile with the lowest polarization, the smoother redox plateaus, the best reversible capacity and CE.^[13]

Parameters (separator choice, electrolyte choice and volume) governing half-cells performance

Before assembling full-cells, it is often necessary to first assess active materials performance. To do so, it is important to assemble half-cells with high reproducibility and importantly with negligible impact of the K metal, separator/electrolyte choice/amount. The goal of this part is thus evaluating the parameters governing half-cells performance.

Note first that careful precautions should be taken when preparing K metal electrodes due to its high reactivity even under Ar glovebox atmosphere,^[15] so that a specific procedure is proposed in the experimental part. Then, the K metal electrode diameter should always be larger than the working electrode one. Otherwise, using an undersized K metal electrode will limit the delivered capacity and lead to inhomogeneous SEI formation at the working electrode, as previously observed in Li-ion half-cells.^[16]

Second, to prevent K dendrites formation, large polarization and low delivered capacity in half-cells, it is mandatory to use a glass fiber separator (noted GF/D or a Solupor membrane;^[17] as proposed in the literature) at the K metal electrode side in addition to a Celgard membrane on the working electrode side. This is more likely explained by an electrolyte wettability issue at the K surface induced by the affinity between the separator and K metal. Indeed, Figure S1 shows that graphite//K cells with 2 Celgard membranes delivered only 41 mAhg^{-1} during the first discharge at C/20 with a very large polarization of 0.74 mV compared to 269 mAhg^{-1} and 0.16 mV when the Celgard at the K metal electrode was replaced by a GF/D separator. The 5th cycle showed an additional polarization increase and thus a capacity decreased with 2 Celgard while nearly no change was observed with the use of a GF/D separator (Figure S1). These results thus highlight the importance of the separator choice when assembling K-ion half-cells.

Third, the electrolyte choice is also of high importance to control the K plating/stripping performance^[1] and thus to not alter the delivered capacity, lifetime and power performance of half-cells. In this study, $0.8 \text{ M KPF}_6 \text{ EC:DEC}$ was selected as it showed much lower polarization from low (0.02 mAcm^{-2}) to moderate (0.8 mAcm^{-2}) currents among the different electrolytes tested (Figure S2). Overall, as K plating/stripping and thus half-cells performance may vary depending on the selected K metal preparation, separator(s), electrolyte salt(s)/solvent(s) and their purity,^[2] it is therefore very important to first determine and select the most suitable combination and not rely only on literature data.

Finally, the electrolyte volume impact on half-cells performance was evaluated (Figure 2) despite that it is usually neglected or not mentioned in the literature. For clarity, Table S1 gather the thickness (μm), porosity (%), diameter (mm) and corresponding porosity volume (μL) for the different components used to assembled K-ion cells in this study, i.e., graphite and KVPFO electrodes, GF/D and Celgard separators as well as the corresponding porosity volume by surface area ($\mu\text{L cm}^{-2}$). From Table S1, it appears that the electrolyte volume needed in our half-cells to fill

both KVPFO or graphite electrode porosity in addition to the separators porosity corresponds to $\sim 17 \mu\text{L}$. Electrolyte volume was thus varied from 30 to $100 \mu\text{L}$. For KVPFO electrodes, using only $30 \mu\text{L}$ led to low reversible capacity and no capacity during the 1st and 5th cycles, respectively (Figure 2). Note that the potential jump observed at about 4.5 V is attributed to the redox phenomenon and structural properties of the KVPFO material.^[13] Between 50 and $70 \mu\text{L}$, similar delivered capacities were observed but using only $50 \mu\text{L}$ led to much higher polarization, indicating possible ionic limitation even at C/10 cycling rate. Increasing further the electrolyte volume from 70 to $100 \mu\text{L}$ significantly increased the irreversible capacity associated with the electrolyte oxidation during the 1st cycle between 4 and 4.6 V. This is likely explained by the oxidation of soluble electrolyte degradation species formed at the K metal for which their amount should increase as the electrolyte volume increases. This phenomenon is also supported by the fact that for graphite electrodes, as no oxidation is possible, the same 1st cycle CE was observed as the electrolyte volume was increased. For graphite electrode, increasing the electrolyte volume increased the delivered

capacities, especially after 5 cycles due to the large electrolyte consumption to form the SEI. However, no significant change was observed between 70 and $100 \mu\text{L}$. To resume, it is thus found that $70 \mu\text{L}$ is the optimal electrolyte volume for both KVPFO and graphite half-cells with our setup, which is about 4 times higher than the total porosity of the electrodes and separators ($\sim 17 \mu\text{L}$, Table S1). This result is thus in good agreement with the literature on Li-ion full coin cells assembly that also used an electrolyte volume of about 3.8 times the porosity volume.^[18]

Impact of the electrolyte volume on full-cells performance

For full KVPFO/graphite cells, increasing the electrolyte volume from 15 to $50 \mu\text{L}$ significantly increased the delivered capacity and CE while decreasing the polarization (Figure 2). This indicates a decrease of the ionic limitation due to a better electrode porosity filling by the electrolyte. However, increasing further the electrolyte volume to $70 \mu\text{L}$ then $100 \mu\text{L}$ significantly decreased the delivered capacity and CE while increasing the polarization, more likely due to

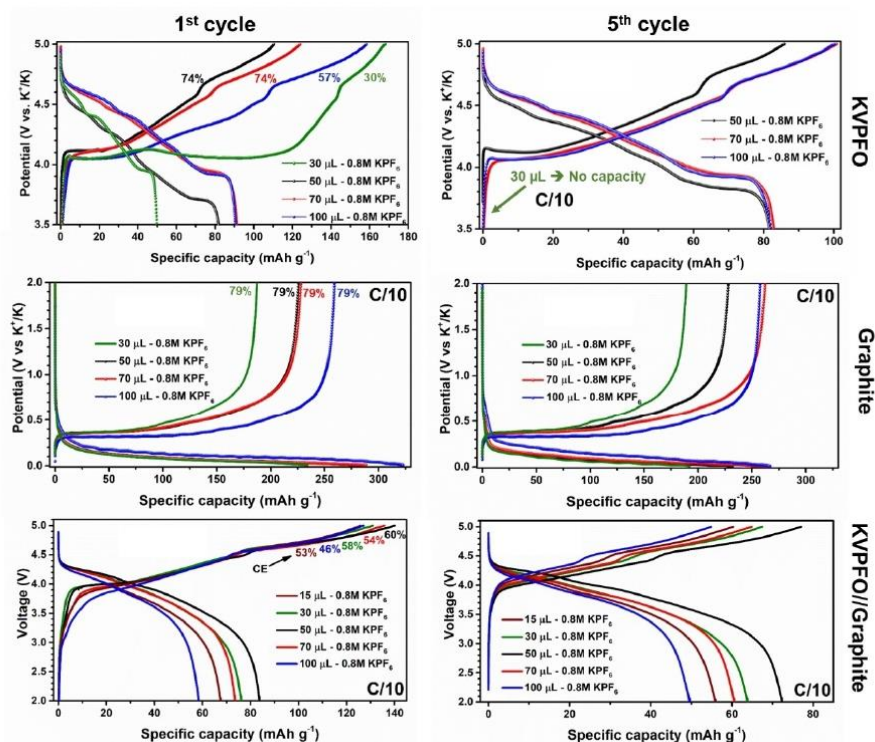


Figure 2. Galvanostatic profiles during the 1st and 5th cycles at C/10 for KVPFO_{0.5}O_{0.5}/K cells (between 3.5–5 V), graphite/K cells (between 2–0.01 V) and KVPFO/graphite cells (between 2–5 V with both negative/positive diameter and capacity ratios of 1.16) as function of the 0.8 M KPF₆ EC:DEC electrolyte volume as indicated.

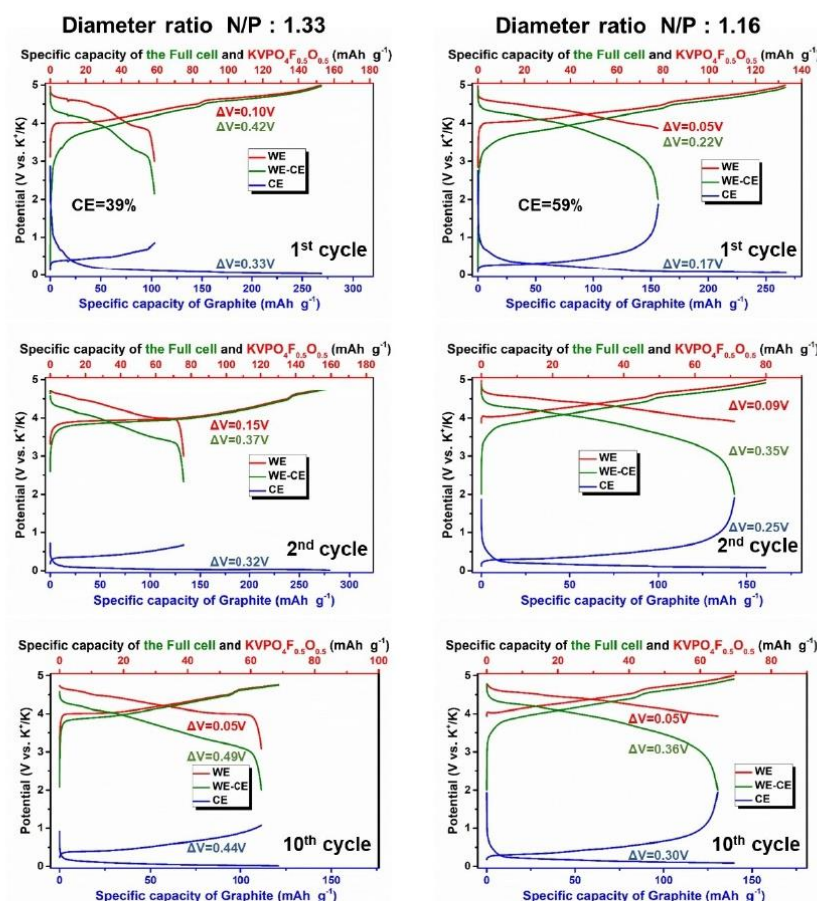


Figure 3. Galvanostatic profiles during the 1st, the 2nd and 10th cycles at C/10 between 3.5–5 V for KVPO//graphite 3-electrodes T-cells with N/P diameter ratio of 12.7/9.5 = 1.33 and 11/9.5 = 1.16. The graphite/KVPO capacity ratio was here fixed to 1.16. Note that ΔV corresponds to the polarization, i.e., the difference between the average potentials.

a too high electrolyte degradation and passivation of the electrodes surface by the SEI. To resume, it is thus found that the optimal electrolyte volume for our KVPO//graphite cells is 50 μL , i.e., about 4 times higher than the total porosity of the electrodes and separators (Table S1), similarly to what was found previously for our half-cells. Note that for the 3-electrodes T-cell study presented after, 100 μL of electrolyte was also used which correspond to ~ 4 times the total porosity of the electrodes and separators (Table S1). Overall, these results highlight that an optimal electrolyte volume should be determined to maximize the delivered capacity, polarization, CE and capacity retention while keeping in mind that excess of electrolyte should be limited in regard to commercial cells.

Impact of the negative/positive diameter on full-cells performance

In this part, 3-electrodes cells were used to evaluate the impact of the negative/positive (N/P) diameter and capacity ratios on the delivered capacity and CE. Note that the optimization of both N/P ratios could have been done using only 2-electrode cells but the interest of 3-electrodes cells is to gain insight on the limiting electrode and the associated phenomenon. To do so, large Swagelok cells were first used but unfortunately it led to high electrolyte degradation with coloration of the K metal reference electrode with such cell design (Figure S3). In addition, a yellow color was observed on the separator in contact with the K metal, indicating a possible contamination of the reference electrode (not showed). As an alternative, smaller

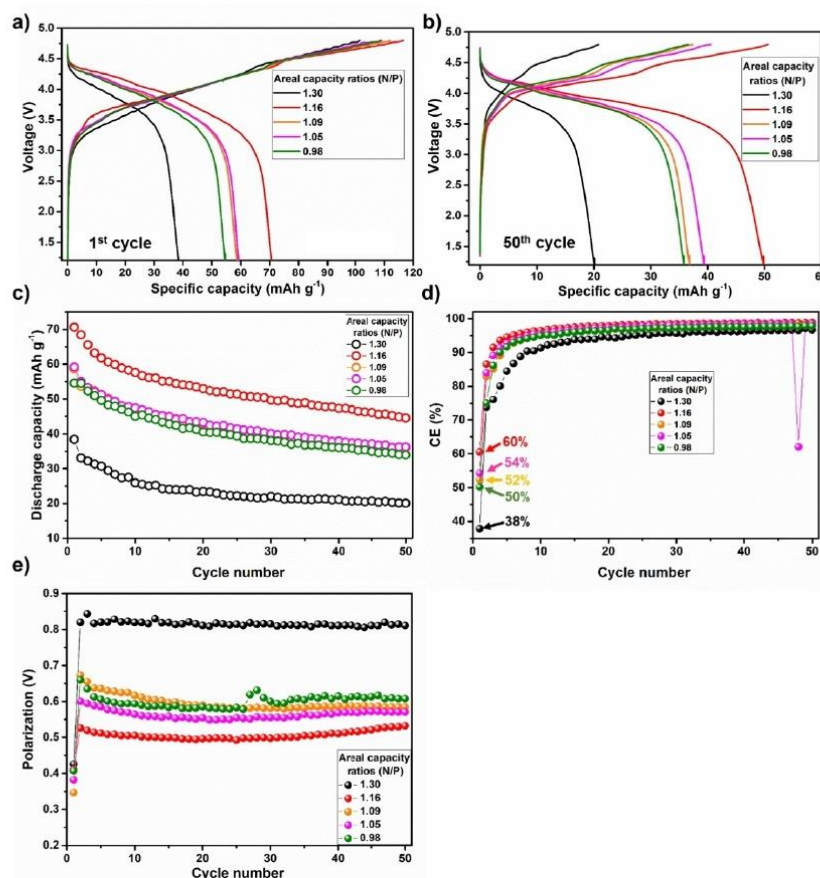


Figure 4. a) 1st and b) 50th galvanostatic cycles profiles between 1.2–4.8 V at C/10 for KVPFO/graphite full coin-cells as function of the capacity ratio. c) Capacity retention, d) coulombic efficiency and e) polarization for the same cells over 50 cycles. The graphite/KVPFO diameter ratio was here fixed to 1.16. Note that the reported capacities were calculated based on KVPFO weight.

Swagelok cells with a T-configuration (K metal placed perpendicularly to the other electrodes) was used with the previously optimized electrolyte volume (100 μL , Table S1). This highlights the importance of the 3-electrodes cell design for KIBs.

The impact of the graphite/KVPFO diameter ratio was then evaluated with the Swagelok T-cells (Figure 3). While using a large diameter ratio of 1.33 (12.7 mm /9.5 mm) may help for the electrode alignment during cell assembly, it also significantly increased the irreversible capacity (61 %) associated with the electrolyte degradation as well as the electrodes/cell polarizations. Indeed, from cycles 2 to 10, the KVPFO electrode could not reach its 5 V cut-off voltage due to a much higher electrolyte degradation between 3.9 and 4.5 V. This is more likely explained by the excess of graphite that needs to passivate and thus produces excess

of soluble electrolyte degradation species that migrate to the KVPFO electrode where they are oxidized. Indeed, for N/P = 1.16, this phenomenon is almost suppressed. After 10 cycles, the KVPFO and graphite electrodes delivered only 62 and 115 mAh g^{-1} , respectively. When the graphite electrode diameter was decreased to 11 mm, corresponding to a N/P diameter ratio of 1.16, the 5 V cut-off voltage of KVPFO was always reached so that both KVPFO and graphite electrodes delivered higher capacity of 66 and 131 mAh g^{-1} after 10 cycles, corresponding to a full-cell capacity of 66 mAh g^{-1} with an average potential of 3.8 V. Overall, while it might be possible to optimize further (i.e., to decrease further) the N/P diameter ratio, a value of 1.16 ± 0.2 is here found satisfying.

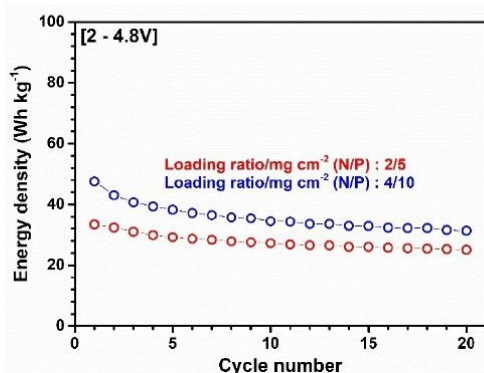


Figure 5. Energy density as function of the cycle number for KVPOF/graphite full coin-cells with N/P loading ratio of 2/5 and 4/10 (in $\text{mg}_{\text{active-material}} \text{cm}^{-2}$) as obtained during cycling between 2–4.8 V at C/10. The diameter and capacity ratios were here both fixed to 1.16. Note that the energy density in $\text{Wh kg}_{\text{device}}^{-1}$ takes into account the mass of both electrodes (including the active materials, carbon additives and binders), the electrolyte and separators.

Impact of the negative/positive diameter on full-cells performance and capacity ratios in full-cells

The impact of the graphite/KVPOF capacity ratio was then evaluated in full coin-cells (Figure 4) and supported by Swagelok T-cells results (Figure S4). Note that here, full coin-cells cycling was performed at C/10 between 1.2–4.8 V after optimization of the voltage limits. The corresponding results will, however, be published in an upcoming study together with SEI analysis. Overall, the N/P capacity ratio of 1.16 led to the highest 1st cycle capacity (71 mAhg^{-1}) and CE (60%), the best capacity retention over 50 cycles (70% with 50 mAhg^{-1}) with the lowest polarization (0.53 V after 50 cycles, Figure 4). Indeed, for a lower N/P capacity ratio of 1.06, the 3-electrodes cell analysis showed that the cells are limited by the excess of KVPOF so that the voltage limit of 5 V couldn't be reached during few cycles while the graphite was fully utilized (Figure S4a). At the opposite, using a higher N/P capacity ratio of 1.3 led to a full utilization of the KVPOF electrode (Figure S4b). However, a very large irreversible capacity was observed (Figure S4b) due to the excess of graphite that need to be passivated by the electrolyte degradation/SEI formation (similarly to the use of a large N/P diameter ratio previously, Figure 3). Also, it leads to high oxidation between 4 and 4.5 V due to the oxidation of excess of soluble electrolyte degradation species formed at the graphite electrode (Figure S4b). Thus, using low and high N/P capacity ratio leads to cells limited by the KVPOF and graphite electrodes, respectively.

Optimized KVPOF/graphite full cells with high loading

In this part, the optimized N/P diameter and capacity ratios were used to assembled KVPOF/graphite coin-cells with high energy, i.e., with high electrodes loadings. Overall, Figure 5 shows that increasing the N/P loading ratio from 2/5 to 4/10 (in $\text{mg}_{\text{active-material}} \text{cm}^{-2}$) allowed reaching an energy density of about 47 Wh kg^{-1} with a retention of 68% after 20 cycles. To our knowledge, this result is probably the highest reported so far in the K-ion full-cells literature especially considering the high electrodes loading used. Finally, if pouch cells can be constructed with a N/P loading of 4/10 (in mg cm^{-2}), an optimized KVPOF electrodes formulation (i.e., at least with 90/5/5 wt.% of KVPOF/carbon/PVDF) and a practical electrolyte volume (1.2 times the total porosity instead of 4 times in coin cells), the energy density could reach about 80 Wh kg^{-1} . This will of course need to be confirmed in the future.

Conclusion

This work demonstrates approaches to assemble reliable K-ion half- and full-cells. Using graphite and $\text{KVPO}_{4.5}\text{F}_{0.5}\text{O}_{0.5}$ based electrodes, it is first illustrated that the separators choice/number and electrolyte choice/volume are key parameters governing half-cells performance. For instance, a glass fiber membrane (GF/D, from Whatman) needs to be added in contact with K metal to optimize the delivered capacity and limit the polarization. Importantly, for both half- and full-cells the electrolyte volume should be fixed to about 4 times the porosity volume of both binder and electrode also to optimize the delivered capacity, CE and polarization. Based on these results and using 3-electrodes cells, the optimal negative/positive (N/P) diameter ratio then the optimal N/P capacity ratio are determined to be 1.16 ± 0.2 . Note that the design of the 3-electrodes cells is also important. Finally, following these approaches, KVPOF/graphite coin-cells with a high N/P loading ratio of 4/10 (in $\text{mg}_{\text{active-material}} \text{cm}^{-2}$) were assembled, leading to cells with an energy density of about $47 \text{ Wh kg}_{\text{device}}^{-1}$. Note that if further improvement can be obtained, such as the KVPOF electrode optimization and the use of pouch cells with lower electrolyte volume, the energy density of KVPOF/graphite cells could reach about 80 Wh kg^{-1} , making K-ion cells promising in the future if sufficient lifetime is obtained. Overall, the approaches followed in this work can be used as a guide to assemble any KIBs full-cell system with high reproducibility and reliability, which is more representative of the practical performance than half-cells. This work should thus help determining the best negative/positive materials combination to accelerate the development of high energy and high power KIBs.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: full cells · graphite · half-cells · $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ · parameters optimization

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Supporting Information

Toward Highly Reliable K-Ion Half and Full Coin Cells

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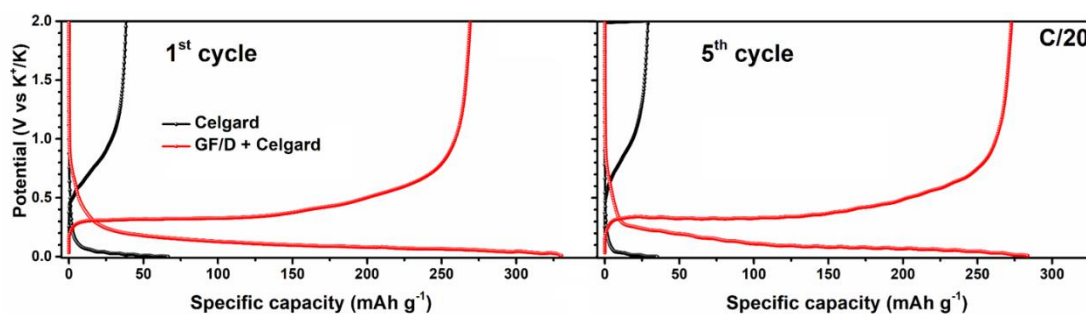


Figure S1. Galvanostatic profiles during the 1st and 5th cycles at C/20 between 0.01-2 V for graphite//K cells with either 2 Celgard membranes or a Celgard membrane + a glass fiber separator (GF/D) at the K metal electrode side.

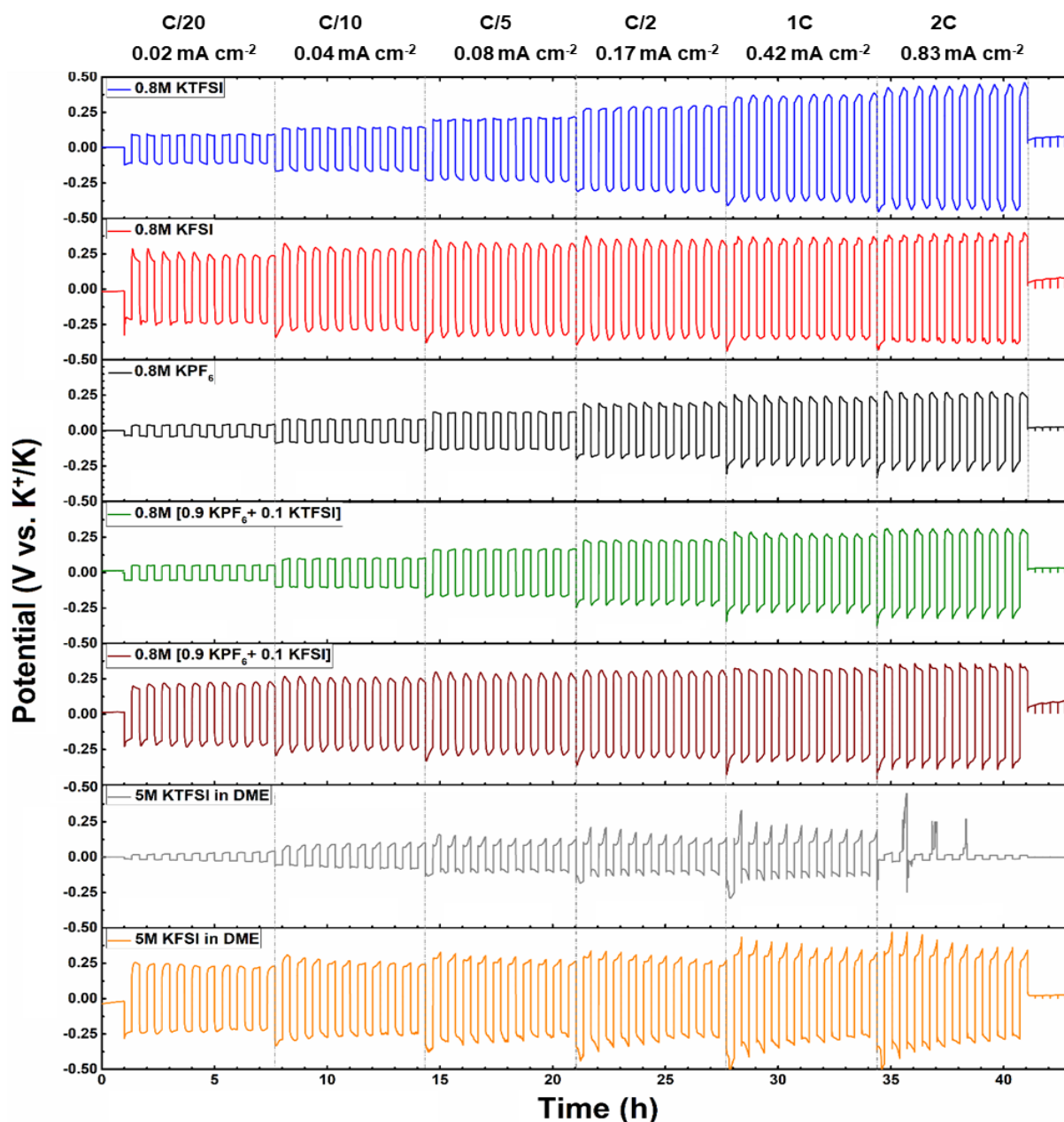
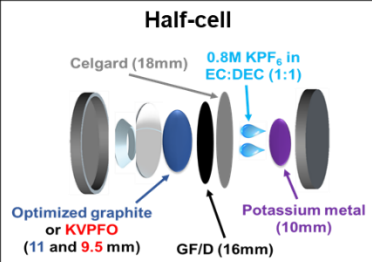
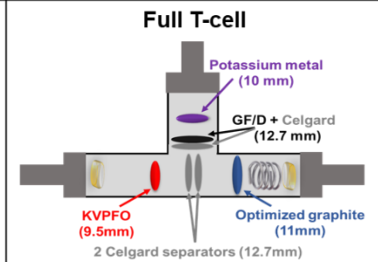
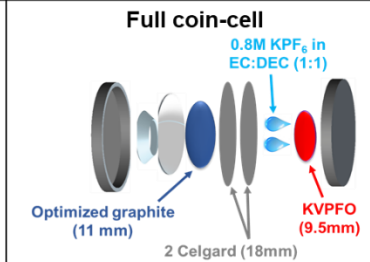


Figure S2. Voltage profiles of K plating/stripping as function of the current density for K//K cells filled with different electrolyte as indicated. Corresponding C rates for our $2.4 \text{ mg}_{\text{graphite}}/\text{cm}^2$ graphite electrodes are also indicated for information. K plating/stripping was performed using 10 cycles for each current density (from 0.02 to 0.83 mA cm^{-2}) with 20 min of constant current for each step while voltage limits were fixed to -10 to $+10 \text{ V}$.

Table S1. (Top) Thickness (μm), porosity (%), diameter (mm) and corresponding porosity volume (μL) for the different components used to assembled K-ion cells in this study, i.e. graphite and KVPFO electrodes, GF/D and Celgard separators as well as the corresponding porosity volume by surface area ($\mu\text{L cm}^{-2}$). (Bottom) Total porosity volume (μL), volume of electrolyte volume added (μL) and ratio added electrolyte/total porosity volume for each cell setup (half coin-cells, full T-cell and full coin-cell) used in this study.

	Thickness [μm]	Porosity [%]	Diameter [mm]	Porosity volume [μL]	Porosity volume/surface area [μL cm ⁻²]
Graphite	30	35	11	1	1.1
KVPFO	46	36	9.5	1.2	1.7
GF/D after assembly (Coin-cells)	145	40	16	11.6	5.8
GF/D after assembly (T-cells)	320	40	12.7	16.2	12.8
Celgard (Coin-cells)	30	60	18	4.6	1.8
Celgard (T-cells)	30	60	12.7	2.3	1.8

Half-cell		Full T-cell		Full coin-cell	
					
Total porosity [μL]	17.4 17.2			25.3	11.4
Added amount [μL]	70			100	50
Ratio : added electrolyte / Total porosity	~4.0			~4.0	~4.4
Suitable electrolyte volume to add (~4 times the total porosity)					

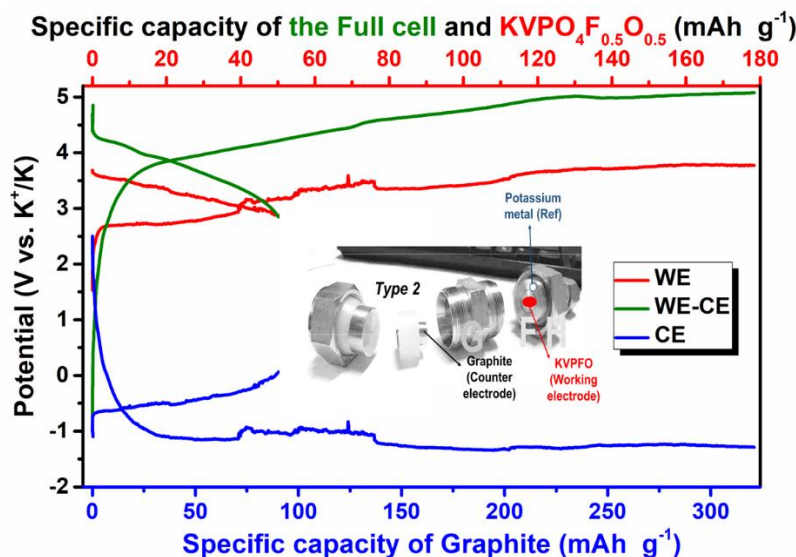


Figure S3. Typical galvanostatic 1st cycle profiles between 3-5 V at C/10 for KVPFO//graphite large 3-electrodes Swagelok cell (as showed in the inserted picture). Note that the electrolyte volume was 200 μ l corresponding to about 4.2 times the total (separator + electrode) porosity.

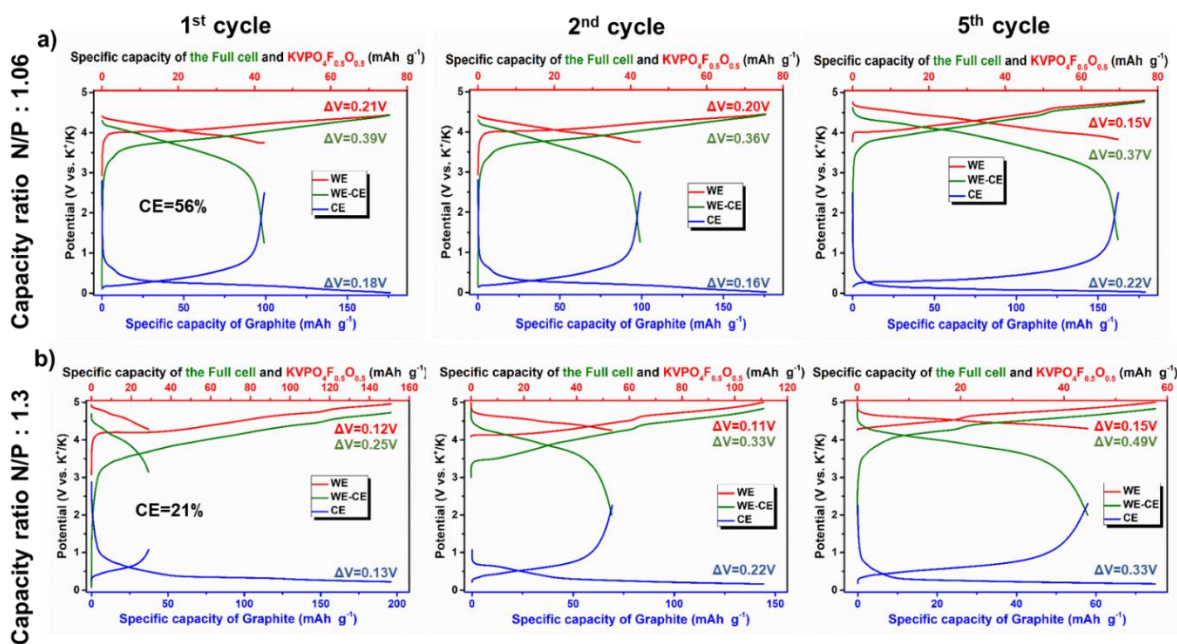


Figure S4. Galvanostatic profiles during the 1st, 2nd, and 10th cycles at C/10 between 1.2-5 V ($E_{\text{KVPFO-graphite}}$) for KVPFO//graphite 3-electrodes T-cells with N/P capacity ratio of 1.3 and 1.06. The graphite/KVPFO diameter ratio was here fixed to 1.16.

Conclusions

Although potassium-ion full cells are in earlier stage compared to lithium-ion and sodium-ion full cells. Research interest in K-ion full cells has surged, resulting in numerous novel full cell designs detailed in the literature. Therefore, in the first section of this chapter, we have provided a comprehensive review summarizing the commonalities and differences in the chemistry and electrochemical properties of potassium-ion full cells.

Furthermore, the second section of this chapter has demonstrated reliable assembly approaches for both K-ion half cells and full cells, utilizing graphite and $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ -based electrodes. Through comprehensive investigations, key parameters governing the performance of half cells, such as separator choice/number and electrolyte choice/volume, have been established. The importance of adding a glass fiber membrane in contact with K metal for optimized capacity and polarization control has been underscored. For both half and full cells, maintaining an electrolyte volume around 4 times the porosity volume of separators and electrodes has been identified as crucial for improving capacity, coulombic efficiency, and decreasing polarization. Furthermore, based on these findings and employing 3-electrode cells, we have determined the optimal negative/positive (N/P) diameter and capacity ratios to be 1.16 ± 0.02 . The design of 3-electrode cells has also been emphasized.

Following these principles, coin-cells featuring KVPFO //graphite with a high N/P loading ratio of 4/10 (in $\text{mg}_{\text{active-material}} \text{cm}^{-2}$) have been assembled, resulting in an energy density of approximately $47 \text{ Wh kg}_{\text{device}}^{-1}$. With potential improvements, such as further optimization of KVPFO electrodes and the use of pouch or 18650 cells with decreased electrolyte volumes, KVPFO //graphite cells could potentially reach an energy density of about 80 Wh kg^{-1} . Thus, the approaches presented in this work serve as a valuable benchmark for assembling high-reproducibility and high-reliability full cell systems for KIBs, which offer a more practical representation of their performance than half cells. By implementing the knowledge gained here, researchers can better determine the most suitable combination of negative/positive materials, accelerating the development of high-energy and -power KIBs.

For the advancement of KIB industrialization, it is critical to focus on full cells. Future research should prioritize evaluating electrode materials and electrolytes in full cell setup, with further

insights on SEI/CEI characterizations, cross-talk mechanisms, and cell design. While challenges persist, conducting comprehensive research to address performance gaps and safety concerns is crucial for efficiently advancing K-ion full cells. Further exploration, especially regarding cylindrical and pouch cells in KIBs, is still lacking, hindering the acquisition of valuable insights into their feasibility and practical applications. This lack of research is a significant obstacle to driving the progress of K-ion battery technology.

Chapter 4

A K-ion full cell: Correlation between XPS SEI studies and electrochemical testing results

I. Published paper: A novel K-ion KVPO₄F_{0.5}O_{0.5}/graphite full cell: Correlation between XPS SEI studies and electrochemical testing results



A novel K-ion KVPO₄F_{0.5}O_{0.5}/graphite full cell: Correlation between XPS SEI studies and electrochemical testing results

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HIGHLIGHTS

- K-ion Full-cell: XPS Unveils SEI/CEI impact on Electrochemical Performance.
- The graphite and KVPO surface layer is thicker at 60   C than at 40   C and 25   C.
- High upper cut-off voltage induces more electrolyte degradation and vanadium dissolution.
- High depth of discharge induces more passivation layer dissolution.

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Upper cut-off voltage
Depth of discharge
SEI
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ABSTRACT

Like Li- and Na-ion batteries, electrolyte reactivity (i.e., salt and solvent decomposition) is important in the electrochemical performance of K-ion batteries (KIBs). Indeed, X-ray photoelectron spectroscopy (XPS) analysis of a solid electrolyte interphase (SEI) in KIBs is still based on K-ion half-cells. This may lead to incorrect interpretations of the results considering the contamination of the studied electrode SEI due to the high K metal reactivity. Therefore, this study aims to provide a reliable XPS study without potassium metal, investigating the impact of various parameters, including open-circuit voltage (OCV) temperature, upper cut-off voltage (UCV), depth of discharge (DOD), and vanadium dissolution, on the electrochemical performance of KVPO₄F_{0.5}O_{0.5}/graphite full cells. This work highlights the importance of SEI preformation, which is more pronounced at higher OCV temperatures. At specific UCV and DOD, the cell provides the best trade-off between the organic and inorganic passivation layer, leading to good electrochemical performance. The study also demonstrates that vanadium dissolution is a potential mechanism affecting capacity fading in K-ion batteries. Finally, understanding these SEI growth mechanisms should help researchers get reliable XPS analysis of the SEI in KIBs and move forward with the practical passivation layer characterizations.

1. Introduction

The market for batteries includes numerous applications, from portable electronics, electric vehicles, grid storage etc. The demand for batteries will continue to grow as the use of electric vehicles and renewable energy sources increases [1], so that alternatives to the Li-ion batteries are needed. In that direction, K-ion batteries (KIBs) present several advantages as a potential battery technology [2]. The most important ones are that potassium is much more abundant (2.1 % by

mass of the earth's crust and the sixth most abundant element dissolved in seawater) and inexpensive than lithium [3]. Moreover, the low standard redox potential of K⁺/K (−2.93 V versus the standard hydrogen electrode (SHE)) [4], which is close to that of Li⁺/Li (−3.04 V versus SHE), implies possible high energy density [5]. In addition, high power density is expected due to the lowest Lewis acidity and desolvation energy of K⁺ compared to Na⁺ and Li⁺, i.e. the higher ionic conductivity and faster diffusion kinetics at the electrode/electrolyte interface, respectively. Also, inexpensive aluminum foil (instead of copper) can be

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used as negative electrode current collector. Finally, similarly to Li-ion batteries, and unlike Na-ion batteries, the reversible electrochemical intercalation of K ions into graphite has been experimentally demonstrated, making K-ion batteries as a potentially more sustainable and cost-effective alternative [3,6].

However, some challenges need to be overcome to develop efficient KIBs. Beyond the active materials choice, the stability of active materials and electrolytes, including the electrode/electrode interfaces upon storage/cycling, are of high interest to understand KIBs failure mechanism and thus optimize KIBs lifetime [7]. To do so, the solid electrolyte interface (SEI) formation and evolution upon storage/cycling as function of solvents/salts/additives needs to be urgently investigated/understood [8–11]. In that direction, some of us recently showed that the electrolyte reactivity at the K metal electrode governs half-cells performance and that more importantly that SEI cannot be study in half cells. Indeed, electrolyte degradation species formed at the K metal surface migrate to the working electrode and thus contaminate the studied electrodes whatever the electrolyte/electrode [11]. Thus, a reliable SEI study requires full-cells to prevent the K metal cross-contamination. However, while many papers have used X-ray photoelectron spectroscopy (XPS) to characterize the SEI layers in K-ion half-cells [9,12–20], to our knowledge, no studies have been performed so far to thoroughly investigate SEI in K-ion full cells [7].

To address these issues, this work investigates the impact of OCV temperature, upper cut-off voltage, depth of discharge, and vanadium dissolution on the electrochemical performance with a correlation to the SEI formation (analyzed by XPS) for $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ /graphite full-cells. To do so, $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ was selected for its electrochemical performance [21] while optimized graphite electrodes [22] and optimized full-cells assembly (with highly reproducible and reliable results) were used [23].

2. Experimental

2.1. Materials and electrodes preparation

Graphite electrodes were prepared following a previously optimized formulation [22]: SLP30 (TIMCAL), Carbon black (CB, C65, MTD), Carboxymethyl Cellulose (CMC-Na, Sigma-Aldrich, Mw ~250000), and carboxylated Styrene Butadiene Rubber (SBR, LITEX LB-420, Synthomer) were mixed with an 85:5:8:2 wt ratio in 1 ml distilled water using ball milling (PULVERISETTE 7) at 500 rpm for 1h. The slurry was coated on aluminum foil (15 μm thickness) by a doctor blade (125 μm corresponding to 2.4 $\text{mg}_{\text{graphite}} \text{cm}^{-2}$). Then the film was dried at room temperature for 1 night and 11 mm diameter electrodes were cut out,

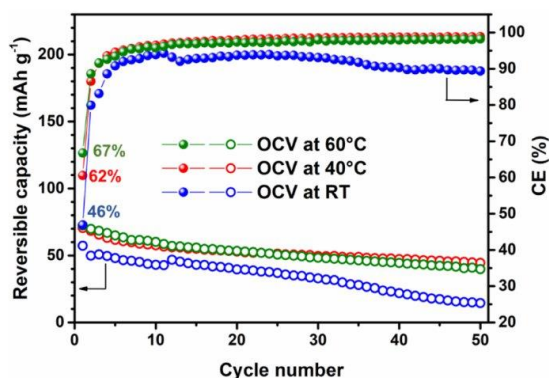


Fig. 1. Capacity retention and coulombic efficiency evolution obtained between 1.2 and 4.8 V at C/10 rate over 50 cycles for $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ /graphite coin-cells.

pressed at 2 tons/ cm^2 (leading to ~35 % electrode porosity), and dried again under vacuum at 80 °C for 12 h.

$\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ (KVFPFO) samples were synthesized by solid-state reaction previously reported [21]. Electrodes were prepared by mixing KVFPFO, CB (C65, MTD), and Polyvinylidene fluoride (PVDF 5130, Solef) with a 75:15:10 wt ratio in 2.5 ml N-Methyl-2-pyrrolidone (2.5 ml NMP for 1g) using ball milling (PULVERISETTE 7) at 500 rpm for 1h. The slurry was coated on aluminum foil (15 μm thickness) by a doctor blade (300 μm corresponding to 5 $\text{mg}_{\text{KVFPFO}} \text{cm}^{-2}$). The film was then dried at 60 °C for 12h under air. Then, 9.5 mm diameter electrodes were cut out, pressed at 3 tons/ cm^2 (leading to ~36 % electrode porosity), and dried again under vacuum at 80 °C for 12 h.

2.2. Electrochemical testing

KVFPFO/graphite cells were assembled using previously optimized cell parameters, i.e. with electrode diameter and capacity ratio fixed to 1.16 and an electrolyte volume of 50 μL . Electrochemical experiments were conducted using a VMP 3 multichannel system (BioLogic, France) in a 20 °C temperature-controlled room. Two pairs of coin cells (CR2032, stainless steel 316L) were assembled for reproducibility, while in the results section, data for only one cell is presented for clarity. The electrolyte was 0.8 M KPF_6 (Sigma-Aldrich, 99 %) EC:DEC (ethylene carbonate, Sigma-Aldrich, 99 %, and diethyl carbonate, Sigma-Aldrich, 99 %) by volume. Two microporous trilayer membranes (PP/PE/PP, from Celgard) were used as separators.

Galvanostatic cycling was made in full coin-cells as follows:

First, the OCV before cycling was done at 25 °C, 40 °C or 60 °C for 12 h to investigate its impact on the pre-formation of SEI analyzed by XPS. Additional cells were then cycled 50 times at C/10 between 1.2 and 4.8 V.

Second, the impact of the upper cut-off voltage on the SEI was performed selecting the OCV at 40 °C followed by 50 cycles at C/10 between 1.2 and 4.5 V, 1.2–4.8 V or 1.2–5.0 V.

Third, the impact of the lower cut-off voltage on the SEI was performed selecting the OCV at 40 °C followed by 50 cycles at C/10 between 1.2 and 4.8 V, 2.0–4.8 V, and 3.0–4.8 V.

Fourth, The rate capability tests were performed at different rates (C/10, C/5, C2, 1C, 2C, 5C, and 10C), the current density corresponding to 1C was 132 mA g^{-1} (corresponding to 1 mol of K^+ deintercalated in 1 h).

2.3. X-ray diffraction and Raman spectroscopy

The X-ray diffraction (XRD) data was collected using a PANalytical X'Pert Pro-MPD diffractometer that employed a copper $\text{K}\alpha$ radiation source with a wavelength of 1.5418 Å and a step size of 0.033°, within a range of 10°–40°. Furthermore, an ex-situ Raman spectrum was acquired using a Horiba Jobin-Yvon LabRAM ARAMIS spectrometer, operated with an excitation wavelength of 473 nm for the measurements.

2.4. Ex situ X-ray photoelectron spectroscopy (XPS)

XPS characterization was performed using an Escalab 250 Xi spectrometer with a monochromatized Al $\text{K}\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). KVFPFO and graphite electrodes, as obtained after the OCV at different temperatures or after 50 cycles as function of the upper and lower cut off voltages, were placed on a sample holder using uPVC insulation tape (3 M part number 655) and transferred to an argon-filled glove box connected to the spectrometer to avoid moisture/air exposure. Analysis was performed using the standard charge compensation mode and an elliptic 325 $\times$ 650 μm X-ray beam spot. Core level spectra were recorded using a 20 eV constant pass energy with a 0.15 eV step size and iterative scans with a dwell time of 500 ms to follow any possible degradation. Using CasaXPS software, the binding energy scale was calibrated from C–C, C–H peak at 285 eV. A non-linear Shirley-type background was used for

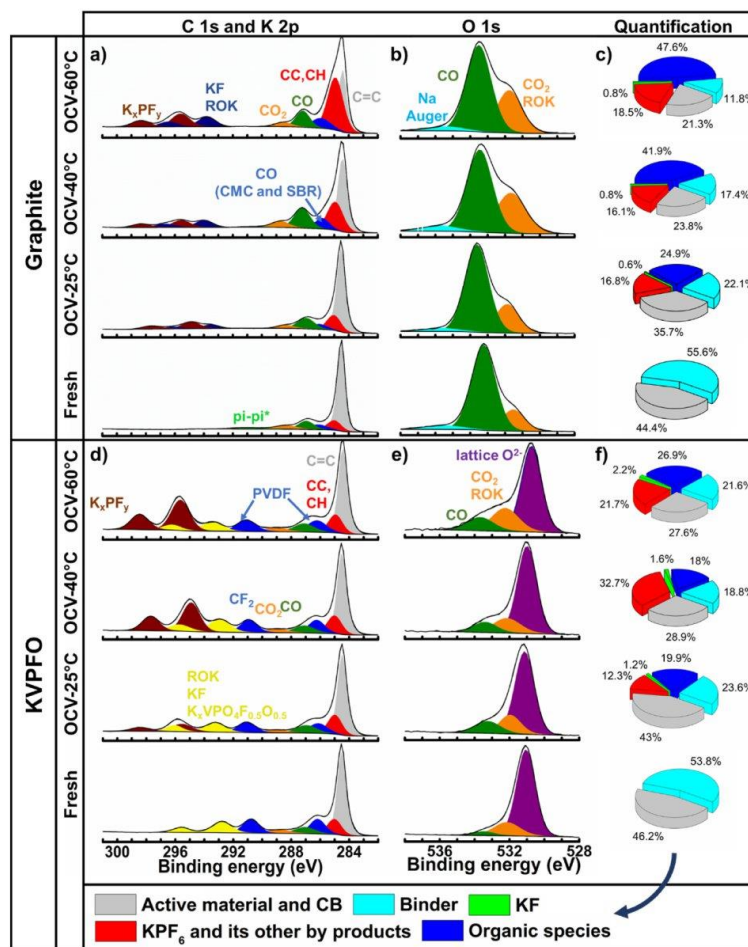


Fig. 2. a) C 1s, K 2p, b) O 1s XPS core level spectra, and c) Surface composition resulting from XPS quantification of graphite d) C 1s, K 2p, e) O 1s XPS core level spectra, and f) Surface composition resulting from XPS quantification of KVPFO electrodes as obtained from KVPFO//graphite cells after OCV at different temperatures (25 °C, 40 °C, and 60 °C) compared to the fresh graphite and KVPFO electrodes.

core peaks analysis while 70 % Gaussian - 30 % Lorentzian Voigt peak shapes (called GL(30)), full width at half-maximum, and position constraint ranges were selected to optimize peak positions and areas. Peak attribution was based on previous studies [14,24], including a K reference compound database previously reported by some of us [25].

For more clarity, the SEI composition resulting from XPS quantification (Tables S1 and S2) of graphite and KVPFO electrodes will be illustrated in a 3D pie chart.

Graphite and KVPFO electrodes were rinsed 2 times during 1 min in 2 ml of pure DEC (anhydrous, >99 % purity, Aldrich) and dried inside the argon-filled glove box for 5h before XPS measurements so that it is assumed that no traces of KPF₆ salt or solvents were left on the electrode surface. After rinsing, electrodes were transferred directly into the XPS machine from an argon-filled glove box connected to the XPS machine, ensuring that the samples never encountered air.

3. Results and discussion

3.1. OCV temperature impact

Fig. 1 Compares the capacity retention of KVPFO//graphite full coin-cells after OCV for 12 h at different temperatures (20, 40 and 60 °C). The cell with an OCV at 20 °C underwent a faster capacity loss than the cells with OCV at 40 °C and 60 °C. Indeed, the three cells were similarly stable during the first 10 cycles while the capacity loss suddenly increased after 10 cycles for the cell with the OCV at 20 °C. The reversible capacities obtained during the first cycle for the three cells suggest that the 12 h of OCV is enough to wet both graphite and KVPFO electrodes. Thus, the observed difference in capacity retention most likely originates from a pre-formation of an SEI spontaneously without cycling during the OCV. This is supported by the increase of the coulombic efficiency (CE) during the first cycle, from 46 % to 62 % then 67 % as the OCV temperature increased from 20 °C to 40 °C then 60 °C. Interestingly, the CE followed CE_{40 °C} > CE_{60 °C} > CE_{20 °C} after only few cycles and until the end of the cycling. Furthermore, Fig. S4a displays the galvanostatic profile of the 1st and 50th cycles of the full cells cycled between 1.2 and 4.8V at room

temperature, 40 °C, and 60 °C. In the 1st cycle, it is observed that the last high potential plateau (around 4.3 V) is more pronounced when the OCV temperature is lower. After 50 cycles, the full cells cycled with an OCV at 40 °C and 60 °C exhibit similar behavior with less irreversibility for the full cell with an OCV at 40 °C. As for the full cell with an OCV at room temperature, it displays low capacity (16.5 mAh g⁻¹) due to the increased cell polarization upon cycling. This underscores the significance of interface preformation (formation of chemical SEI). These results thus highlight that high-temperature OCV minimizes the irreversible capacity in the first cycle due to the pre-formation of a SEI, which leads to better CE and capacity retention for prolonged cycling. Overall, the cell with an OCV at 40 °C shows the best CE evolution and capacity retention compared to other cells. In contrast, an OCV at 60 °C can be here considered too extreme to pre-form efficiently the SEI. Finally, after 50 cycles, the KVPFO//graphite cells with 12 h OCVs at 25, 40, and 60 °C delivered 13, 48, and 41 mAh g⁻¹ with a capacity retention of 23, 70, and 57 %, respectively.

Then, XPS analysis was performed to confirm the pre-formation of a passivation layer and to evaluate the impact of the temperature on this phenomenon. Fig. 2 shows the relevant XPS core level spectra (C 1s, K 2p, and O 1s) of fresh graphite and KVPFO electrodes, along with the electrodes as obtained from KVPFO//graphite cells after OCV at 25 °C, 40 °C, and 60 °C. For clarity, Fig. 2 also shows the main compounds (in at.%) as obtained from XPS quantification for the corresponding electrodes while the full XPS quantification can be found in Tables S1 and S2.

First, regarding the peak attribution, the C 1s and K 2p of the graphite electrode (Fig. 2 a and b) display different peaks at 284.4, 285.0, 285.8 eV corresponding to C=C (carbon black and graphite), hydrocarbon contamination, carbon atoms in the C-O environment, respectively. The CMC and SBR binders display two characteristic peaks at 287 and 288.7 eV, assigned to CO- and CO₂-like carbon atoms, respectively [26]. At about 291.5 eV is a shake-up satellite (pi-pi* transitions of carbon black). The K 2p peaks at 293.5 (K 2p_{3/2}) and 296.3 (K 2p_{1/2}) eV are assigned to KF and ROK components [25]. The other K 2p peaks at 294.8 and 297.4 eV are ascribed to K_xPF_y [27]. Moreover, The O 1s core peaks spectra show the presence of ROK and CO₂ environment at 531.8 eV. The peak displayed at 533.5 eV relates to CO based species [11].

For KVPFO (Fig. 2 d and e), C1s core peaks spectra exhibit different components at 284.5, 287, 288.7 eV attributed to C=C (carbon black) and carbon atoms in the CO and CO₂ environments, respectively. The PVDF binder shows two characteristic peaks at 286 and 290.5 eV, allocated to CH₂- and CF₂-like carbon atoms, respectively [14]. The K 2p peaks at 292.6 (K 2p_{1/2}) and 295.4 (K 2p_{3/2}) eV are assigned to KF, KVPFO, and ROK components [16]. The other K 2p peaks at 294.7 (K 2p_{1/2}) and 297.5 (K 2p_{3/2}) eV are ascribed to the K_xPF_y component. In addition, The O 1s core peaks spectra show the presence of a KVPFO oxygen lattice (O²⁻) at 530.7 eV [28]. The peak displayed at 532.2 eV is related CO and ROK, and the peak at 533.8 eV is assigned to a C-O environment [25]. Thus, quantification details for the graphite and KVPFO electrodes are given in Tables S1 and S2 (supplementary information).

Regarding the electrodes surface composition, the comparative passivation layer evolution of fresh and assembled graphite and KVPFO electrodes by XPS at several OCV temperatures for 12h is displayed in Fig. 2 a, b, d, and e. The graphite and KVPFO passivation layers get thicker as a function of temperature without cycling with a remarkable increase in the CH, CO, KF, ROK, and K_xPF_y peak areas, indicating more salts and solvents decomposition at high OCV temperature (at 40 and 60 °C). The 60 °C OCV provides a large degradation of the solvents (Fig. 2 c and f), which is confirmed by the high initial coulombic efficiency of 67 % and exhibited by the considerable increase in the CH, CO, and ROK peaks areas (Fig. 2 a, b, d, and e, Tables S1 and S2) [7]. As shown in Fig. 2 c and f, the amounts of organic byproducts containing carbon and oxygen, as well as a smaller fraction of potassium,

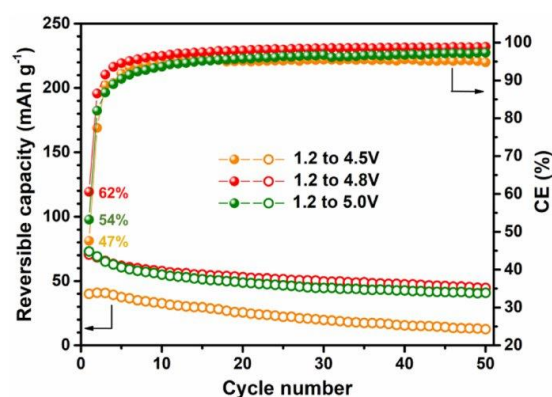


Fig. 3. Capacity retention and coulombic efficiency evolution obtained between 1.2 and 4.5 V, 1.2–4.8 V, and 1.2–5.0 V at C/10 rate over 50 cycles for KVPFO//graphite coin-cells.

phosphorus, and fluorine inorganic species are more significant for graphite and KVPFO with a 60 °C OCV. Thus, a more organic SEI appears unsuitable for the electrochemical performance (long-term cycling). Furthermore, Fig. 2 c and f show a 3D pie chart resulting from the SEI composition obtained from XPS quantification for fresh and assembled electrodes at different wetting temperatures. The passivation layer components have been divided into four parts: KPF₆ and its other by-products, organic species, KF, and binder. Indeed, increasing the OCV temperature involves more SEI growth; quantification of passivation layer for graphite electrodes with OCV temperatures of 25, 40, and 60 °C could be respectively considered as 42.2, 58.8, and 66.9 %. For KVPFO electrodes, the quantification of passivation layer could be respectively considered as 33.4, 52.3, and 50.8 % with OCV temperatures of 25, 40, and 60 °C. The high-temperature OCV can eliminate inhomogeneous reactions before cycling and minimize the irreversible capacity in the first cycle due to the pre-formed passivation layer, which is consistent with the electrochemical results. For the rest of the study, the 12h OCV at 40 °C was selected as an optimal parameter.

3.2. Upper cut-off voltage impact

The upper cut-off voltage (UCV) also affects the capacity retention. In this part, three full-cells were cycled at a C/10 rate to upper cut-off voltages of 4.5, 4.8, and 5 V over 50 cycles (Fig. 3). When the upper cut-off voltage of 4.5 V is applied, the reversible capacity decreases faster upon cycling compared to 4.8 and 5 V. This effect can be explained by the fact that total potassium intercalation into graphite occurs at potentials above 4.5 V, and the last KVPFO plateau was not reached. In addition, the larger capacity loss could also originate from a non-passivating and/or non-stable SEI formation at 4.5 V, the plateau at 4.3V disappears upon cycling, as shown at the 50th cycle (Fig. S4b). When cycled above 4.5 V, the SEI is expected to be thicker, which may lead to better passivation. Indeed, increasing the upper cut-off voltage to 4.8 V leads to an initial CE of 62 % while a further increase to 5 V negatively impacts the first CE (53 %) due to the irreversible plateau between 4.8 and 5V (i.e., enhanced electrolyte degradation), as depicted in Fig. S4b. Moreover, after 50 cycles, the CE reaches 99 % and 96 % corresponding to a capacity retention 70 % (48 mAh g⁻¹) and 63 % (45 mAh g⁻¹) when cycled at 4.8 V and 5 V, respectively. Overall, the 4.8 V upper cut-off voltage can be considered as good compromise to limit the electrolyte reactivity (i.e., SEI formation) without decreasing too much the delivered capacity while the 5 V CU limit can be considered too extreme due to the much higher electrolyte degradation. The SEI formed at 5 V is thus more likely thicker but more unstable and/or non-

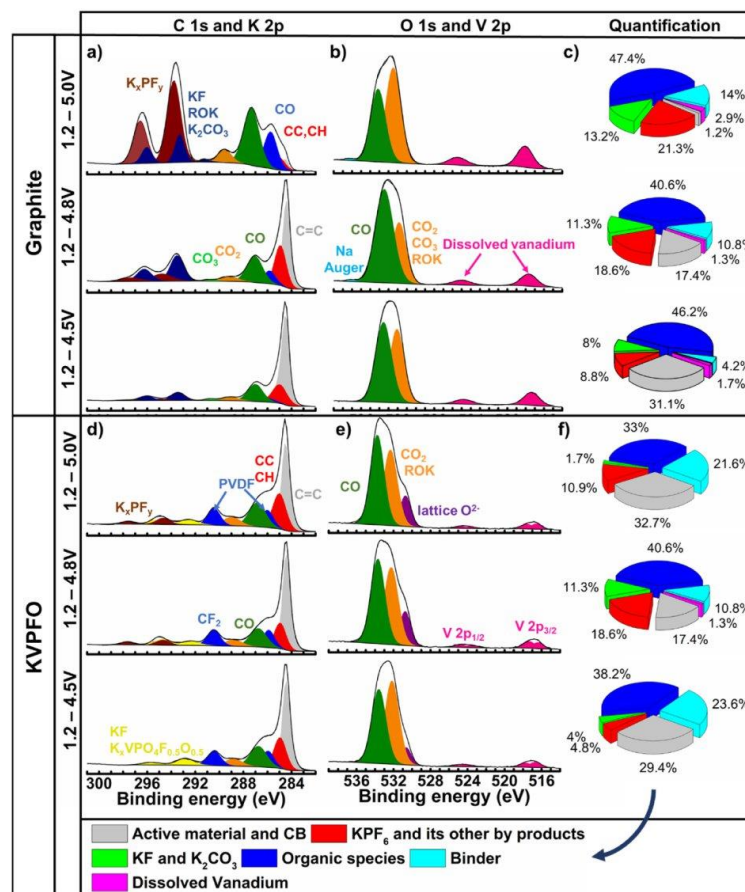


Fig. 4. a) C 1s, K 2p, b) O 1s XPS core level spectra, and c) Surface composition resulting from XPS quantification of graphite d) C 1s, K 2p, e) O 1s XPS core level spectra, and f) SEI composition resulting from XPS quantification of KVPFO electrodes as obtained from KVPFO//graphite cells after 50 cycles at different upper cut-off voltages (4.5, 4.8, and 5.0V).

passivating compared to the SEI formed at 4.8 V. Note that optimizing the KVPFO/graphite capacity ratio as function of the upper cut-off voltage would be necessary and would more likely help to further increase the CE and capacity retention, but this evaluation is out of the scope of this study.

Moreover, XPS analysis was used to observe the electrode/electrolyte interfaces by investigating the elemental compositions and the SEI growth built on the surfaces of the graphite and KVPFO electrodes and thus impacting their electrochemical performance. Fig. 4 illustrates the combined regions of C 1s, K 2p and O 1s, V 2p core levels spectra of graphite and KVPFO at the three different UCVs after 50 cycles mentioned previously.

The C 1s and K 2p core spectra indicate that the passivation layer is thin on both electrodes at 4.5 UCV, as evidenced by the presence of characteristic peaks of the fresh materials. This result could be attributed to insufficient SEI growth and huge electrolyte depletion during 50 cycles, implying thus poor electrochemical performance [29].

The spectra and quantification tables for KVPFO show no significant differences between the UCVs of 4.8 and 5V (Table S2, Fig. 4c and f). However, in the case of the graphite electrode, increasing the UCVs results in a greater passivation layer. This layer exhibits organic composition at 4.5V due to the high degradation of EC and DEC solvents.

Specifically, only 8.8 % of KPF₆ and its by-products, as well as 46.2 % of organic species. At 5V, both salt and solvent degradation is higher with 21.3 % of KPF₆ and its by-products, and 47.7 % of organic species.

Furthermore, the evolution of the atomic percentage of both electrodes detected by XPS at several UCVs is displayed in Fig. 4 c and f. It illustrates different behaviors concerning passivation layer covering depending on the UCV chosen. Indeed, inner inorganic SEI to a certain amount should be preferred because compounds including K₂CO₃, KF, and other salt by-products improve SEI stability [30]. The passivation layer should present the best compromise between organic and inorganic compounds to ensure high SEI stability. Based on the electrochemical performance and XPS quantification (Figs. 3 and 4), UCV of 4.8 provide the best trade-off between organic and inorganic passivation layer (11.3 % of K₂CO₃ and KF, 18.6 % of KPF₆ and its other by-products, as well as 40.6 % of organic species).

In addition to the chemical environment of the native material before cycling (Fig. 2), the O 1s and V 2p graphite core spectra show the presence of additional peaks (V 2p_{3/2} and V 2p_{1/2}) at UCVs of 4.5, 4.8, and 5.0V. These peaks are related to vanadium dissolution resulting from the degradation of KVPFO and/or active material surface defects, which could explain partially the capacity losses over 50 cycles. This vanadium dissolution is more pronounced at a 5 V UCV (2.9 %), as

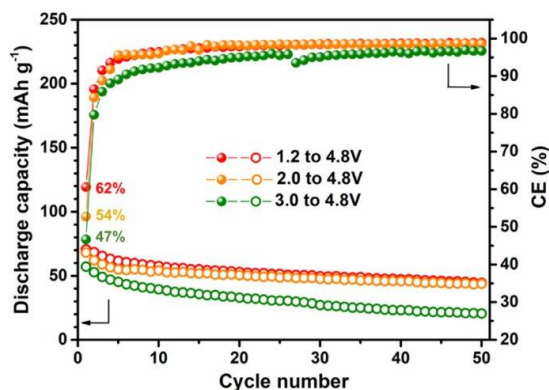


Fig. 5. Capacity retention and coulombic efficiency evolution obtained between 1.2 and 4.8 V, 2.0–4.8 V, and 3–5.0 V at C/10 rate over 50 cycles.

shown in Fig. 4. The 4.8 V UCV appears as an optimal cut-off voltage for the next part of the study.

3.3. Depth of discharge impact

The depth of discharge (DOD) has a significant impact on cell degradation due to both different SEI formation mechanisms (including SEI rearrangement/dissolution at higher DOD) and volume change of particles, which may result in electrolyte drying, stress, and cracking [30,31].

KVPFO//graphite full-cells were cycled with a selected upper cut-off voltage of 4.8 V and discharged to various DODs, i.e. to 1.2, 2.0, and 3.0 V (Fig. 5). A DOD of 3 V provided the largest loss of capacity and lowest CE upon cycling. Note that at 3V, the deintercalation of potassium ions from the graphite does not reach the final stage, which is consistent with the low CE that remains lower than 97 % and a continuous SEI growth over cycles. Fig. S4c illustrates that with a voltage cutoff of 3V, the plateau at 4.3V at the 1st cycle disappears after 50 cycles, accompanied by a noticeable increase in polarization. This increase in polarization could be attributed to an unstable SEI (i.e., significant dissolution and reformation), leading to an increase in charge transfer resistance upon cycling. In contrast, the 1.2 and 2.0 V DODs have similar

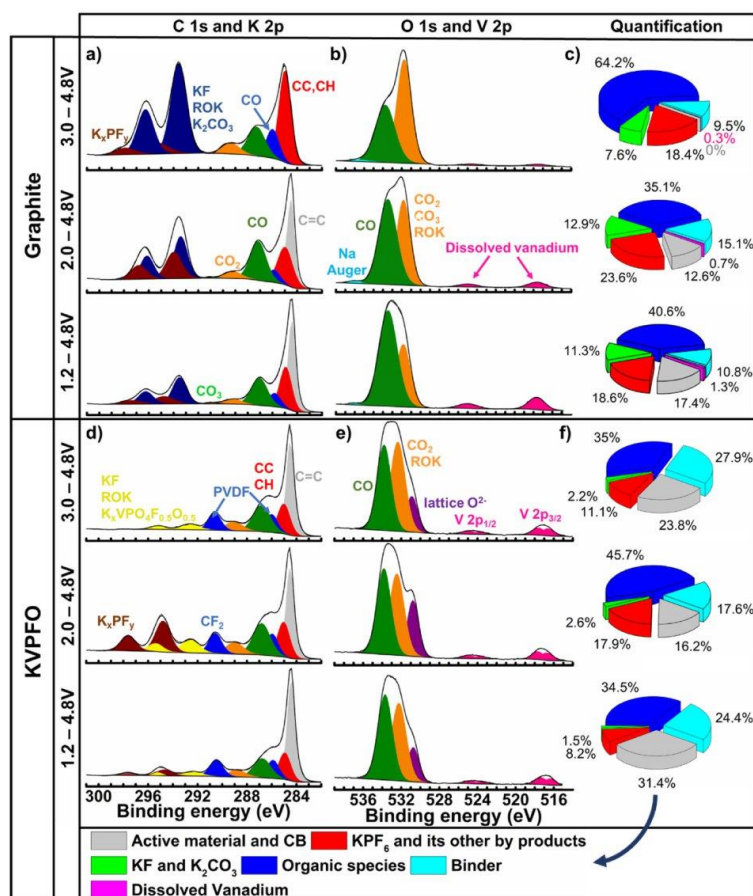


Fig. 6. a) C 1s, K 2p, b) O 1s XPS core level spectra, and c) Surface composition resulting from XPS quantification of graphite d) C 1s, K 2p, e) O 1s XPS core level spectra, and f) SEI composition resulting from XPS quantification of KVPFO electrodes as obtained from KVPFO//graphite cells after 50 cycles at different lower cut-off voltages (1.2, 2.0, and 3.0V).

electrochemical performance: a capacity retention of 70 % with a capacity of 48 mAh g⁻¹ and a CE of 99.3 % after 50 cycles. Overall, while higher DODs (i.e., lower discharge voltage) generally result in higher capacity fade and impedance growth, the opposite is observed here, which needs to be understood by the SEI analysis.

C 1s and K 2p core peaks spectra of the graphite electrode show that the passivation layer is thicker by increasing the discharge potential (from 1.2 to 3 V). As shown in Fig. 6 a, b, d, and e. This could be justified by the greater SEI dissolution/reorganization at higher DOD (1.2 V). Moreover, the O 1s and V 2p graphite core spectra show the presence of additional peaks (V 2p_{3/2} and V 2p_{1/2}). As noted, the vanadium dissolution related peaks resulting from the degradation of KVPFO or/and framework defects; this vanadium dissolution is more pronounced at a higher DOD of 1.2 V (1.3 %), as shown in Fig. 6. On the other hand, KVPFO follows the same trend as graphite for 1.2 and 2V DODs except for 3V, where the SEI is much thinner (Fig. 6 c and f). This may be a result of the excessive consumption of electrolytes upon the SEI growth on the anode, and the dissolution of the organic passivation layer on the cathode, since there will be no total deintercalation of potassium ions from the graphite at 3 V, thus fewer desolvation phenomena that reduce the thickness of the SEI. Finally, we can conclude that a thick SEI on the anode and a thin passivation layer on the cathode are observed. These results are consistent with CE evolution shown in Fig. 5, demonstrating the process (charge/discharge) irreversibility due to the inhomogeneous passivation layer growth at 3 V DOD. Fig. 6 c and f show that the inorganic/organic species ratio of graphite electrodes provides 0.73, 1.1, and 0.4 for 1.2, 2.0, and 3.0 V, respectively. These results confirm that the more inorganic SEI is suitable for high electrochemical performance, as mentioned previously. Moreover, the passivation layer is more important in the case of graphite which suffers from several drawbacks; in particular, during potassiation the volume expansion (>60 %) and the graphene layers exfoliation in the case of an unstable SEI, contrary to KVPFO, which has a three-dimensional framework that is more stable [21].

As previously mentioned, a partial capacity loss comes from the dissolution of vanadium from the cathode, which is deposited on the anode surface and might contaminate the SEI of the graphite. The mechanism of vanadium accumulation's detrimental effect on the graphite electrode in KIBs is poorly studied in the literature compared to transition metal dissolutions in Li-ion batteries, especially in the spinel structure-type [32,33]. Indeed, the oxidation state of vanadium species on the graphite electrode is critical for thoroughly understanding these processes. The vanadium oxidation state present in the pristine KVPFO material is V³⁺. Fig. S1 B shows a shift to high binding energy at the V 2p_{3/2} peaks after the first cycle (i.e., a degree of oxidation slightly higher than 3⁺) on the graphite electrode, which indicates that oxidized vanadium dissolution takes place at high potential and before to be reduced on the graphite negative electrode. As depicted in Fig. S1 a and b, in an actual battery cell, the consequence could be ongoing active potassium loss and increased SEI growth, exhibited by the continual CE increase. Accordingly, this vanadium dissolution starting from the first cycle might be the underlying mechanism causing the enhanced capacity fading observed for graphite/KVPFO full cell when operating under conditions favoring vanadium dissolution (i.e., high upper cut-off voltages).

To examine the structural stability of graphite under various potentials after 50 cycles, XRD was conducted as part of further investigation (Fig. S3). For KVPFO, It was previously demonstrated by Wernert et al. [21], that the material exhibited a stable structure even after undergoing up to 5V. Furthermore, Fig. S3 shows the main characteristic Bragg peak (002) of graphite at 22°. After cycling a shoulder in the graphite peak (002) is systematically observed whatever the potential windows used [34]. This peak shoulder highlights the presence of potassium ions inserted within the electrode structure, as also shown from the peaks labeled KC₃₆ at 23° and KC₂₄ at 20° which are intermediate potassiated phases. The presence these peaks and the absence of KC₈

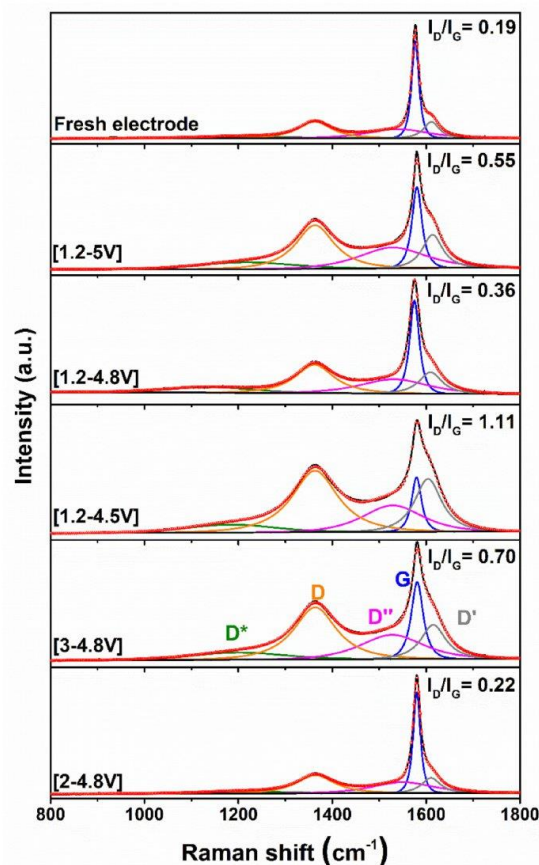


Fig. 7. Raman spectra of graphite electrodes from full-cells after 50 Cycles at different potential windows.

characteristic peak (16.6°) are in line with a limited potassiation [35]. For further investigations, Raman spectroscopy analysis was carried out on the same set of electrodes.

Fig. 7 shows two characteristic bands of defective or disordered carbon around 1360 cm⁻¹ (D-band) and graphitized sp² carbon around 1580 cm⁻¹ (G-band). These peaks were fitted with a Lorentzian shaped-bands to determine the I_D/I_G ratio with precision, where I_D and I_G are the intensities of the fitted D-peak and G-peak, respectively [36–38].

The rise in the ratio of D-band and G-band intensities (I_D/I_G) observed in the Raman spectrum of a graphite electrode is usually attributed to three factors: the trapped K ions into the graphite structure, intercalation process, and the structure exfoliation, indicating a decrease in the graphite crystallinity, which could be one of the key factors behind the capacity decay [39].

On the one hand, with an UCV of 4.5V (1.2–4.5V) and a DOD of 3V (3–4.8V) after 50 cycles the spectra presents the highest I_D/I_G of 1.11 and 0.70, respectively, which is due to the trapping of K ions into the graphite structure upon cycling, agreeing with the electrochemical results (Figs. 3 and 5). On the other hand, cells cycled at potential windows of [1.2–5V], [1.2–4.8V], and [2–4.8V] exhibit lower I_D/I_G of 0.55, 0.36, and 0.22 respectively. Thus, the Raman spectra after 50 cycles at voltage window of [2–4.8V], showing a close I_D/I_G ratio to that of fresh electrode, which indicates that the structure of graphite is intact after

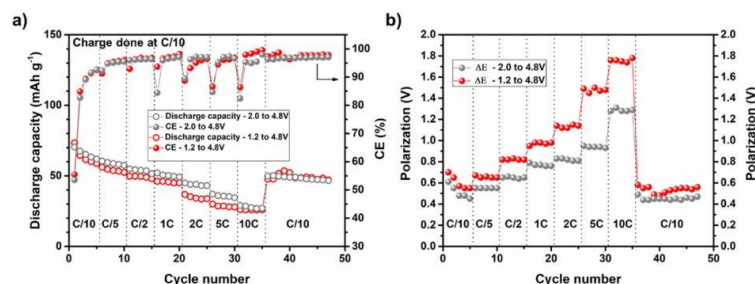


Fig. 8. a) Galvanostatic rate performance at 1.2V and 2.0V DODs from C/10 to 10C and b) corresponding polarization of graphite/KVPFO full coin cells.

repeated K-ion intercalation/deintercalation, which is consistent with the previously discussed electrochemical performance and SEI characterization.

3.4. Power performance

In this part, a rate capability test was performed using the 4.8 V upper cut off-voltage and the 1.2 and 2 V DODs as they were similar in term of capacity retention. Note that high rate at low discharge voltage may result in K plating, higher polarization, and cell degradation [22, 40]. As expected, Fig. 8 shows that using 2 V as DOD led to higher capacity at high rate ($\sim 50 \text{ mAh g}^{-1}$ at 2C with a polarization of 0.8 V), which is quite satisfying for such relatively high KVPFO/graphite loading ratio ($2/5 \text{ mg cm}^{-2}$). In contrast, the 1.2 V DOD led to only $\sim 35 \text{ mAh g}^{-1}$ at C/2 with a higher polarization of 1.1 V, indicating an impedance growth due to a different SEI formation. Overall, these results highlight that KVPFO/graphite full-cells with relatively high energy ($42 \text{ Wh kg}_{\text{device}}^{-1}$ at C/5 and $31.5 \text{ Wh kg}_{\text{device}}^{-1}$ at 2C) and high power ($8.4 \text{ W kg}_{\text{device}}^{-1}$ at C/5 and $63 \text{ W kg}_{\text{device}}^{-1}$ at C/5) can be obtained. Note that the energy and power values given here include the active materials, binder, carbon additive, electrolyte, and current collector masses. Moreover, further improvement is expected, especially as the KVPFO electrode (i.e., coating or/and other interface/surface treatment) [20] and the electrolyte formulation still need to be optimized (addition of additives).

4. Conclusions

This work studied the impact of OCV temperature, UCVs, DODs and rates of cycling of KVPFO/graphite full cells on the electrochemical performance through SEI studies. After cycling, cells underwent XPS analysis to study the mentioned parameters on the passivation layer. The main results of this work can be summarized as follows:

- Passivation layer preformation on KVPFO and graphite is more pronounced by increasing the OCV temperature, likely to rise the electrode wetting by electrolyte. A OCV temperature at 40°C for 12h leads to a main inorganic behavior, and consequently to good electrochemical performance compared to 25°C and 60°C .
- The passivation layer is nearly absent on both cathode and anode electrodes at 4.5 UCV, leading to critical electrochemical results. In contrast, UCV of 4.8 provided the best trade-off between the organic and inorganic passivation layer, leading to both good capacity retention and coulombic efficiency evolution, compared to 4.5 and 5 V UCVs.
- Greater SEI dissolution at 1.2V compared to 2V DODs lead to a thinner SEI. Furthermore, the ratio of SEI inorganic/organic species for graphite electrodes are 0.73, 1.1, and 0.4 for 1.2, 2.0, and 3.0 V. Suitable electrochemical performance is observed when this ratio is close to 1 corresponding likely to a stable passivation layer.

- For graphite/KVPFO full cell, capacity loss comes partially from vanadium dissolution that started from the 1st cycle.
- 1.2V DOD presented lower capacity at a high rate, indicating an impedance growth at higher DODs, confirmed by the increase of polarization as a function of current density. In contrast, 2 V DOD led to higher capacity at a high rate.

This work highlights the correlation between SEI investigation and electrochemical performance. This study could be completed in the future by the coating and optimization of KVPFO electrode, as well as the formulation of new innovative electrolytes to mitigate the vanadium dissolution and improve the passivation layer stability.

CRedit authorship contribution statement

Badre Larhrib: Investigation, Conceptualization, Formal analysis, Visualization, Original draft writing. **Lénaïc Madec:** Conceptualization, Validation, Review & Editing, Supervision. **Laure Monconduit:** Validation, Review & Editing, Supervision. **Hervé Martinez:** Resources, Management, Validation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2023.233743>.

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Supporting Information:

A Novel K-ion KVPO₄F_{0.5}O_{0.5}/graphite full cell: Correlation between XPS SEI Studies and Electrochemical testing results

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Table S1. Atomic percent (at.%) obtained from XPS quantification for graphite electrodes at different conditions.

	Name	Position	FWHM	Pristine	25°C OCV	40°C OCV	60°C OCV	1.2 to 4.5V	1.2 to 4.8V	1.2 to 5V	2 to 4.8V	3 to 4.8V
C 1s	C=C	284.4	0.6-0.8	44.4	35.3	23.8	21.3	31.1	17.4	1.2	12.8	-
	C-C, CH	285.0	1.1-1.4	8.0	9.3	14.2	22.5	10.4	11.5	1.9	9.3	16.7
	C-O	285.8	1.1-1.4	5.1	3.4	4.8	3.1	2.3	3.7	6.4	2.4	5.5
	C=O	287.0	1.3-1.6	7.5	8.0	10.1	8.2	9.7	10.3	12.0	10.3	7.4
	O-C=O	288.7	1.3-1.6	4.8	2.3	3.4	1.6	2.3	2.0	2.4	2.0	2.9
	CO ₃ ²⁻	290.1	1.3-1.6	-	-	-	-	0.7	0.4	0.3	0.1	-
	pi pi*	291.5	3	2.7	-	0.4	-	-	-	-	-	-
K 2p	K 2p _{3/2} (1)	293.5	1.2-1.5	-	1.0	1.5	1.6	1.4	3.3	2.8	3.1	6.9
	K 2p _{3/2} (2)	294.8	1.7-2.0	-	2.0	1.5	2.4	0.3	1.4	4.9	2.3	1.3
	K 2p _{1/2} (1)	296.3	1.2-1.5	-	1.0	1.5	1.8	1.5	3.2	2.9	3.3	7.0
	K 2p _{3/2} (2)	297.4	1.7-2.0	-	2.0	1.5	2.4	0.3	1.3	5.0	2.3	1.3
F 1s	KF	685.0	1.7-2.0	-	0.3	0.4	0.4	2.3	3.2	6.3	6.1	3.8
	K _x PF _y	687.8	1.7-2.0	-	8.3	9.3	10.0	3.1	8.4	3.6	11.0	9.4
	Org F (1)	689.0	1.7-2.0	-	2.7	1.0	0.6	1.8	1.4	6.9	1.0	2.6
	Org F (2)	690.8	1.7-2.0	-	0.9	1.6	-	1.2	0.3	-	0.2	3.1
V 2p	Dissolved V (total)	-	-	-	-	-	-	1.7	1.3	2.9	0.7	0.3
O 1s	ROK, O-C=O, CO ₃ ²⁻	531.8	1.7-2.0	2.5	3.9	3.6	4.5	10.5	6.5	15.5	8.4	12.5
	C=O, C-O	533.5	1.7-2.0	10.4	6.9	11.1	9.0	12.7	12.9	11.5	11.3	9.2
	Na Auger	537.2	1.1-1.3	0.8	0.6	0.6	0.6	-	0.1	0.2	0.2	0.3
P 2p	KPF ₆ by products	133.9	1.2-1.5	-	0.1	0.1	0.2	1.8	1.9	2.8	2.1	0.8
	KPF ₆ by products	134.8	1.2-1.5	-	0.1	0.1	0.2	1.8	1.8	2.7	2.1	0.9
	KPF ₆ by products	135.8	1.2-1.5	-	1.9	0.2	0.2	0.4	0.5	0.6	0.8	0.1
	KPF ₆ by products	136.7	1.2-1.5	-	1.8	0.2	0.2	0.4	0.4	0.5	0.7	0.1
	K _x PF _y	137.7	1.5-1.7	-	0.2	1.6	2.6	0.5	1.4	0.8	1.1	2.2
	K _x PF _y	138.5	1.5-1.7	-	0.2	1.5	2.5	0.6	1.5	0.8	1.2	2.3
Na 1s	Na 1s (CMC and SBR)	1071.5	-	13.7	7.8	6.2	4.2	1.5	3.8	5.0	5.4	3.4

Table S2. Atomic percent (at.%) obtained from XPS quantification for KVPFO electrodes at different conditions.

	Name	Position	FWHM	Pristine	25°C OCV	40°C OCV	60°C OCV	1.2 to 4.5V	1.2 to 4.8V	1.2 to 5V	2 to 4.8V	3 to 4.8V
C 1s	C=C	284.5	0.6-0.8	30.8	26.8	19.1	21.5	23.3	24.0	20.9	12.7	20.9
	CC, CH	285.0	1.1-1.3	7.8	8.7	5.8	6.2	10.2	10.2	9.6	8.0	8.6
	CH-CF ₂	286.0	1.4-1.6	8.3	5.9	4.7	5.4	5.9	6.1	5.5	4.4	6.4
	CO	287.0	1.4-1.6	2.6	1.5	1.2	1.2	10.8	7.6	9.3	7.9	10.4
	O-C=O	288.7	1.4-1.6	1.4	1.8	1.5	1.6	3.6	3.4	3.7	3.4	4.0
	CF ₂	290.5	1.4-1.6	8.3	5.9	4.7	5.4	5.9	6.1	5.5	4.4	5.7
K 2p	KF, KVPFO, ROK	292.6	1.1-1.4	2.6	2.0	2.0	1.5	1.2	0.8	0.8	1.3	0.9
	K _x PF _y	294.7	1.1-1.4	-	1.6	3.7	4.5	-	0.9	0.7	2.6	-
	KF, KVPFO, ROK	295.4	1.1-1.4	2.1	1.9	1.9	1.5	1.0	0.7	0.7	1.3	1.0
	K _x PF _y	297.5	1.1-1.4	-	1.5	3.6	4.4	-	0.9	0.7	2.5	-
F 1s	KF	684.90	1.8-2	0.6	0.8	1.1	0.7	2.0	0.7	0.9	1.3	1.1
	K _x PF _y and/or PVDF	687.6	1.7-2	14.5	18.1	28.8	19.7	14.3	16.0	18.6	26.1	15.8
	Org F	689.5	1.5-1.8	5.6	6.5	5.9	13.2	-	4.4	0.4	1.2	0.9
V 2p (total)	-	-	-	1.6	1.3	1.0	0.6	0.6	0.5	0.6	0.7	0.8
O 1s	Lattice O ₂ ⁻	530.7	1.3-1.6	5.8	4.7	3.6	2.5	1.2	1.7	2.1	3.1	2.6
	O-C=O, ROK	532.2	1.6-1.8	2.7	3.4	2.6	3.4	8.5	7.1	6.6	5.8	8.3
	CO	533.8	1.6-1.8	2.3	1.4	1.1	1.2	7.6	7.0	9.7	6.8	8.5
P 2p	KVPFO	133.0	1.5-1.8	1.5	1.2	0.9	0.7	0.9	0.7	0.9	1.0	0.9
	KVPFO	133.9	1.5-1.8	1.6	1.4	1.0	0.8	0.9	0.8	1.0	1.2	1.1
	KPF ₆ by products	135.8	1.5-1.8	-	-	-	-	1.1	0.4	0.2	0.2	1.2
	KPF ₆ by products	136.6	1.5-1.8	-	-	-	-	1.2	0.4	0.2	0.2	1.1
	K _x PF _y	137.9	1.2-1.5	-	1.4	2.9	1.8	-	0.8	0.8	1.8	-
	K _x PF _y	138.7	1.2-1.5	-	1.5	3.1	2.0	-	1.0	0.9	2.1	-

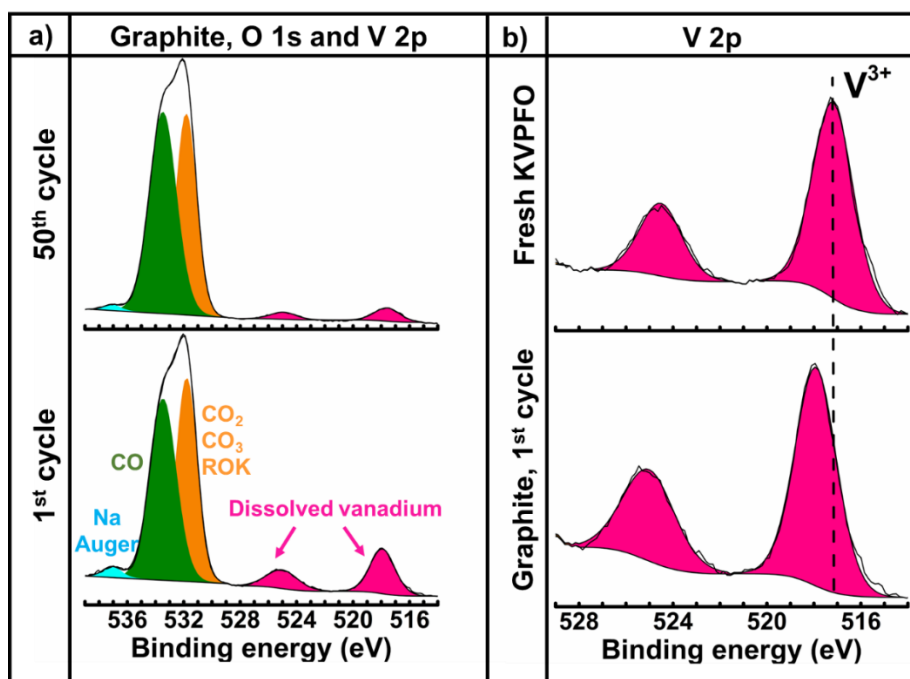


Fig. S2. a) O 1s and V 2p XPS core spectra of graphite electrode obtained after the 50th cycle (top) and 1st cycle (bottom). b) V 2p XPS core spectra of pristine KVPFO (top) and graphite electrode obtained after the 1st cycle (bottom).

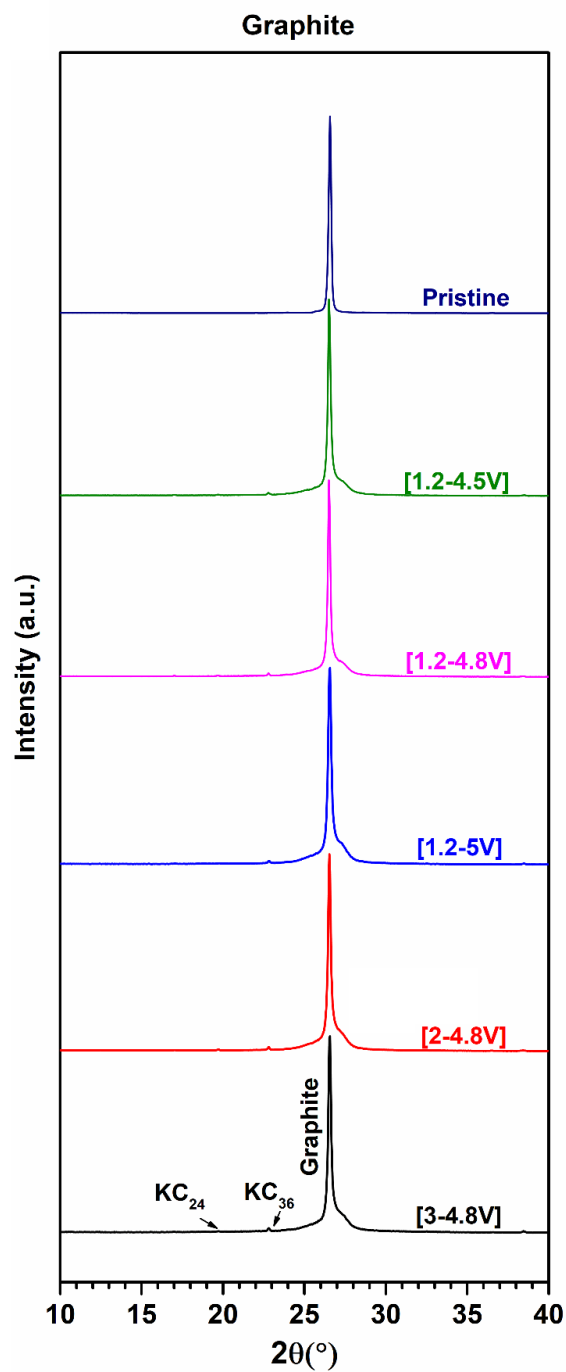


Fig S3. XRD patterns of graphite samples as obtained from KVPFO/graphite cells after 50 cycles (at end of full cell discharge) at different UCVs (4.5, 4.8, and 5V) and DODs (1.2, 2, and 3V) compared to the pristine material.

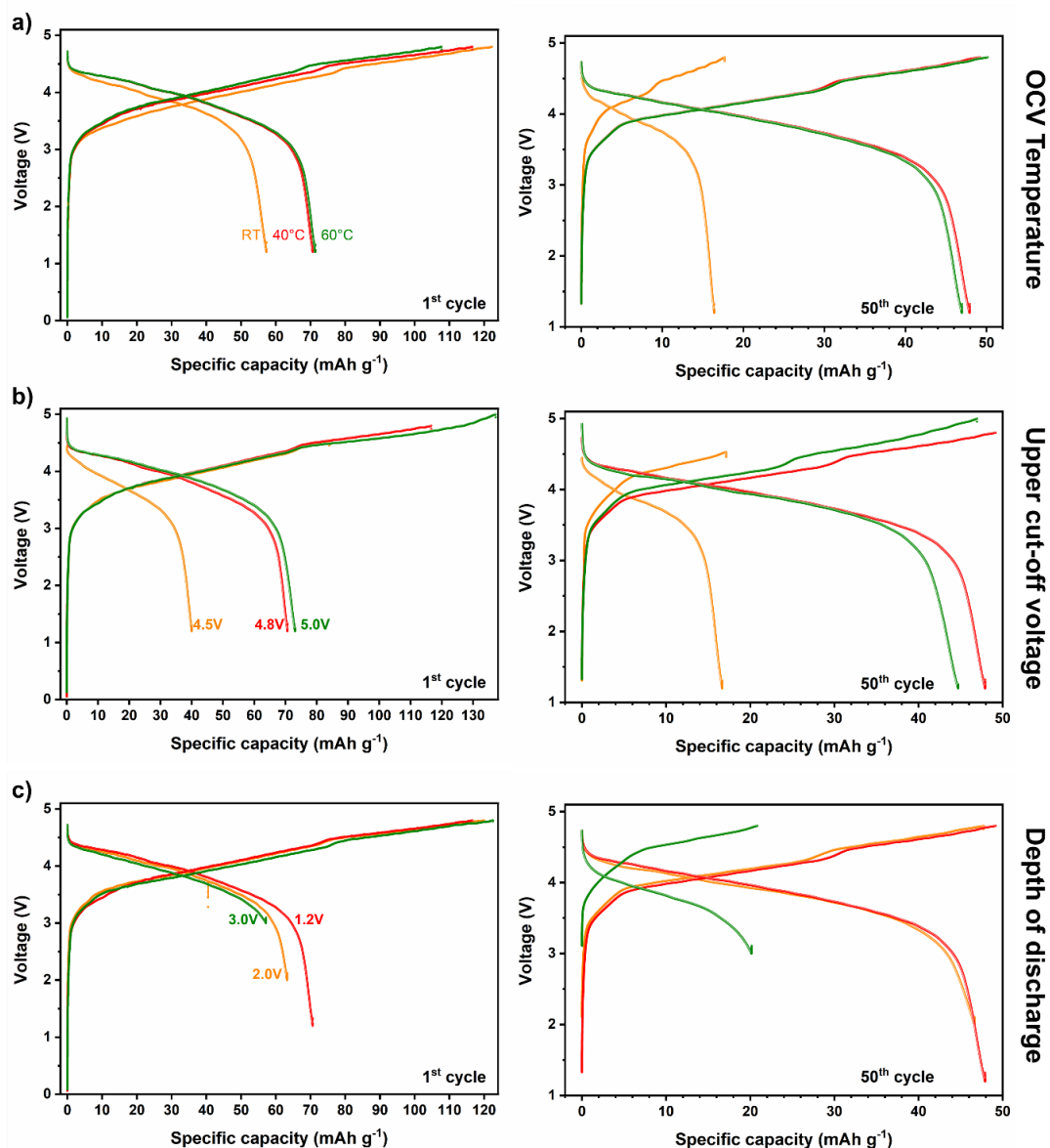


Fig S4. a) 1st and 50th charge/discharge profiles obtained between 1.2-4.8 V at different OCV temperatures, b) 1st and 50th charge/discharge profiles obtained between 1.2-4.5V, 1.2-4.8V, and 1.2-5.0V, and c) 1st and 50th charge/discharge profiles obtained between 1.2-4.8V, 2.0-4.8V, and 3.0-4.8V at C/10 rate for KVPFO/graphite full coin-cells.

Conclusions and Perspectives

The increase in renewable energy production - essential for the creation of a sustainable society - implies a growing need for stationary energy storage systems. Currently, lithium-ion batteries are the most widely used due to their high mass and volumetric energy densities. In parallel with the optimization of their performance, new research has emerged to develop batteries with more abundant and cost-effective components. The success of sodium-ion technology has inspired research into potassium-ion technology, which appears promising for stationary storage due to the low standard potential of the K^+/K couple and the low desolvation energy of the K ion, which are favorable for the development of high-energy and -power density batteries. Optimizing anode and cathode formulation is crucial for the development of this technology, as the impact of the electrode design on electrochemical performance has been studied for several years. Thus, an electrode formulation study was conducted and is discussed in Chapter 2, comparing different graphite electrode compositions to strike a balance between electronic and ionic percolation networks while maintaining a 35% porosity. Our investigations revealed a substantial improvement in the volumetric expansion and electrochemical performance of the graphite electrode, achieved with a composition of 85:5:2:8 for Graphite:CB:SBR(2):CMC. Furthermore, in the same chapter, another study explored hard carbons synthesized by Louiza Larbi (IS2M & ICGM) at varying temperatures using a composition of 90:5:5 for the active material:CB:PVDF. Notably, while the optimized graphite composition did not yield satisfactory results for hard carbons, we identified that HCs synthesized at 1500°C displayed favorable electrochemical performance. This enhancement can be attributed to the presence of oxygen-functional groups, desirable porosity, low close porosity, and edge defects, all of which enhance adsorption. This hard carbon sphere-based material exhibits significant promise for power applications. To advance towards the development of reliable full cells, this chapter also explores the study of positive electrodes. In pursuit of this goal, we focused on two electrode families: fluorophosphates ($KVPO_4F_{0.5}O_{0.5}$ – Synthesized by Romain Wernert - ICMCB) and Prussian Blue Analogs ($K_{1.7}Mn_{0.65}Fe_{0.35}[Fe(CN)_6]_{0.92} \cdot 0.5H_2O$ – Synthesized by Phuong Nam Le Pham - ICGM). Our investigations revealed that these electrodes exhibit impressive capacities of 93 and 111 mAh g⁻¹, with average potentials of 4.2 and 4 V, respectively.

As a critical step towards full cell development, chapter 3 focuses on K-ion full cells. The chapter provides emphasizes the significance of full cell research for advancing K-ion battery technology, even though it is in earlier stages compared to other battery types like lithium-ion and sodium-ion. A review of commonalities and differences in potassium-ion full cells is provided, revealing persistent challenges requiring attention and resolution. These challenges include the imperative avoidance of electrode precycling before full cell assembly, a lack in comprehensive research relating to electrolyte and electrode design, the essential demand for dependable cell prototypes, and a obvious deficiency in positive electrode materials that satisfactorily fulfill a set of criteria. Specifically, these specifications involve characteristics such as high tap density, significant capacity within the voltage range of 2 to 4.3V, high average potential, facile synthesis, and other essential parameters. Addressing these challenges is imperative for the advancement of potassium-ion battery technology, paving the way for its broader integration and practical use within the scientific and technological landscape. In the same chapter, a guideline for assembling K-ion half cells and full cells is presented, using specific electrode materials (graphite and $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$). Key parameters that influence half cell performance, such as the choice of separator and electrolyte, are discussed, and the importance of using a glass fiber membrane in contact with potassium metal is highlighted. Maintaining a specific electrolyte volume in relation to the porosity of the electrodes and separators is crucial for enhancing capacity and efficiency. The chapter also outlines the optimal ratios for electrode diameter and capacity. The practical application of these findings is demonstrated in coin-cells with a high loading ratio, resulting in promising energy density. Thus, to industrialize KIBs, future research should prioritize full cell studies, focusing on electrode materials, electrolytes, and other aspects like characterizing the electrode/electrolyte interfaces and understanding how cells interact.

To address the previously mentioned issues, chapter 4 investigates the impact of several key parameters on the electrochemical performance of $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ /graphite full cells was investigated. Higher open-circuit voltage (OCV) temperatures were found to enhance the preformation of the passivation layer, leading to improved electrochemical performance, particularly at 40°C for 12 hours. An upper cut-off voltage (UCV) of 4.8 V provided a favorable balance between organic and inorganic passivation layers, resulting in enhanced capacity retention and coulombic efficiency compared to other UCV values (i.e., 4.5 and 5.0V). The depth of discharge (DOD) was also a crucial factor, with a DOD of 1.2 V leading to lower capacity at higher

cycling rates due to increased impedance, while a DOD of 2 V resulted in higher capacity under such conditions. These findings shed light on factors influencing the electrochemical behavior of $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$ /graphite full cells, offering valuable insights for optimizing their performance and stability.

Overall, this thesis began in October 2020 as part of the ANR TROPIC project initiated in November 2019, in collaboration with IPREM, ICGM, and ICMCB, primarily due to the initial research on potassium-ion batteries by Vincent Gabaudan (ICGM), then by Laure Caracciolo who was in her third year of doctoral studies at IPREM at that time. Over the course of a year, we collaborated on the study of materials, synthesized by ICMCB, $\text{KVPO}_4\text{F}_{0.5}\text{O}_{0.5}$. All the work conducted since then, some of which has been published in peer-reviewed journals, has provided an initial understanding of potassium-ion batteries' functioning and has opened up exciting prospects in the field. This collaboration between IPREM, ICGM, and ICMCB has strengthened through the research efforts of Louiza Larbi (IS2M/ICGM) on Hard Carbon as negative electrode materials and the development of new carbon coatings for positive electrodes, aimed at reducing electrolyte degradation at the active material's surface. Furthermore, research by Phuong Nam Le Pham (ICGM) explores the impact of concentrated electrolytes on electrochemical performance and various mechanisms of intercalation and insertion into graphite and prussian blue analogues.

Finally, this work will pave the way for further studies aimed at enhancing our understanding of potassium-ion technology. These studies may include conducting ex-situ characterizations in full cells to mitigate the reactivity of potassium metal, exploring cross-talk phenomena in full cells to design suitable electrolytes for each system, and addressing the formulation of electrode materials, which is currently lacking in the potassium-ion literature. It is hoped that this thesis will serve as a catalyst for future projects toward the first potassium-ion prototype (i.e., 18650 cells), which holds promise for various applications.

Appendix I : Glossary

LIBs	Li-ion batteries
SHE	Standard hydrogen electrode
KIBs	K-ion batteries
PVDF	Polyvinylidene fluoride
CMC	Carboxymethylcellulose
NMP	N-methyl pyrrolidone
NIBs	Sodium-ion batteries
NaSICON	Sodium superionic conductors
KFSI or KFSA	Bis(fluorosulfonyl)imide potassium salt
CNFs	Carbon nanofibers
EC	Ethylene carbonate
DEC	Diethyl carbonate
KPF₆	Hexafluorophosphate potassium salt
PTCDA	Perylene-3,4,9,10-tetracarboxylic dianhydride
PAQS	polyanthraquinone sulfide
T_M	Transition metals
PB	Prussian blue
PBA	Prussian blue analogue
DMC	dimethyl carbonate
PC	Propylene carbonate
KClO₄	Perchlorate de potassium
KTFSI or KTFSA	Bis(trifluorosulfonyl)imide potassium
GBL	γ -butyrolactone
SEI	Solid electrolyte interphase
C₃C₁pyrr	N-methyl-N-propylpyrrolidinium
HAXPS	Hard X-ray Photoelectron Spectroscopy

XPS	X-ray Photoelectron Spectroscopy
ES	Ethylene sulfite
FEC	Fluoroethylene carbonate
VC	Vinylene carbonate
CEI	Cathode electrolyte interphase
SPI	Solid permeable interface
LUMO	Lowest unoccupied molecular orbital
HOMO	Highest occupied molecular orbital
LCL	Loss of cyclable lithium
HC	Hard Carbon
SBR	Styrene butadiene rubber
CB	Carbon black
DME	Dimethoxyethane
PC	Propylene carbonate
CE	Coulombic efficiency
BET	Brunauer-Emmett-Teller
L_c	Crystallite height
L_a	Crystallite width
HCS	Hard carbon spheres
ASA	Active surface area
SSA	Specific surface area
Gr	Graphite
KVPFO	KVPO ₄ F _{0.5} O _{0.5}
KIFC	K-ion full-cell
QSSKFC	Quasi-solid-state potassium full-cell
ASSKFC	All-solid-state potassium full-cell
LKIFC	Liquid potassium-ion full-cell

KQ26DS	Oxidized potassium 9,10 -anthraquinone-2,6-disulfonate
GF	Glass fiber
OCV	Open circuit voltage
RT	Room temperature
UCV	Upper cut-off voltage
DOD	Depth of discharge
PANa	Sodium polyacrylate

Appendix II : Article “Impact of Hard Carbon Properties on Their Performance in Potassium-Ion Batteries”

Impact of Hard Carbon Properties on Their Performance in Potassium-Ion Batteries

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and Camelia Matei Ghimbeu*



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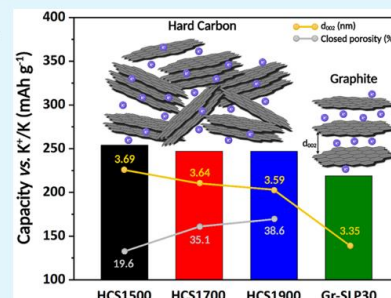
Article Recommendations



Supporting Information

ABSTRACT: This work reports on the synthesis of hard carbon spheres (HCS) and the impact of the pyrolysis temperature (1500 to 1900 °C) on the properties of HC and its relationship with the electrochemical performance in potassium-ion batteries (KIBs). Comparison with commercial graphite performance is provided as well. Spherical morphology, disordered structure, and low surface area were obtained for the HCSs. Most properties (interlayer space, active surface area, and oxygen-based functional groups) were found to decrease with increasing pyrolysis temperature, except for the helium density and closed porosity, which increase. However, graphite presents a flake-like morphology with a larger particle size, a higher helium density, an ordered structure with a smaller interlayer distance, and no closed pores. Electrochemical tests in a half-cell vs K⁺/K showed that HCSs perform better than graphite with higher initial Coulombic efficiency (ICE) and better specific capacities. The HCSs pyrolyzed at 1500 and 1700 °C exhibit the best initial Coulombic efficiency, ICEs of 54 and 62%, and specific capacities of 254 and 247 mAh g⁻¹ (C/20, 11.5 mA g⁻¹), respectively. The ICE is affected by multiple surface and bulk parameters but also by electrolyte formulation (67% for 0.8 M KFSI vs 62% for 0.8 M KPF₆). The capacity is governed by diffusive phenomena, and a larger interlayer graphitic spacing and defects favor a better insertion of K ions. Closed pores did not lead to an improvement in capacity. Furthermore, HCSs exhibit significantly better capacity retention (97%) than graphite (84%), especially when cycled at high current rates (up to 10C depotassiation rate).

KEYWORDS: Hard carbon, Graphite, Anodes, Potassium-ion batteries, Energy storage



1. INTRODUCTION

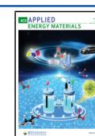
Since their commercialization in 1990, lithium-ion batteries (LIBs) have been the most common and widely used systems for various applications.¹ They deliver a high energy density with an acceptable lifespan. However, the increased demand for LIBs triggered a consequent lithium consumption and raised concerns about the depletion of lithium resources, which already suffer from poor abundance and heterogeneous localization over the world. To address this dilemma, the development of new advanced battery systems, as an alternative to LIBs, is strongly required. In this regard, sodium ion batteries (NIBs) have been studied for several years while the attention on potassium ion batteries (KIBs) has only begun recently,² mainly due to the high natural abundance of Na and K, which could ensure long-term availability, lower cost, and long lasting technology. One of the first works on KIBs was reported in 2004 by Eftekhari,³ but KIB research was only recently extended, as testified to by the upward spark in publications.⁴ Among the advantages of KIBs, we can cite (i) the similarities between Li and K, as both are alkali metals sharing the same chemistry and have a close standard potential; (ii) potassium being the seventh most abundant

element in the Earth's crust is nearly 1000 times more abundant than lithium and equally available throughout the world;^{4,5} and (iii) the possibility of using aluminum as a current collector for both electrodes instead of the more expensive copper used for Li anodes. All of these assets should lead to a relatively lower cost for KIB technology than that of LIBs, with the condition to deliver a longer lifetime than LIBs.⁶ As potassium presents a slightly lower standard potential than lithium in the solvents used in electrolytes (PC or EC/DEC), the expected energy density of KIBs will be slightly higher than that of LIBs in a full cell. Furthermore, solvated potassium ions are smaller than lithium due to its weaker Lewis acidity; consequently, solvated K⁺ shows higher transport numbers and ionic conductivity,^{5,7} so that high-power KIBs are expected.

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Despite these positive aspects, potassium presents some issues, such as its higher weight compared to its analogues Li and Na, as well as its larger radius (1.38 Å) compared to lithium (0.76 Å). These limitations may cause volume expansion and poor kinetics limiting the K^+ intercalation in the host electrode materials (i.e., graphite),⁸ leading to poor cycling stability and rate capability. Furthermore, the high reactivity of potassium metal with organic electrolytes and the impact of salt anions on K metal reactivity are major inconveniences in half-cells.⁹ In recent studies,^{4,10} it was demonstrated that the potassium metal strongly reacts with different electrolytes and other parts of the cell, causing battery performance degradation (large ohmic resistance and fast electrolyte degradation) and electrode polarization increases. Furthermore, the lower melting point of potassium (63.38 °C) vs lithium (180.54 °C) might limit its applicability under certain conditions. Both of these aspects can cause security problems and need to be considered.^{4,11}

Several materials were investigated as negative electrodes for KIBs such as carbons (graphite, hard carbon),¹² metal alloys (Sn, Sb, Bi and P based alloys...),^{13–15} metal oxides (Fe_xO_y , SnO_2 ...),¹⁶ and metal sulfides (MoS_2 , SnS_2 ...).¹⁶ However, carbonaceous materials appear to be the most promising for KIB negative electrodes due to their high electronic conductivity, good chemical stability, eco-friendliness, availability, and low price.^{17–19} Jian et al.²⁰ reported that graphite, the most used anode material in LIBs, allows the insertion of K^+ to form the KC_8 compound. However, the gravimetric capacity is still lower, i.e., 278 mAh g^{-1} compared to 372 mAh g^{-1} in LIBs with the formation of LiC_6 .²¹ Furthermore, the formation of intercalated graphite compounds triggers a large volume expansion in KIBs, approximately 61% vs 10% in LIBs, causing capacity fading during the electrochemical cycling and a limited life span of the KIBs.²² To circumvent this problem, various alternative forms of carbon materials have been studied i.e., commercial expanded graphite,²³ heteroatom doped graphene,²¹ reduced graphene,²⁴ carbon nanofiber,²⁵ carbon-based composite materials, soft carbons, and hard carbons (HCs).²⁶

Among these materials, hard carbon delivers high electrochemical performance (capacity and cycle life) as an anode in both LIBs and NIBs due to its structural stability.^{14,27,28} HCs can be obtained from organic precursors, by a simple pyrolysis of biomass,²⁹ resins (phenolic resin, epoxy resin, polyfurfuryl alcohol, etc.),^{27,30} and/or biopolymers.³¹ HC refers to a carbon material, which does not graphitize even under high temperatures (>2000 °C) and is characterized by a complex structure. As described by Dahn et al.³² in the “falling cards” model, HCs are composed of a mixture of disordered and graphitic domains with open and closed pores. HCs can thus accommodate the insertion/extraction of large K ions.^{33,34} Furthermore, the disordered structure and the greater graphene interlayer distance of HC vs graphite limit the volume expansion during K^+ insertion/extraction. In this direction, different approaches have been proposed to overcome the volume expansion and improve the electrochemical performance of HCs in KIBs, especially by focusing on the structure engineering of hard carbons, i.e., by playing on the carbon precursor, developing new synthesis processes, controlling the properties (morphology, structure, texture, functionalities), and active material utilization (electrode formulation). These approaches can help to understand/optimize multiple properties, such as the diffusion efficiency of K ions, the volume expansion rate, the

kinetic reaction, the contact between the electrolyte and the active materials, and electrochemical properties such as Coulombic efficiency (CE) and rate performance.¹²

For example, Liu's group reported the impact of structure in K-ion storage by synthesizing active hollow nanospheres with a broad graphene interlayer spacing (0.408 nm), at 800 °C using scalable self-template strategy, followed by a KOH activation process. The improved structure of the carbon nanospheres after activation resulted in a high initial charge capacity of 370.2 mAh g^{-1} at 0.2 A g^{-1} . Furthermore, *ex situ* X-ray diffraction (XRD) and transmission electron microscopy (TEM) on post-mortem electrodes (first cycle) showed that a high interlayer spacing can accommodate volume fluctuation and facilitate reversible intercalation of K ions.¹⁸ However, such material presents a low initial CE (ICE) of 44%. Furthermore, Qiu et al.³⁵ reported the influence of texture on the storage of K ions by synthesizing HC through a pyrolysis process (900, 1000, 1300, and 1500 °C) of a preheated rice husk, followed by a washing step with strong and hazardous acids (HF and HCl). It was noticed that the specific surface area (SSA) decreases (from 365 to 17 m² g^{-1}) by increasing the pyrolysis temperature (from 900 to 1500 °C). When tested as an anode in KIBs, the sample with the lowest SSA (carbonized at 1500 °C) delivered the best charge capacity and ICE (244 mAh g^{-1} , 49%).

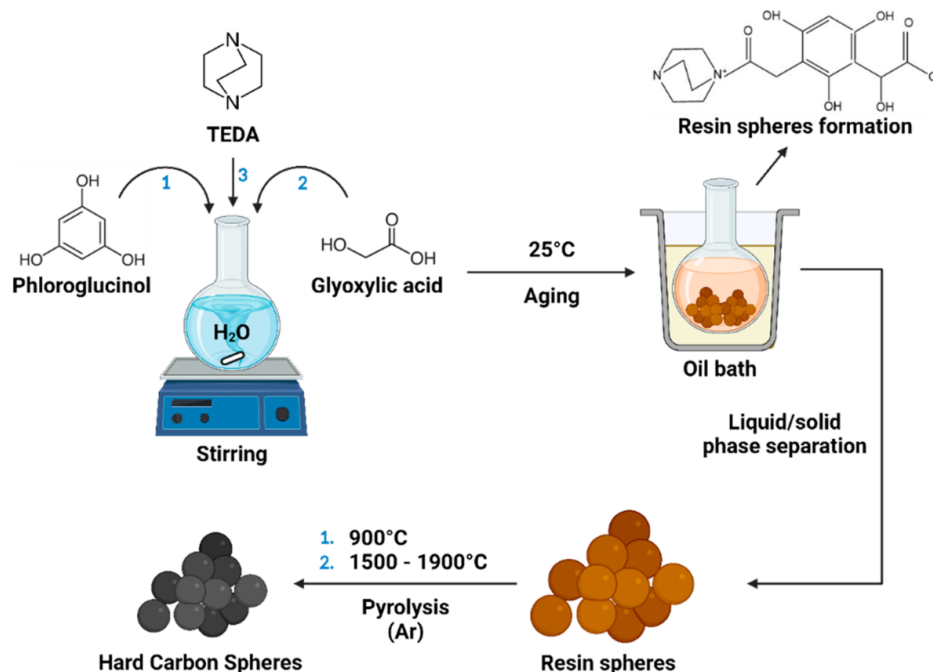
In addition, a hydrothermal strategy was reported by Ji et al.³¹ for the synthesis of HC spheres, using an aqueous solution of sucrose. Narrow and uniform particle sizes were obtained after a pyrolysis step at 1000 °C. The material exhibits an interlayer space of 0.4 nm, an SSA of 65 m² g^{-1} , and a capacity of 262 mAh g^{-1} (at 28 mA g^{-1}) with an ICE of 61.8%.³¹ Moreover, Chen et al.³⁶ reported a carbonization-etching strategy to obtain HC microspheres codoped with sulfur and oxygen. The material delivered a reversible capacity of 221.3 mAh g^{-1} (at 50 mA g^{-1}) and an ICE of 61%. Although the above-mentioned works present interesting strategies to improve the performance of HC, most of the processes used are difficult to implement and generally require pretreatments, the addition of activation agents, a chemical washing step, high pressure or high temperature conditions, etc. Moreover, there is a lack of general understanding of the factors that affect both the K ion storage mechanisms and performance.

In this work, we synthesized hard carbon spheres using an environmentally friendly approach (polymerization-precipitation process) in water at room temperature, followed by a pyrolysis step (1500 to 1900 °C), under an atmosphere of argon. Different characterizations were carried out to determine the influence of the pyrolysis temperature on both the physicochemical properties of the HCS and the electrochemical performance when used as anodes for KIBs. A comparison of electrochemical performance was done with a commercial graphite (Gr-SLP30). HCSs have been shown to deliver better performance than graphite material, i.e., higher initial CE, higher reversible capacity, and better capacity retention at high rates. This result could be explained by the difference in the structural, textural, and surface chemistry of the materials.

2. EXPERIMENTAL SECTION

2.1. Material Synthesis. HCSs with controlled particle size and different physicochemical properties were prepared using an eco-friendly and simple precipitation polymerization method, inspired by our previous works.^{37,27} In a typical synthesis (Scheme 1),

Scheme 1. Schematic Representation of the Synthesis Process of the Hard Carbon Spheres (HCS) [Created by the Authors with BioRender.com]



phloroglucinol (4.1 g) and glyoxylic acid (3.6 g) were dissolved in water (200 mL), under magnetic stirring, followed by the addition of triethylenediamine (TEDA, 1.8 g) as a cross-linker. After 15–30 min of stirring, this mixture was left to aging (without stirring) for 24 h at 25 °C, and the solid phenolic resin formed was recovered and dried at 80 °C for 12 h. Subsequently, the material was pyrolyzed first at 900 °C for 1 h under an argon flow (5 °C min⁻¹ heating rate) in an alumina tube furnace and then in a second step at 1500, 1700, and 1900 °C in a graphitic tube furnace. The obtained materials are denoted HCST (where T-indicates the final pyrolysis temperature). The synthesis results in ~2.5–3 g of carbon/synthesis batch. No grinding is required, which is advantageous for industrial applications. Graphite material called Gr-SLP30 was graciously provided by Timcal (actually called Imerys) and was used without any other modification. It was selected on the basis of its low surface area and active sites, according to our previous study,³⁸ for comparison purposes with hard carbon spheres.

2.2. Material Characterization. The morphology of the obtained HCSs and graphite was observed by scanning electron microscopy (SEM) using FEI Quanta 400 scanning electron microscopy, whereas the particle size distribution was determined by ImageJ software by counting ~600 particles of different SEM images. Structural characterization of the materials was performed by X-ray diffraction (XRD) using a Bruker D8 Advanced diffractometer with flat Bragg–Brentano θ – θ geometry and a copper wavelength of 1.5406 Å. The distance between the graphene planes, d_{002} , was calculated using the graphite diffraction peak (002) and the Bragg equation.³⁹ The height (L_c) and the width (L_a) of the stacked graphene layers were calculated from the full width at half-maximum (fwhm) of the diffraction peaks (002) and (100), respectively, based on the Scherrer formula.³⁹

Raman spectroscopy was performed with a LabRAM BX40 instrument (Horiba Jobin-Yvon) equipped with a He–Ne excitation source (532 nm wavelength). Nine spectra were acquired for each sample by doing a mapping. The average spectrum was used for a good representation of the structure to calculate the I_D/I_G report after

fitting with a Gaussian function. The stacked graphene plane width (L_a) was calculated by Raman spectroscopy according to the literature.⁴⁰ The local structure has been examined by high-resolution microscopy (HRTEM) using a JEOL instrument (ARM-200F model) operating at 200 kV.

Textural characteristics such as specific surface area, SSA (at $P/P_0 = 0.01$ – 0.30); total pore volume, V_T (at $P/P_0 = 0.99$); and pore size distribution were evaluated with a Micromeritics ASAP 2420 instrument using N₂ adsorbate gas (77 K) and a Micromeritics ASAP 2020 instrument using CO₂ adsorbate gas (273 K) as described elsewhere.⁴¹

Materials density was measured with an Accupyc 1330 pycnometer from Micromeritics working under helium gas. Before analysis, the materials were first outgassed at 300 °C for 12 h under a vacuum to remove the physisorbed molecules. For each sample, 100 cycles were performed, and the average value of density was taken for every sample. The closed and opened porosity ratios were calculated based on the total pore volume measured by N₂ sorption, and the helium density of HCSs and graphite were calculated according to the equations reported in the literature.^{42,43}

The chemical composition and the functional groups of the HCS surface (3 to 9 nm in thickness) were determined by X-ray photoelectron spectroscopy (XPS) using a SE-2002 (VG SCIENTA) spectrometer equipped with a monochromatic X-ray source (Al K α = 1486.6 eV). Thermal programmed desorption coupled with mass spectrometry (TPD-MS) was used to obtain insights on the nature and the amount of oxygen-based functional groups in the bulk of the materials. Furthermore, the same technique allows the quantification of the active surface area (ASA). The analysis of TPD-MS was performed on laboratory (IS2M) made equipment. A quantity of ~500 mg of HCS was heated under a secondary vacuum of 10^{-6} to 10^{-7} mmHg from 25 to 950 °C with a heating rate of 5 °C min⁻¹. The released gases were quantitatively detected and analyzed using a quadrupole mass spectrometer (MS) that is already calibrated using the following reference gases, i.e., H₂, H₂O, CO, and CO₂. Before each

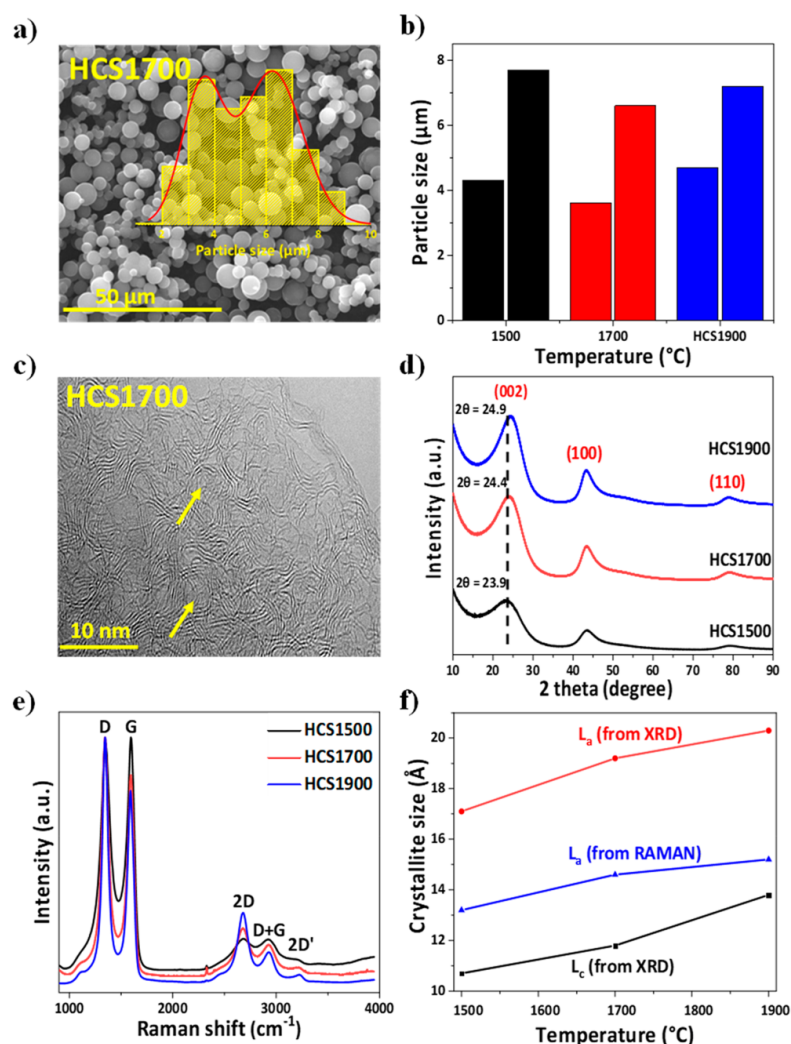


Figure 1. (a) SEM image and the particle size distribution of HCS1700 (inset). (b) Average particle size corresponding to the two peaks for HCS1500, HCS1700, and HCS1900. (c) HRTEM image of HCS1700. (d) XRD diffractograms of HCSs. (e) Raman spectra of HCSs. (f) Evolution of crystallite height (L_c) and width (L_a), calculated from XRD and Raman data, with the pyrolysis temperature.

analysis, a measurement of N_2 sensibility was performed to allow further quantification of other gases.^{27,38,44,45} Subsequently, the material is exposed to oxygen chemisorption at 300 °C for 10 h, and after cooling down, a second TPD-MS is performed up to 950 °C with a heating rate of 10 °C min⁻¹. This allows quantification of the structural defects or the active surface area (ASA) of the materials. More details about this procedure can be found elsewhere.^{27,46}

2.3. Electrochemical Characterization. 2.3.1. Electrode Preparation. The working electrodes were prepared by mixing in a ball miller (PULVERISETTE 7) at 500 rpm for 1 h the active material (synthesized HCSs and commercial graphite), the polyvinylidene fluoride (noted PVDF from Solef 5130) binder, and carbon black (Super C65 from Imerys), with a mass ratio of 90:5:5 respectively, in the presence of 1-methyl-2-pyrrolidone solvent (noted NMP (purity ≥ 99) from Sigma-Aldrich).

The obtained slurry was coated on an aluminum current collector (20 μm thickness) using the doctor blade method (150 μm

thickness), then dried under a vacuum for one night at 80 °C. The electrode foil obtained was cut into round pieces using a precision punch, to obtain electrodes with a diameter of 9.5 mm and a mass load of ~1.4–1.9 mg cm⁻². The electrodes were dried in a Buchi oven under a vacuum for one more night at the same temperature (80 °C) before being introduced into an argon-filled glovebox (MBRAUN).

2.3.2. Battery Testing Conditions. Electrochemical analyses were performed using 2032-type coin cells in a controlled temperature room (~25 °C) with a multichannel VMP 3 system (BioLogic, France), by assembling at least two cells for each material to ensure the reproducibility of the results. The mean error was estimated to be a maximum of 5%.

Coin cells were assembled using HCS and Gr-SLP30 electrodes, a microporous trilayer (PP/PE/PP, Celgard) and glass microfiber filter (Whatman, grade GF/D) as separators, and potassium metal as a counter electrode. It is worth mentioning that K metal electrodes were prepared from K ingots (Alfa Aesar, 99.95%) in the following way.

Teflon tweezers were used to place K metal pieces between two latex surfaces, followed by pressing them with the help of an 8 cm diameter Teflon roller. Then, 10 mm diameter K metal disks were punched out, and the K metal disks were removed from the latex using Teflon tweezers, then placed on a stainless-steel spacer (1 mm thick, 16 mm diameter) and finally scratched with the back of the tweezers, to remove the oxide layer from the surface.

Most tests were performed using as an electrolyte 0.8 M potassium hexafluorophosphates (KPF₆, Sigma-Aldrich, ≥99%) dissolved in a mixture of ethylene carbonate (EC, Sigma-Aldrich, ≥99%) and diethyl carbonate (DEC, Sigma-Aldrich, ≥99%) in a 50:50 v/v ratio. In addition, for the most promising material, complementary tests were conducted with other electrolytes: 0.8 M of potassium bis(trifluoromethanesulfonyl) imide (KTFSI, Solvionic), 0.8 M of potassium bis(fluorosulfonyl)imide (KFSLI, Solvionic), 0.8 M of a mixture of KPF₆ (90%) and KTFSI (10%), and 0.8 M of a mixture of KPF₆ (90%) and KFSLI (10%) in the same solvent mixture. Two concentrated electrolytes were also tested, which are 5 M KTFSI and KFSLI in 1,2-dimethoxyethane (DME, Sigma-Aldrich).

Galvanostatic charge/discharge tests were performed between 2.0 and 0.01 V (vs. K⁺/K) in half-cells at C/20 for the first five cycles then at C/10 (23 mA g⁻¹) for 50 cycles. Cycling voltammetry (CV) was performed at different scan rates from 0.02 to 0.2 mV s⁻¹ to discriminate the capacitive and diffusive behaviors of HCS materials using the Dunn method.⁴⁷

The evaluation of the rate performance was done according to several distinct protocols:

- Conventional galvanostatic cycling test: five cycles at C/20 and 45 cycles at C/10; then five cycles at C/10; five cycles at C/5, C/2, C, 2C, 5C, and 10C; followed by five cycles at C/10
- First (1st) alternative test: five cycles at different C rates, i.e., C/10, C/5, C/2, C, 2C, 5C, and 10C with potassiation (insertion) kept at C/10 between C/5 to 10C (to reduce the impact of the K metal stripping polarization) followed by five cycles at C/10 to verify the capacity
- Second (2nd) alternative test: four cycles at C/10, potassiation at C/10 followed by successive depotassiation (at xC from x = 10, 5, 1, 0.5, 0.2, 0.1, and 0.05, i.e., from 5C to C/10) and 2 h relaxation steps; the aim of this test was used to evaluate only the depotassiation (extraction) rate capability

3. RESULTS AND DISCUSSION

3.1. Morphology, Structure, Texture, and Surface Properties. The morphology of the materials examined by SEM (Figure 1a and Figure S1a–c) shows individual, well-marked, and uniform spherical particles. HCS has a particle size range of 2 to 10 μm with a bimodal distribution for all materials, centered at a maximum of ~3.6–4.7 μm and 6.6–7.7 μm, as shown in the particle size distribution of the HCS1700 inset (Figure 1a) and for all materials (Figure 1b). The uniformity of the particles along with the size obtained are important parameters to optimize the electrode and achieve high performance in NIBs.²⁷ On the other hand, Gr-SLP30 presents a flake-like morphology, with rounded particle contours (Figure S1c) and an average particle size of 32 μm.³⁸

The material structure was analyzed by complementary techniques, i.e., HRTEM, XRD, and Raman. As shown by HRTEM (Figure 1c), HCS1700 reveals a structure that combines a mixture of disordered graphene domains randomly orientated and pseudo-graphitic domains, where short graphenes (3–6 nm) are stacked in 3–5 layers. Such a structure is typical for hard carbon materials.¹² The same structure is observed for the other HCS, as illustrated by the images provided in Figure S1d,e. The presence of closed pores (empty spherical spaces surrounded by few stacked parallel graphene layers) can also be observed, as indicated by the yellow arrows

in Figures 1c and S1d. On the contrary, the graphite Gr-SLP30 shows a highly ordered structure with several parallel stacks of graphene (up to 25 layers), which have a long lateral size (15–30 nm) and no closed pores, as shown in Figure S1f.

As illustrated in Figure 1d, the XRD patterns of all of the HCS samples exhibit three distinct broad diffraction peaks indexed as (002) at 2θ ≈ 23°, (100) at 2θ ≈ 44°, and (110) at 2θ ≈ 80°, indicating the formation of a disordered-like carbon structure. In particular, the diffraction planes (002) reveal a small shift to higher 2θ angles and an increase in the intensity with the increase of the pyrolysis temperature (from 1500 to 1900 °C), suggesting an improvement in the structural organization of the material. A decrease of the interplanar distance, *d*₀₀₂ from 3.69 to 3.59 Å, is observed, in agreement with other works.^{27,48,49} However, the *d*₀₀₂ remains greater than that of Gr-SLP30 (3.35 Å). The larger interlayer distance of HCSs might manage the volume change associated with K-ion insertion/extraction.¹² For the graphite material (Figure S2a), an intense and narrow peak at 26°, specific to the (002) diffraction plane, indicates a very organized structure corresponding to hexagonal graphite (COD 9011577). Other small peaks (inset Figure S2a) between 42° and 46° correspond to a mixture of hexagonal and rhombohedral phases.³⁸

The crystallite height (*L*_c) along the *c* axis and the crystallite width (*L*_a) along the *a* axis were calculated using the Scherrer formula from the XRD data, the peaks (002) and (100), and the average number of graphene layers was also estimated as *L*_c/*d*₀₀₂ (Table 1). Gr-SLP30 presents the highest *L*_c, *L*_a, and *L*_c/*d*₀₀₂ due to its highly organized structure. Regarding HCSs, the HCS1900 has the highest *L*_c and *L*_a values, i.e., 13.8 and 20.3 Å, respectively, and the smallest *d*₀₀₂ (3.59 Å). This confirms the increase of graphene layers stacking when increasing the pyrolysis temperature, i.e., ~2–3 for HCS1500 and ~4 for HCS1900.

Table 1. Hard Carbon Spheres and Graphite Physico-Chemical Characteristics: Particle Size, Graphite Interlayer Distance (*d*₀₀₂), Crystallite Height (*L*_c), Crystallite Width (*L*_a), Number of Graphene Layers (*L*_c/*d*₀₀₂), *I*_D/*I*_G Ratio, Specific Surface Area (SSA), Total Pore Volume (*V*_T), Active Surface Area (ASA), Oxygen (O) and Carbon (C) Surface Amount, Oxygen-Based Functional Groups (CO_x), Amount, He Density, and Closed Porosity Ratio

material properties	HCS1500	HCS1700	HCS1900	Gr-SLP30
particle size (μm)	4.1	6.3	6.4	32
<i>d</i> ₀₀₂ ^a (Å)	3.69	3.64	3.59	3.35
<i>L</i> _c ^a (Å)	10.7	11.8	13.8	284
<i>L</i> _a ^a (Å)	17.1	19.2	20.3	707
<i>L</i> _c / <i>d</i> ₀₀₂ ^a	3	3	4	84
<i>I</i> _D / <i>I</i> _G ^b	1.46	1.32	1.27	0.31
N ₂ SSA (m ² g ⁻¹)	3.6	1.4	1.0	6.5
<i>V</i> _T (cm ³ g ⁻¹)	0.006	0.004	0.003	0.021
CO ₂ SSA (m ² g ⁻¹)	18	14	8	5
ASA (m ² g ⁻¹)	1.6	0.1	0.1	0.4
O (atom %)	5.35	1.59	1.46	3.3
C (atom %)	92.4	98.2	98.2	96.7
CO _x (mmol g ⁻¹)	0.04	0.005	0.003	0.04
He density (g cm ⁻³)	1.86	1.50	1.42	2.30
closed porosity ratio (%)	19.6	35.1	38.6	0.8

^aDetermined from XRD. ^bFrom Raman spectroscopy.

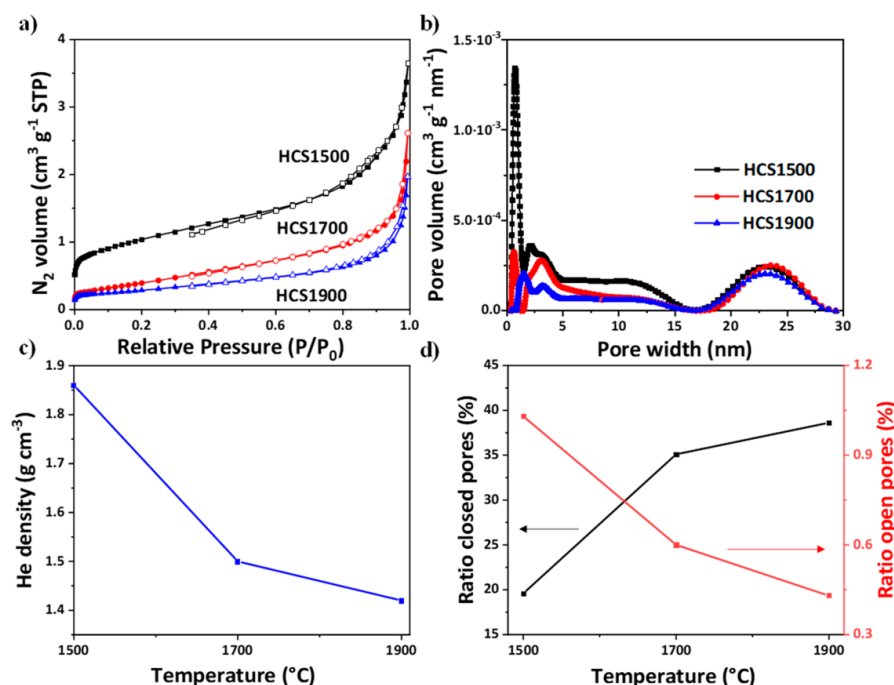


Figure 2. (a) N₂ adsorption–desorption isotherms of HCS materials. (b) Pore size distribution determined using the N₂ adsorption branch and the two-dimension nonlocal density functional theory (2D-NLDFT) model. (c) Helium density evolution with pyrolysis temperature. (d) Closed and open porosity ratio evolution with pyrolysis temperature.

The local structure and defects of HCS were estimated by Raman spectroscopy (Figure 1e). All materials show two intense and sharp peaks at ~ 1340 and 1590 cm^{-1} corresponding to the D and G bands. The D band is related to disordered carbon, while the G band is associated with organized graphite (hexagonal carbon structure), respectively, which are typical features of carbon materials.^{50,51} Both can be used to characterize the degree of graphitization and defects by calculating the I_D/I_G ratio.^{19,44} The D band has a lower intensity than the G band in organized materials, which is the case for Gr-SLP30 (Figure S2b), while the D band is more intense than the G band for HCSs, indicating a more disordered structure.^{52–54} The I_D/I_G ratio is calculated to be 1.46, 1.32, and 1.27 (Table 1) for HCS1500, HCS1700, and HCS1900, respectively, suggesting a higher degree of graphitization at a higher pyrolysis temperature for HCSs. Gr-SLP30 shows a very low I_D/I_G ratio of 0.3 (Table 1) due to its more organized structure, which is in line with the XRD and HRTEM results. At a higher Raman shift ($2500\text{--}3500\text{ cm}^{-1}$), other peaks with lower intensity were detected (Figure 1e and Figure S2b) and associated with 2D, D+G, and 2D'. The 2D band is characteristic for bulk graphite and gives information about the degree of graphitization in the material. The D+G band was reported as a defect activated peak, and the 2D' band is the harmonic of the Raman inactive fundamental mode in ordered carbons.^{50,51} The intensity of this band in HCSs increases with increasing the pyrolysis temperature, confirming the formation of graphitic domains at a high temperature in addition to the disordered ones.^{54,55} This band is very intense in the case of graphite, Gr-SLP30.

The evolution of the crystallite width (L_a) calculated from Raman spectra for HCS (Figure 1f) shows the same trend with the pyrolysis temperature (13.2, 14.6, and 15.2 Å for HCS1500, HCS1700, and HCS1900, respectively) as L_c deduced by XRD results, although some differences in the values are observed, and related to the specificity of each technique.

The textural properties of the materials were determined by N₂ adsorption–desorption and CO₂ adsorption. The obtained N₂ isotherms (Figure 2a) for HCS are type II characterized by low porosity or nonporous materials and a mixture of type II/IV for Gr-SLP30 (Figure S3a) with small hysteresis starting around $P/P_0 = 0.40$, indicating capillary condensation of the mesopores. Furthermore, we can observe a significant increase in adsorbed volume at high relative pressure due to the contribution of intergranular porosity.³⁸ All samples have a very low BET specific surface area $<10\text{ m}^2\text{ g}^{-1}$ as reported in Table 1, which is favorable for potassium ion storage because it can limit electrolyte decomposition and excessive SEI formation.⁵⁶ From the published works in the literature (Table S1), it can be seen that a small SSA limits irreversible capacity.

Based on the N₂ adsorption results, the pore size distribution of HCS and Gr-SLP30 was determined (Figure 2b and Figure S3b). Two regions of porosity were revealed for HCSs: first, the micropores with a pore diameter $<2\text{ nm}$ with a small presence of mesopores at $\sim 3\text{ nm}$ and, second, at $\sim 20\text{--}30\text{ nm}$, which can be associated with intergrain porosity. Gr-SLP30 presents the same trend as HCS in terms of porosity with

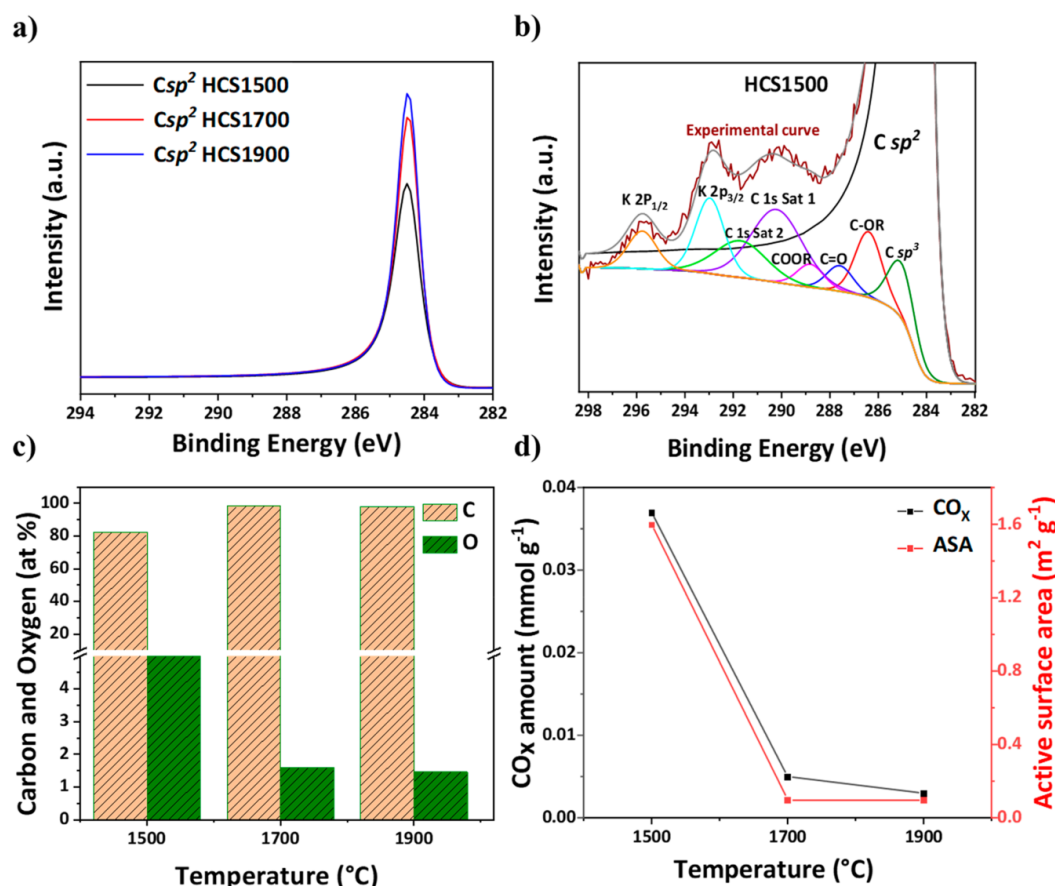


Figure 3. (a) XPS C sp^2 high-resolution peak of the HCSs. (b) XPS C 1s high-resolution deconvoluted spectra of HCS1500. (c) Carbon and oxygen amount evolution with pyrolysis temperature as determined by XPS. (d) The amount of oxygen-based functional groups (CO_x) and the active surface area (ASA) vs pyrolysis temperature assessed by TPD-MS.

micropores <2 nm, small mesopores (~ 2.5 to 7.5 nm), and an important contribution of intergrain porosity.

To better understand the texture of HCS, CO_2 adsorption was performed since this gas allows greater diffusion, accessibility, and rapid kinetics in narrower pores (<0.7 nm).⁴⁴ The CO_2 adsorption isotherm (Figure S4a) shows a slightly higher adsorbed volume than N_2 and BET surface area (Table 1), but the values are still very low (<10 m² g⁻¹) and decrease with increasing pyrolysis temperature. This reveals the presence of some ultramicropores (pores below 1.0 nm) as shown in the pore size distribution (Figure S4b). It can be assumed that this kind of porosity can have an impact in K-ion storage, as already shown in NIBs.²⁷ However, this impact is not yet elucidated for KIBs, and a limited effect is expected herein due to the low values of CO_2 SSA.

The He density of the materials was measured (Figure 2c and Table 1), and the values are 1.86, 1.50, and 1.42 g cm⁻³ for HCS1500, HCS1700, and HCS1900, respectively, while the helium density of Gr-SLP30 is much higher, i.e., 2.3 g cm⁻³. If the electrode density is calculated according to the protocol provided in the SI, the same trend was observed as for He density, i.e., decreases of electrode density by increasing the

pyrolysis temperature for the HCS materials, e.g., 0.82, 0.63, and 0.62 g cm⁻³ for HCS1500, HCS1700, and HCS1900, respectively. On the other hand, Gr-SLP30 presents an electrode density of 0.88 g cm⁻³. The decrease in HCS He and electrode densities by enhancing the pyrolysis temperature might be explained by the formation of a closed porosity. Therefore, the closed- and open-porosity ratios of HCS were calculated using the helium density values and the total pore volume obtained by nitrogen adsorption. As noted (Figure 2d and Table 1), closed porosity increases from 19.6% for HCS1500 to 38.6% for HCS1900. Gr-SLP30 has a closed porosity ratio of 0.8%, which is very low compared to HCS. However, open porosity decreases as the pyrolysis temperature increases for HCSs and is the lowest for Gr-SLP30 ($\sim 5\%$). These differences between HCS and Gr-SLP30 are due to the type of carbon precursor and the preparation conditions, such as the temperature of pyrolysis. Furthermore, the impact of closed porosity in K-ion storage is rarely discussed in the literature. This is noted in the different published articles in the literature, such as the ones reported in Table S1.

X-ray photoelectron spectra (XPS) on HCSs were recorded to provide a view of the surface chemistry of the materials,

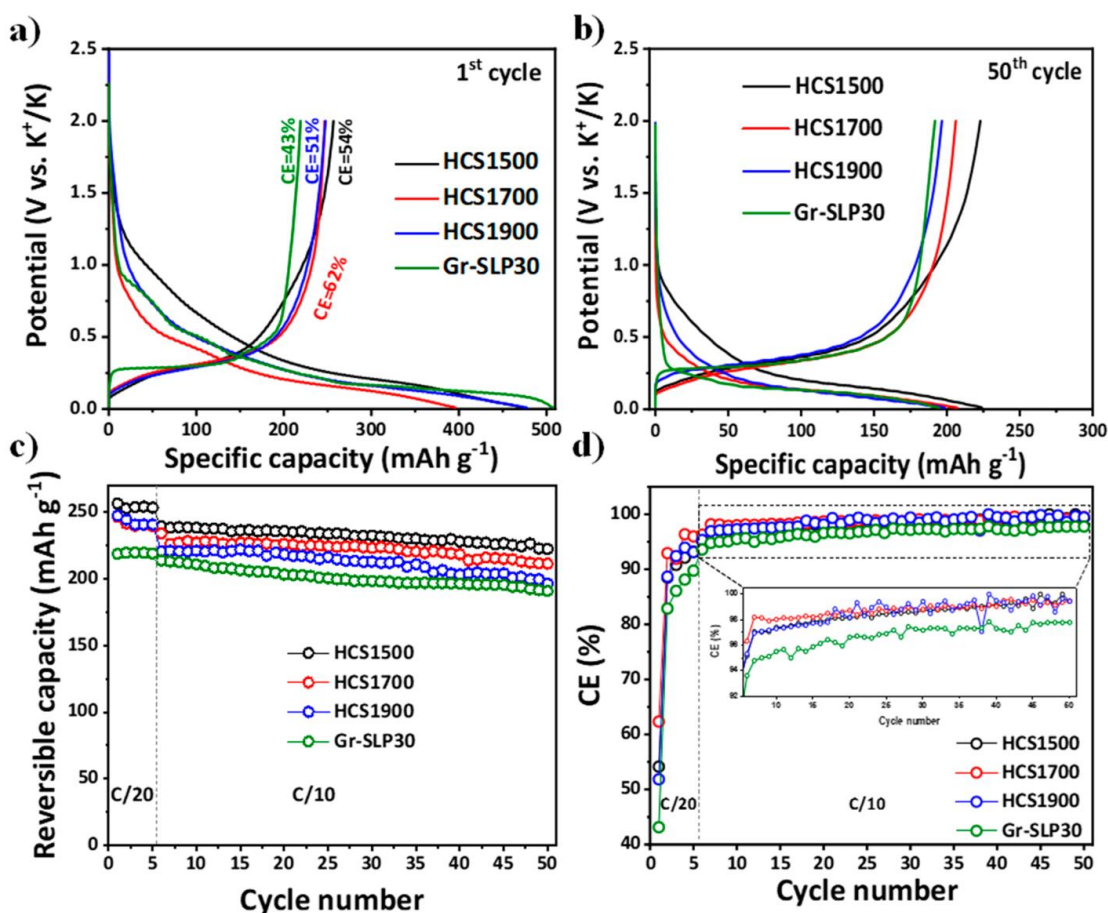


Figure 4. Galvanostatic profiles of the (a) first and (b) 50th cycle at C/20 and C/10, respectively. (c) Capacity retention. (d) Coulombic efficiency at C/10 rate after five formation cycles at C/20 obtained between 2.0 and 0.01 V for HCS1500, HCS1700, HCS1900, and Gr-SLP30 electrodes.

namely, the nature of the functional groups and the binding energy on the surface of the material (10–15 nm) compared to the TPD-MS analysis, which provides information on bulk.

The high-resolution C1 XPS spectra of the HCS materials are recorded, and an intense peak corresponding to C sp^2 is observed, which increases with increasing pyrolysis temperature (Figure 3a). In addition, other small peaks were detected as shown for HCS1500 in the high resolution deconvoluted spectra of C1s (Figure 3b). The peaks can be associated with C sp^3 and oxygen-based functional groups (i.e., carbonyl, CO, ethers, COR, and carboxyl COOR).⁴⁵ Some small peaks of K 2p_{1/2} and K 2p_{3/2} are only observed for HCS1500 and are associated with some contamination impurities. As shown in Figure 3c and Table 1, the amount of oxygen detected by XPS decreases (from 5.3 to 1.5 atom %) by increasing the temperature of the pyrolysis. This can be beneficial for K-ion storage because it can limit electrolyte decomposition, causing SEI formation, and has high irreversible capacity in the first cycle. However, a small amount of oxygen can ensure good wettability of the carbon material by the electrolyte. On the other hand, the amount of carbon is increased (from 92.4 to

98.2 atom %) with the pyrolysis temperature. This might help to have more insertion sites for a larger number of K⁺. Regarding Gr-SLP30, an intense peak of C sp^2 is observed (Figure S5a), confirming the high structural order. Additionally, oxygen groups such as C=O, C–OR, and O=C–O can be seen as well (Figure S5a').

Figure S6a–d shows the TPD-MS profiles of the desorbed gases during the heating under a vacuum for the different samples. The oxygen-based functional groups were decomposed into CO and CO₂ groups. The latter were attributed according to their decomposition temperature to specific functional groups, as described in the literature.^{45,57} For HCS and Gr-SLP30 materials, the desorption profiles show peaks of CO₂ desorption between 200 and 700 °C, indicating the decomposition of carboxylic acids at low temperature, followed by lactones and anhydrides, at much higher temperatures. The CO desorption exhibits peaks in the range of 300 to 900 °C resulting from the degradation of ethers, phenols, and quinones. The total amount of CO₂ and CO released (namely, CO_x, Figure 3d and Table 1) decreases for HCS with increasing temperature.

For the graphite material, the CO and CO₂ profiles have intensities higher than those of the HCS materials. As a consequence, the total amount of CO_x is more than 10 times higher for graphite than HCS1900 but similar to that of HCS1500. However, the values are very low compared to reported data for other HCs and graphites.^{27,38} Other gases were also desorbed such as H₂ (~600 °C) due to the C–H bond cleavage, in greater quantities for HCS series, indicated more disorganized materials. Water is also released (50 to 600 °C)⁴⁵ due to physisorption into the pores and/or secondary reactions occurring between neighboring oxygen-functional groups (–COOH, –OH, etc.).

Both of the TPD-MS and XPS techniques showed the presence of oxygen based functional groups in the HCSs, which decrease as the pyrolysis temperature increases.

Surface defects can be involved in the storage mechanism of K ions and irreversible capacity, similar to Na and Li ions, as shown with both hard carbons and graphite.^{27,38,58} Therefore, a quantification of the edge defects and active sites was carried out by measuring the active surface area (ASA) after the surfaces of the materials were cleaned during the first TPD-MS analysis. Figure 3d shows the evolution of the active surface ASA vs pyrolysis temperature for HCS. Very low ASA values were obtained for HCS and decreased from 1.6 m² g^{−1} for HCS1500 to ~0.1 m² g^{−1} for HCS1700 and HCS1900. The latter have 4 times lower ASA values (0.1 m² g^{−1}) than Gr-SLP30 (0.4 m² g^{−1}). Moreover, ASA quantification is absent in the literature for carbons used in KIBs, contrary to that for NIBs. For example, this property was not mentioned in the published works presented in Table S1.

3.2. Electrochemical Properties. The performance of HCS and Gr-SLP30 materials as negative electrodes in KIBs, in terms of CE, capacity retention, and rate performance, were determined and further correlated to the carbon properties (structure, texture, and chemistry).

Figure 4a,b depict the galvanostatic charge/discharge profiles for HCS1500, HCS1700, HCS1900, and Gr-SLP30 electrodes during the first cycle at C/20 and the 50th cycle at a C/10 rate.

The shape of the curves presents two distinct regions: a sloping region from 2.0 to 0.35 V and a plateau-like region from 0.35 to 0.01 V. When we compare the first plateau region between HCS materials (Figure 4a), we noticed that the lengths are longer for HCS1700, HCS1900, and Gr-SLP30 compared to HCS1500, which presents a higher slope region (i.e., capacitive behavior). After 50 cycles (Figure 4b), the slope region becomes less pronounced for all materials. Therefore, a considerable decrease in irreversible capacity is remarked upon along with a decrease in reversible capacity.

The high irreversible capacity is essentially attributed to the formation of SEI involving the reduction of the electrolyte on the electrode surface and the trapping of K⁺ in porosity or/and structure.^{59,60} Although there is not yet a complete agreement on the association of these regions with a precise mechanism, several works^{61–63} suggest that K-ions are adsorbed to defective sites or pores in the sloping region, while insertion of K ions between graphene layers or filling in closed pores occurs in the plateau region.

In addition, the arrangement of the graphene layers might affect the adsorption/diffusion phenomena. Graphite presents a highly organized structure and small interplanar distances (3.35 Å), and the K-ion diffusion through the planes can be unidimensional, while the hard carbon materials present a

disordered structure with randomly orientated planes and higher interlayer distances (3.59 to 3.69 Å). Therefore, the diffusion of the K ion is multidimensional (in different directions) and more easily occurs. Figure 4c shows the capacity retention over 50 cycles. HCS1500 has 88% capacity retention compared to 83%, 79%, and 87% for HCS1700, HCS1900, and Gr-SLP30, respectively (Table 2). In terms of

Table 2. Electrochemical Characteristics of HCSs and Gr-SLP30 Including ICE, the First Charge Capacity, the Capacity Retention, and the CE after 50 Cycles

materials	ICE (%)	first charge capacity (mAh g ^{−1})	capacity after 50 cycles (mAh g ^{−1})	capacity retention after 50 cycles (%)	CE after 50 cycles
HCS1500	54	254	221	88	99
HCS1700	62	247	205	83	99
HCS1900	51	247	195	79	98
Gr-SLP30	43	219	190	87	97

CE evolution (Figure 4d), for HCS1700, it reaches 98% after 10 cycles, while CE for HCS1500 and HCS1900 reaches 98% after 18 cycles. Concerning Gr-SLP30, it does not reach 98% even after 50 cycles. High retention is maintained for all materials after 50 cycles (Table 2). Based on these results, HCS1500 shows the best trade-off based on reversible capacity, capacity retention, and CE evolution. It is important to mention that other factors that are not related to the electrodes contribute as well to the low ICE observed. For example, it was shown that the reactivity of K-metal might induce electrolyte degradation and SEI formation.⁶⁴ The electrolyte itself, in particular, the anion, plays an important role in the formation of SEI. As will be explained later in the manuscript (Figure 8a,b), a better ICE is obtained when KTFSI and KFSI electrolytes are used compared to KPF₆ in EC:DEC.

To gain insight into the mechanisms that occur in these materials, CV analyses were performed (Figure S7). Similar CV profiles for HCS1500, HCS1700, and HCS1900 with two redox peaks (O₁/R₁) reflecting the insertion/extraction of K ions (diffusive behavior) are seen. For a given scan rate, the hysteresis between the two redox peaks (anodic and cathodic pics) increases with the pyrolysis temperature. This suggests a decrease in polarization and a rate capability improvement. By enhancing the scan rate, the peaks become more intense, no matter the material, indicating that capacitive phenomena are promoted. If the capacitive (adsorption) and diffusive (insertion) contributions are determined based on CV curves and the Dunn method, the increase of capacitive phenomena can be clearly seen with the scan rate to the detriment of the diffusive process (Figure 5a,b). The evolution of both capacitive and diffusive contributions between 0.02 and 0.2 mV s^{−1} scan rate CVs shows that the diffusion contribution is predominant (~70 to 90%) compared to the capacitive one (~10 to 30%). HCS1500 and HCS1900 have similar behavior, while HCS1700 shows more pronounced diffusive behavior. Furthermore, the capacitive contribution depicted in Figure 5a is sustained by the capacitive contribution (slope zone in the galvanostatic curves), which is larger for HCS1500 and HCS1900 compared to a tiny slope region for HCS1700 (Figure 4a).

Moreover, the low ICE in the whole series can also be explained by the PVDF strong swelling characteristics.⁶⁵

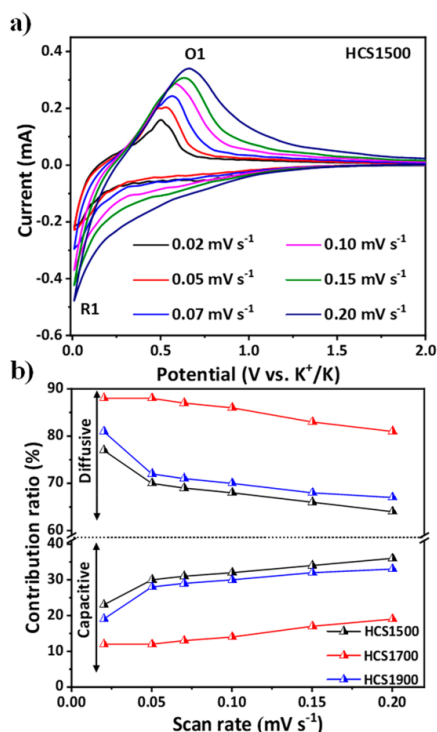


Figure 5. (a) Cyclic voltammetry at different scan rates for HCS1500. (b) Diffusive and capacitive contribution at different scan rates of HCS1500, HCS1700, and HCS1900.

Regarding capacity, HCS1500 has the best initial charge capacity of 254 mAh g^{-1} , followed by HCS1700 (247 mAh g^{-1}) and HCS1900 (247 mAh g^{-1}), while graphite material delivers the lowest capacity, i.e., 219 mAh g^{-1} . It seems that the obtained values decrease with increasing pyrolysis temperature. It is worth it to remind that various properties such as interlayer space, open porosity, and defects are decreasing with the temperature while the closed porosity shows an opposite trend. These properties are known to affect the insertion/adsorption sites of K^+ ions.²² If we attempt to correlate the first charge capacity with the interlayer space, d_{002} (Figure 6a,b), we can see that the capacity increases with the expansion of d_{002} and, therefore, with the decrease of the pyrolysis temperature. This is in agreement with other works^{48,49} and is emphasized in Table S1. For example, Kubota et al.⁶⁶ showed that when the pyrolysis temperature is increased from 1300 to 2000 °C, the reversible capacity decreases. Therefore, larger interlayer spaces allow for better accommodation of K^+ considering their size, which is larger than that of Li^+ .

Defects are also claimed to play a role in K-ion adsorption. As seen in Figure 6a,c, the capacity is enhanced with an increasing defect ratio (I_D/I_G). The important role of defects in the insertion capacity has already been observed in hard carbon used in KIBs and NIBs.⁴⁰

Concerning the possible impact of closed pores on the capacity, one can see (Figure 6a,d) within the HCS series that the capacity tends to increase (HCS1500) with the decrease of the porosity. In the case of graphite, which has much lower

closed porosity, the capacity is reduced. These results suggest that closed porosity does not contribute to K-ion storage. The mechanisms suggesting the closed pore contribution in Na-ion storage have been widely debated in NIBs^{67,68} and are still controversial in the K-ion counterpart.

HCS1700 has the highest ICE (62%) followed by that of HCS1500 (54%) and finally HCS1900 (51%) and Gr-SLP30 (43%). The higher ICE of HCS1700 can be related to its low SSA, low ASA, and optimal d_{002} compared to its analogues prepared at 1500 and 1900 °C. Indeed, HCS1500 presents much higher SSA, ASA, and CO_x functional groups that could favor SEI formation. For HCS1900, although it presents an SSA and ASA similar to HCS1700, it has a smaller d_{002} that can lead to irreversible trapping of K ions and thus to a lower ICE. Gr-SLP30 has the lowest initial ICE of 43%, which can be attributed to its higher active surface area and oxygen functionality amount, which could contribute to higher electrolyte degradation and thus more abundant SEI formation.³⁴ In addition, ICE appears to be higher when the closed porosity is higher, except for HCS1900. However, the variation of other parameters is simultaneously occurring when the pyrolysis temperature increases (SSA, ASA, CO_x); therefore, it is difficult to distinguish the real impact of the closed porosity on ICE in this case. Furthermore, the smallest interlayer space of HCS1700 and Gr-SLP30 (3.35 Å) can irreversibly trap K ions and likely contribute to the lower ICE.³⁴

Therefore, the trend of ICE evolution with temperature is not clear because of the contribution of several parameters. The same conclusion can be reached by analyzing data from the literature collected in Table S1, which show no clear correlation of ICE with the physicochemical properties. Nevertheless, the ICE values obtained in this work are among the best reported in the literature (Table S1), when using a similar electrode formulation (based on PVDF binder). In addition, the use of only 5% of the binder is another advantage of the electrodes reported herein.

To further discriminate the impact of disordered carbon materials (HCS) and well-ordered carbon material (Gr-SLP30), the C-rate performance was evaluated after 50 cycles (Figure S8). All carbons show a dramatic loss of capacity when the rate is increased. HCS1500 withstands better at high C rates, although its capacity decreased from $\sim 235 \text{ mAh g}^{-1}$ at the C/10 rate to $\sim 125 \text{ mAh g}^{-1}$ at the C/2 (115 mA g^{-1}) rate. This is comparable to SLP50⁶⁹ (Table S1), which delivers a capacity of 100 mAh g^{-1} at 140 mA g^{-1} after 50 cycles.

The current limit beyond which the delivered capacity is zero is 2C, C/2, and C/5 for HCS1500, HCS1700, and HCS1900, respectively. The improved results for HCS1500 are explained by the larger d_{002} that can contribute to the faster insertion/disinsertion of K ions and more efficient rate capability. The oxygen-functional groups, porosity, and defects might also favor the K ion adsorption on this material, particularly at high rates, where the capacitive behavior is enhanced. Indeed, Kubota et al.⁶⁶ suggested that the presence of hydrogen terminated edges at a low pyrolysis temperature (1300 °C) will allow a better adsorption compared to higher temperature pyrolysis (i.e., 1800 or 2000 °C). At C/2, Gr-SLP30 delivered a lower capacity than HCS1500 but a larger capacity than HCS1700 and HCS1900. Active surface area and oxygen-based groups are higher for Gr-SLP30, which might positively contribute to a capacity increase through adsorption.

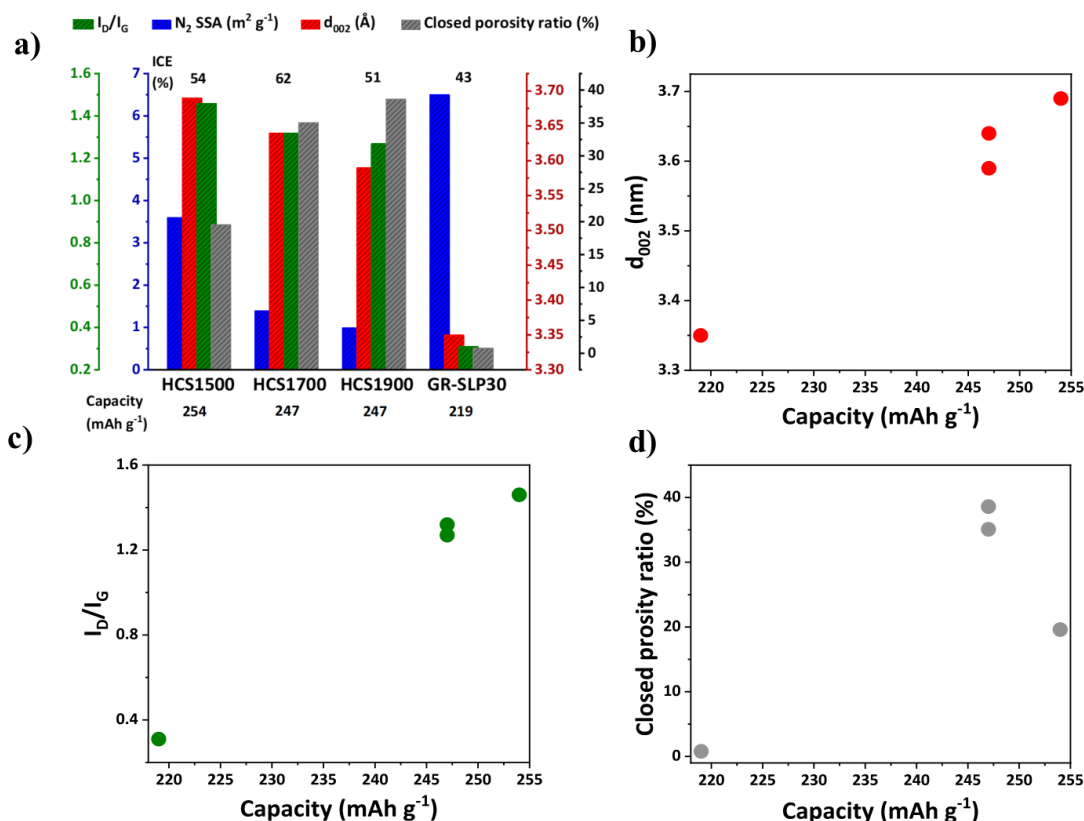


Figure 6. (a) Correlation between the N₂ specific surface area, d_{002} , I_b/I_g , closed porosity ratio, and electrochemical performance (initial Coulombic efficiency and first charge capacity). (b, c, and d) Correlation between d_{002} , I_b/I_g , closed porosity ratio, and the first charge capacity.

In addition, K metal passivation upon cycling (i.e., K metal stripping polarization increase) is also at the origin of the capacity decay observed during the conventional rate test in half cells.⁷⁰ As a result, the potassiation rate is restricted by the polarization of the potassium metal stripping.

To tackle this issue, two alternative cycling tests were performed at different rates. In the first alternative test (Figure 7a), the potassiation rate was kept at C/10, while the depotassiation rate varied from C/10 to 10C. Compared to the conventional rate test, substantially higher depotassiation capacities were obtained. Using this rate capability test (Figure 7a), HCS1500 delivered 230 mAh g⁻¹ after depotassiation at 10C, compared to 0 mAh g⁻¹ using the conventional test (Figure S8). These results show that HCS materials can give high capacities at high depotassiation rates when the hard carbon potassiation is not limited by the K metal stripping polarization. After cycle 32 at 10 C in depotassiation (Figure 7a), HCS delivers high capacities of 230, 228, and 214 mAh g⁻¹ for HCS1500, HCS1700, and HCS1900, respectively, compared to 147 mAh g⁻¹ for Gr-SLP30.

These high capacities for HCS are associated with a small potential hysteresis (polarization) in the 32nd cycle, especially at a high depotassiation rate (10C) when the potassiation of HCS (C/10) is not limited by the stripping polarization of K metal (Figure 7b). Furthermore, when the current goes back to

lower values (C/10) after 35 cycles, HCS recovers nearly all of its initial capacities, but Gr-SLP30 only recovers 83% of its first capacity (Figure 7a). Moreover, this large difference in capacities between graphite and HCSs may be explained by the lower polarization of the latter compared to the high polarization of graphite, which exceeds 0.8 V at 10C. The large volume changes of graphite applying extra stress on the binder and protective SEI explains the graphite behavior as well.

A second rapid alternative test (see the Experimental Section) was performed to evaluate only the capability of the depotassiation rate, overcoming potassium aging and reactivity (Figure S9). In general, much higher depotassiation capacities were obtained compared to the conventional rate test mentioned above (Figure S8). For instance, the HCS1500 delivered 245 mAh g⁻¹ during depotassiation at 10C (254 mAh g⁻¹ at C/10) using the rapid alternative test, compared to 202, 214, and 195 for HCS1700, HCS1900, and Gr-SLP30, respectively, at a 10C depotassiation rate. These results also confirm that HCS1500 delivers high capacities due to the large interlayer space and a higher amount of defects. This offers easy potassium adsorption/insertion without significant structural damage.

The material showing the best ICE (HCS1700) was tested using different electrolytes at C/10 in half-cells vs K metal: (i) using nonconcentrated 0.8 M of electrolytes (KPF₆, KFSI,

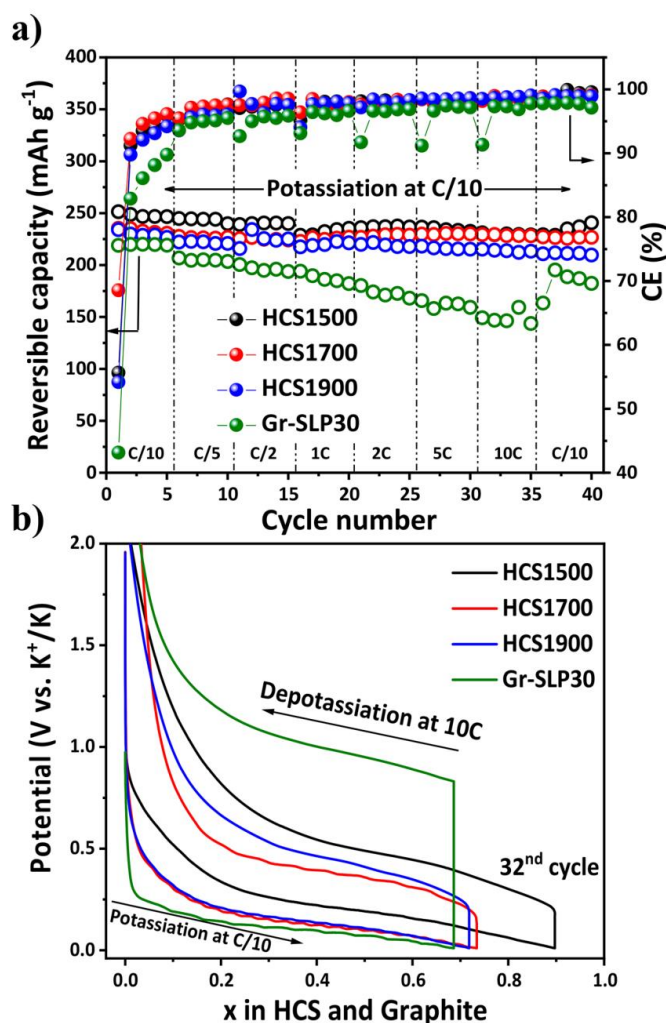


Figure 7. (a) First alternative galvanostatic rate performance from C/10 to 10C depotassiation and C/10 potassiation and CE evolution. (b) Galvanostatic profiles of the 32nd cycle at C/10 potassiation and 10C depotassiation obtained between 2.0 and 0.01 V for HCS1500, HCS1700, HCS1900, and Gr-SLP30 electrodes.

KTFSI), (ii) a mixture of 0.8 M (0.9 KPF₆ and 0.1 KTFSI) and a mixture of 0.8 M (0.9 KPF₆ and 0.1 KFSI) both in EC/DEC, and (iii) two concentrated electrolytes, i.e., 5 M KTFSI and 5 M KFSI in DME. The corresponding galvanostatic charge/discharge curves are shown in Figure 8a, and two regions are observed, a slope and a plateau region for all of the electrolytes, with two pronounced peaks at ~1 V for 5 M KFSI and 0.8 V for 5 M KTFSI, associated with SEI formation. The 0.8 M KTFSI electrolyte exhibits a higher ICE (72%) than the 0.8 M KPF₆ electrolyte (62%) but a lower first charge capacity of 187 mAh g⁻¹ (0.8 M KTFSI) vs 247 mAh g⁻¹ for 0.8 M KPF₆. A good compromise is observed for the 0.8 M KFSI electrolyte, which showed an improved ICE (67%) with a similar first charge capacity (247 mAh g⁻¹) compared to the 0.8 M KPF₆ electrolyte used in this preliminary study.

In addition, when using highly concentrated electrolytes (5 M KTFSI in DME and 5 M KFSI in DME), it is noticed that the same ICE (62%) with 0.8 M KPF₆ is obtained, while both of them have a lower capacity of 213 mAh g⁻¹ vs 247 mAh g⁻¹. Furthermore, the mixture of 0.8 M (0.9 KPF₆ + 0.1 KFSI) and 0.8 M (0.9 KPF₆ + 0.1 KTFSI) delivers ICEs of 59% and 67% and capacities of 232 mAh g⁻¹ and 207 mAh g⁻¹.

The evolution of specific capacity and Coulombic efficiency during 12 cycles for HCS1700 using the different electrolytes are shown in Figure S10a,b. It was noticed that 0.8 M KFSI and 0.8 M KPF₆ in EC/DEC electrolytes deliver the best cycling stabilities (capacity retention). The 0.8 M KPF₆ shows better cycling stability until the sixth cycle, while 0.8 M KFSI behaves better for the rest of the cycles. Regarding the impact on the Coulombic efficiency, all electrolytes lead to improved values compared to 0.8 M KPF₆, except 0.8 M (0.9 KPF₆ +

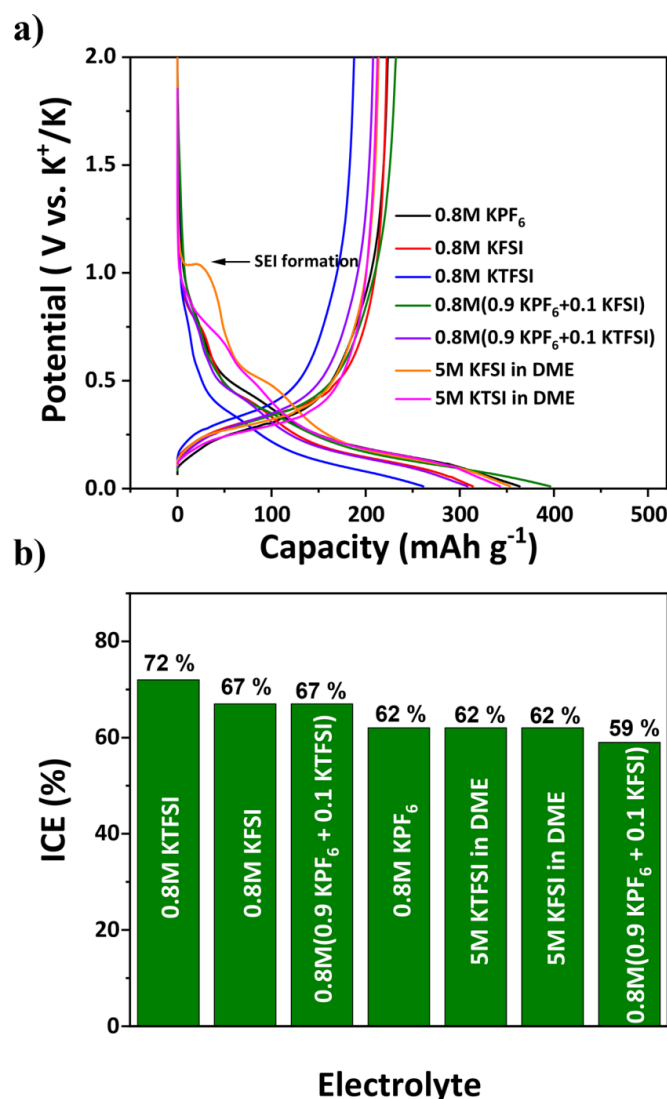


Figure 8. (a) Galvanostatic first charge/discharge profiles and (b) corresponding ICE for HCS1700 obtained between 2.0 and 0.01 V at C/10 using different electrolytes.

0.1KTFSI) in EC:DEC. Finally, 0.8 M KFSI in EC:DEC seems to present the best compromise (capacity/Coulombic efficiency) during cycling. Although, long-term cycling and rate performance tests should be performed to select the best electrolyte, these results already highlight that improvement can be obtained by tuning the electrolyte formulation (including the use of electrolyte additives) in the future.

CONCLUSIONS

Hard carbon sphere (HCS) materials synthesized from a green precursor at different pyrolysis temperatures were designed to understand the influence of temperature on the physicochemical and electrochemical properties. The results obtained were then compared to a commercial graphite (Gr-SLP30). The

increasing pyrolysis temperature (1500 to 1900 °C) impacted the physicochemical properties of the HCSs. The interlayer space (d_{002}), the specific surface area, and the amount of oxygen-based groups and defects decreased with increasing temperature. However, both helium density measurements and closed porosity have an opposite trend. Compared to HCS, Gr-SLP30 presents a different morphology (flakes vs spheres), lower interlayer space, no closed porosity, and high density. Moreover, it reveals a higher particle size, He density, and active surface area (ASA) than HCS.

The correlations between the physicochemical properties and electrochemical performance, i.e., higher capacity and capacity retention when the pyrolysis temperature is decreased, showed that the increase of the interplanar graphitic distance

and defect ratio is desirable for higher performance. Regarding the ICE, the correlations were less obvious since many parameters may impact it, i.e., surface chemistry, defects, and interlayer space. HCSs present better ICE and capacity compared to graphite. Furthermore, conventional C-rate tests showed rapid fading of the capacity with increasing C rate. The alternative rate tests implemented allow the achievement of high capacities (230, 228, and 214 mAh g⁻¹) at high depotassiation rates (10C) when the potassiation of the HCSs materials is not limited by the K metal polarization. Among the materials, the HCS1500 delivers the best capacities due to its structure, which combines the larger space between the graphene layers, defects, and functionalities.

Finally, this work will contribute to the development of high-energy KIBs by providing hard carbon with suitable properties which are tuned by the synthesis conditions. Furthermore, there is no doubt that electrolyte formulation will allow for further improvements of the HC-based KIB, as shown here with preliminary results.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.3c00201>.

SEM and HRTEM images of hard carbons and graphite; XRD and Raman spectra of graphite; CO₂ sorption isotherms and pore size distribution of hard carbon materials; XPS C 1s high resolution spectra of graphite; TPD-MS gas desorption profiles of the three hard carbon and graphite materials; electrode density calculation explanations; cyclic voltammetry of hard carbon materials; rate performance after 50 cycles of hard carbons; alternative rate performance test and depotassiation capacities obtained using the alternative rate performance of hard carbon and graphite materials; specific capacity and evolution of Coulombic efficiency of HCS1700 during cycling using different electrolytes; comparison table of physicochemical properties and electrochemical performance of the as-prepared materials with other reported carbons in the literature (PDF)

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Notes

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Supporting Information

Impact of hard carbon properties on their performance in potassium-ion batteries

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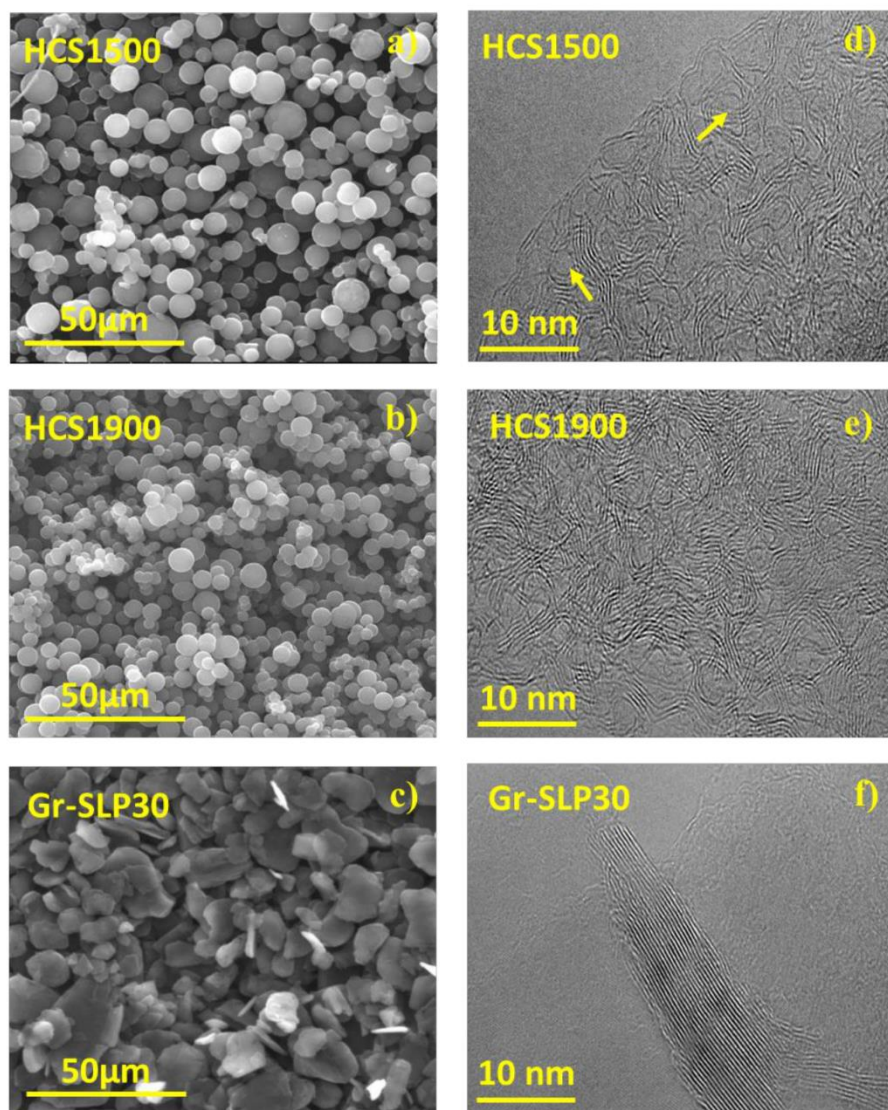


Figure S1: (left) SEM images of (a) HCS1500, (b) HCS1900 and (c) Gr-SLP30; (right) HRTEM images of (d) HCS1500, (e) HCS1900 and (f) Gr-SLP30.

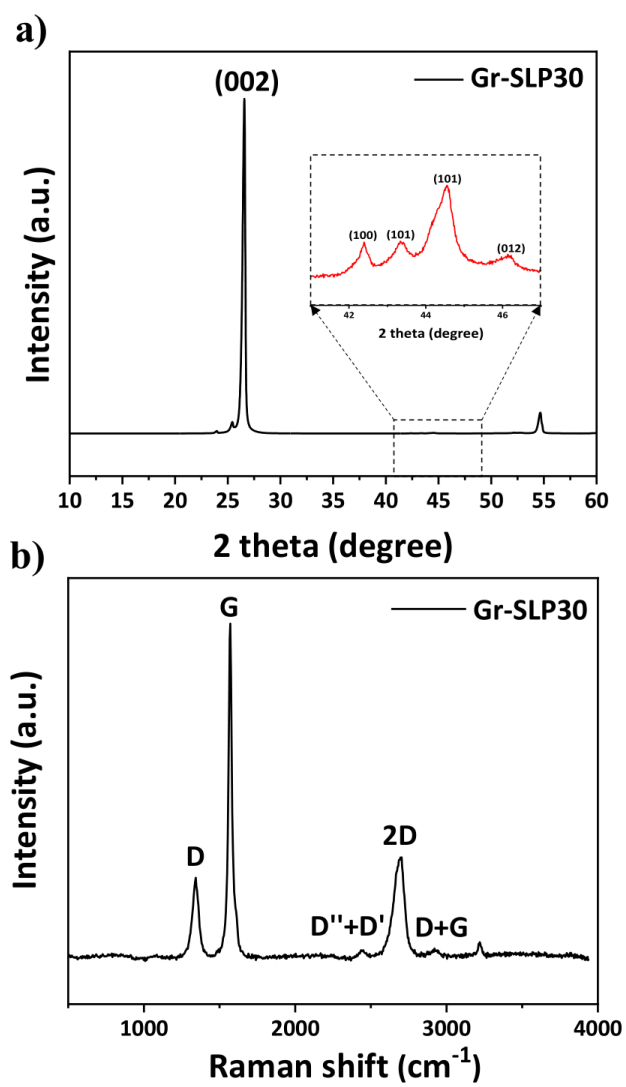


Figure S2: (a) XRD diffractograms and (b) Raman spectrum of Gr-SLP30.

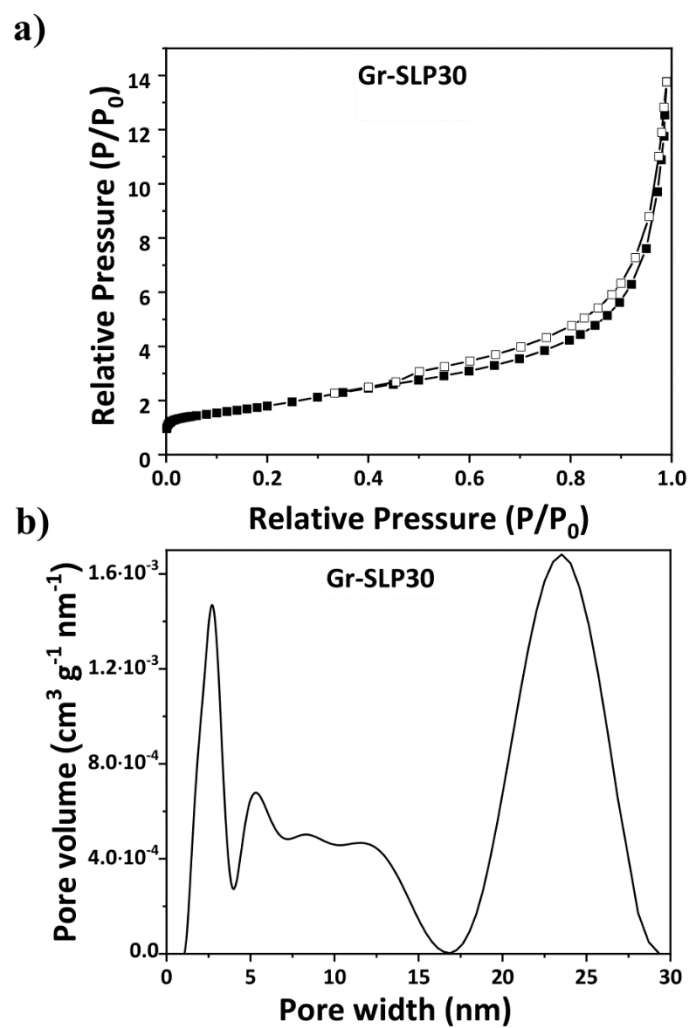


Figure S3: (a) N_2 adsorption - desorption isotherms of Gr-SLP30 material; (b) 2D-NLDFT pore size distribution based on N_2 adsorption branch.

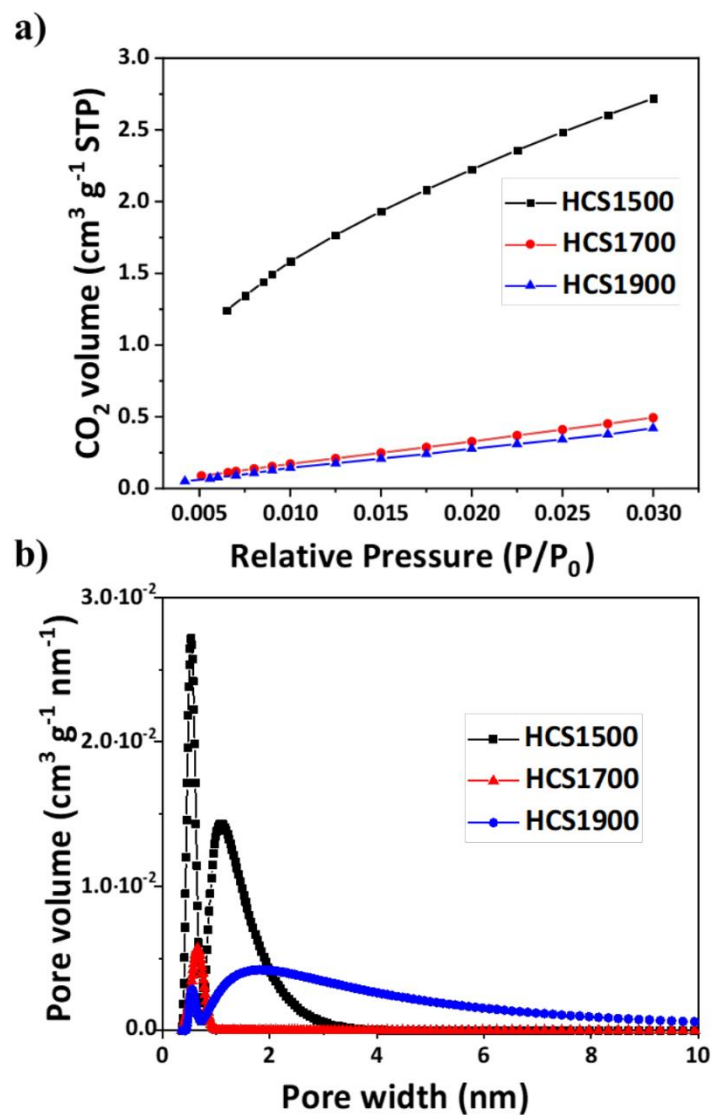


Figure S4: (a) CO₂ adsorption isotherms of HCS materials; (b) 2D-NLDFT pore size distribution based on CO₂ adsorption branch.

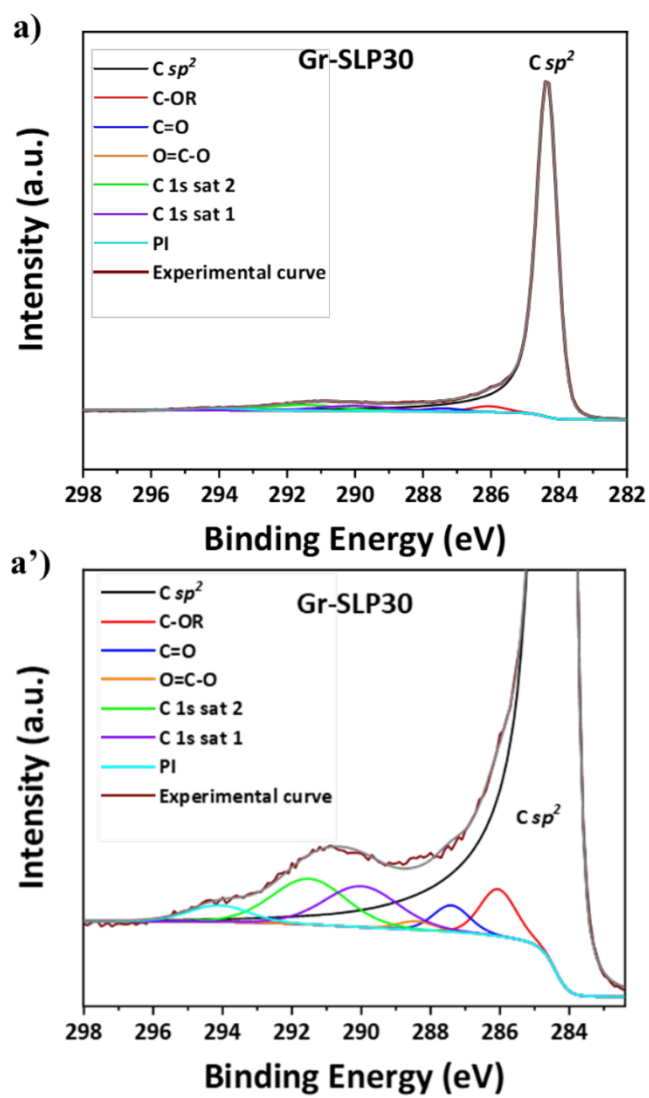


Figure S5: XPS C1s high-resolution spectra of (a) Gr-SLP30 and (a') zoom in oxygen functional groups region.

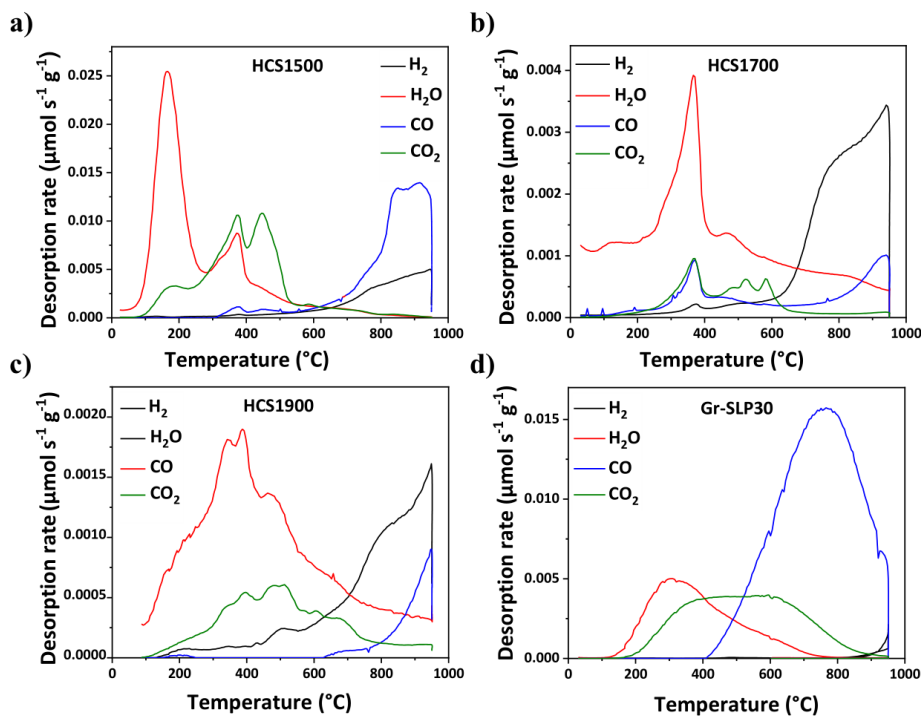


Figure S6: Desorbed gases evolution during TPD-MS analysis for HCSs: (a) HCS1500, (b) HCS1700 (c) HCS1900, and (d) Gr-SLP30.

Electrodes density calculation:

The electrodes density was calculated via the following formula:

$$\rho = (\text{Masse of the active material}) / \text{Volume of the electrode} \quad (1)$$

Where:

Masse of electrode = total mass of the electrode containing current collector (Al) – mass of the current collector (Al)

Volume of the electrode = $S \times h$

S: surface of the electrode

h: the electrode thickness (total thickness of electrode containing the Al current collector – thickness of the current collector)

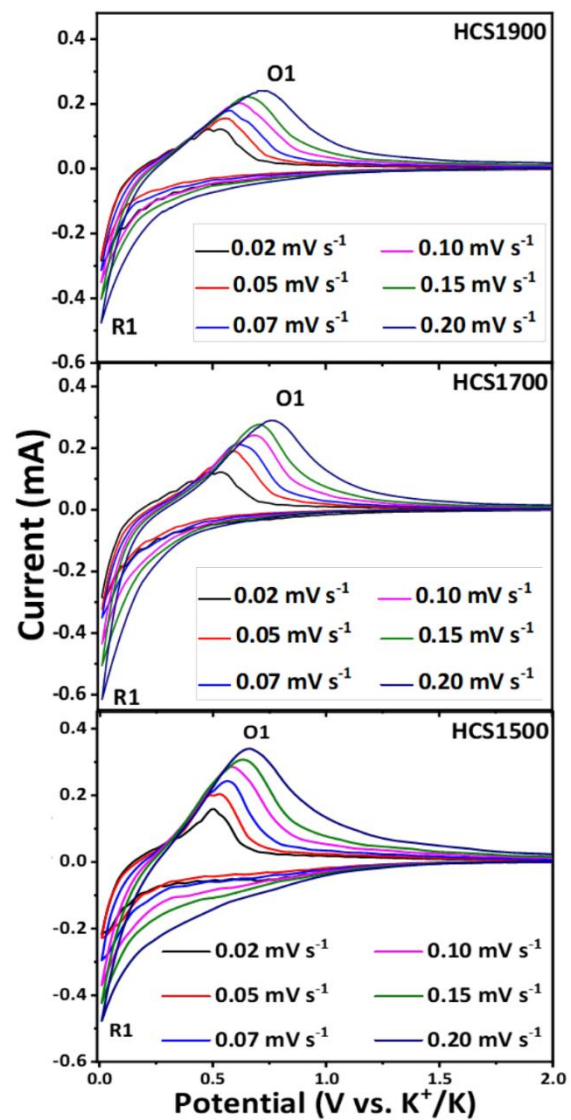


Figure S7: Cyclic voltammetry at different scan rates for HCS1500, HCS1700, and HCS1900.

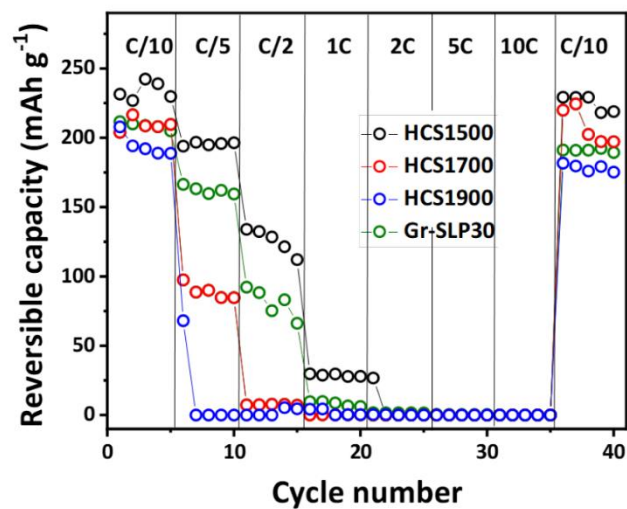


Figure S8: Conventional rate performance after 50 cycles from C/10 to 10C obtained between 2.0-0.01V for HCS1500, HCS1700, HCS1900, and Gr-SLP30 electrodes.

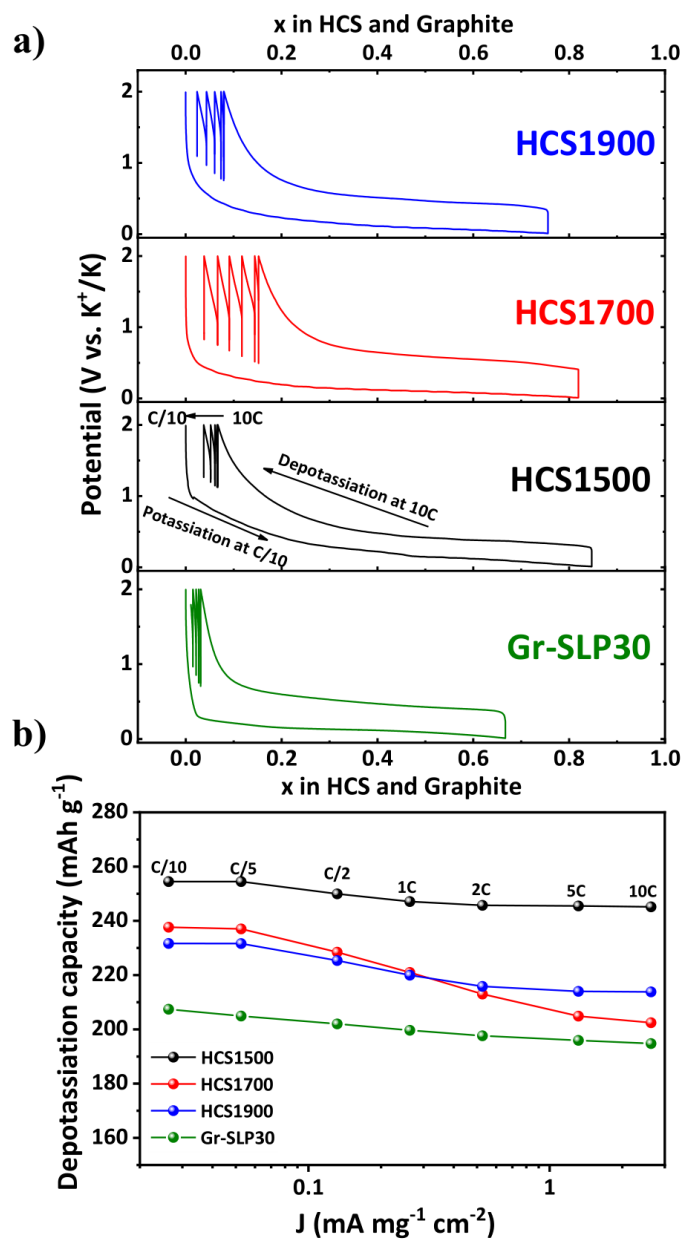


Figure S9: (a) Second alternative rate performance, (b) depotassiation capacities obtained using the alternative rate performance during the 5th cycle (successive depotassiation / 2h relaxation steps) between 2.0-0.01 V for HCS1500, HCS1700, HCS1900, and Gr-SLP30 electrodes.

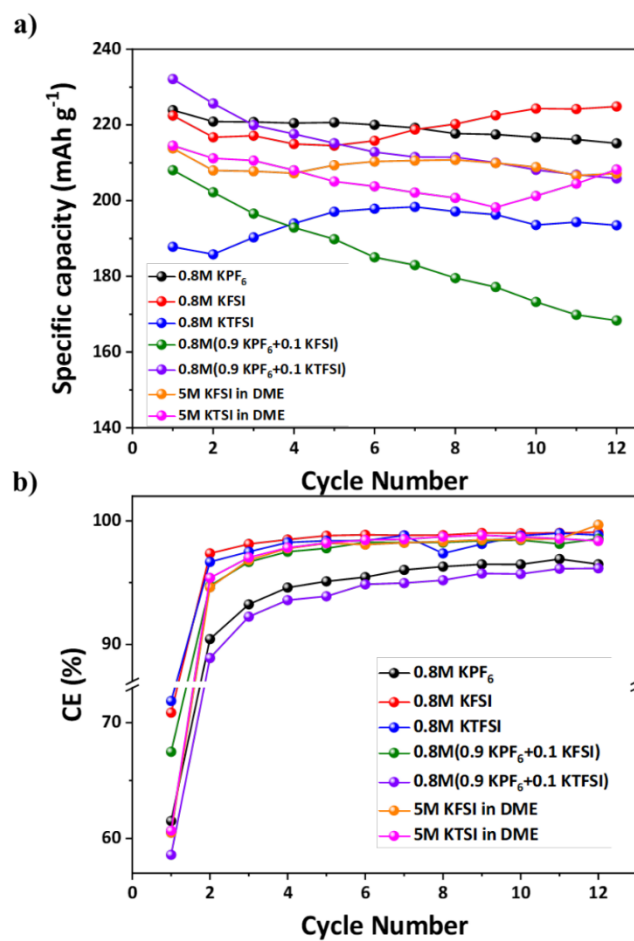


Figure S10: (a) Specific capacity and (b) Coulombic efficiency evolution of HCS1700 during cycling using different electrolytes.

Table S1: Comparison table of the physico-chemical properties and electrochemical performance of the as-prepared HCSs and the commercial Gr-SLP30 with other reported carbon materials in literature.

Material	Pyrolysis temperature (°C)	d ₀₀₂ (nm)	I _D /I _G	SSA (m ² g ⁻¹)	Formulation and electrolyte	Current rate (mA g ⁻¹)	ICE (%)	Charge / Discharge (mAh g ⁻¹)	Retention (%)	Ref
RHC-900 RHC-1100 RHC-1300 RHC-1500	900 1100 1300 1500	0.393 0.388 0.378 0.370	0.32 0.58 0.72 0.76	365.4 115.4 87.3 17.2	80:10:10 AM:CB:PVDF ----- 0.8 M KPF ₆ in (EC:DEC)	30	36.68 <40 49.56 <40	176.9/482.5 n.a 244.9/490.0 n.a	n.a n.a 83 at 30 mA g ⁻¹ (100 cycles) n.a	1
A-700 A-900 A-1100 A-1300 A-1500	700 900 1100 1300 1500	0.355 0.376 0.377 0.350 0.344	1.84 2.60 2.67 1.61 1.36	4.49 2.84 3.82 5.09 5.70	80:10:10 AM:Acetylene black: PVDF ----- 0.8M KPF ₆ in (EC:DEC)	100	~35 ~56.8 53 ~37 ~26	~180/490 213/375 ~ 210/390 ~140/370 ~120/455	n.a ~77 at 100 mA g ⁻¹ (100 cycles) n.a n.a n.a	2
SP-HC 1000 SP-HC 1200 SP-HC 1400 SP-HC 1600	1000 1200 1400 1600	0.387 0.385 0.382 0.375	0.415 0.494 0.534 0.558	41.6 18.3 15.1 9.5	80:10:10 AM:CB:PVDF ----- 0.8 M KPF ₆ in (EC:DEC)	27.9	50 58 57 54	269/538.0 284/489.6 278/487.7 250/462.9	68.4 81.6 73.1 65.6 at 27.9 mA g ⁻¹ (100 cycles)	3
CSHC-8 CSHC-10 CSHC-12	800 1000 1200	0.389 0.386 0.377	3.26 2.95 2.60	217.5 78.5 9.3	90:5:5 AM: acetylene black:CMC ----- 0.8 M KPF ₆ in (EC:DEC)	30	72.7 75.0 74.4	246.9/338.8 254.5/239.3 250.7/336.9	87.5 82.1 83.1 At 100 mA g ⁻¹ (100 cycles)	4
HCSs AHCSs	800 800	0.375 0.410	0.96 1.08	481.4 757.8	80:10:10 AM:Acetylene black:PVDF ----- 0.8 M KPF ₆ in (EC:DEC)	200	41.3 44.2	306.2/742.2 370.2/836.4	~62 at 200 mA g ⁻¹ (5000 cycles)	5
HCS	1100	0.4	n.a	65	80:10:10 AM:CB:PVDF ----- 0.8 M KPF ₆ in (EC:DEC)	27.9	76	260/344	89 at 13.95 mA g ⁻¹ (440 cycles)	6
HC-H ₂ O HC-HCl	1200 1200	0.385 0.388	1.01 1.01	132 354	80:10:10 AM:CB:PVDF ----- 1.0 M KPF ₆ in DME	40	72 73	221/300 253/348	87 at 40 mA g ⁻¹ (150 cycle) 92 at 40 mA g ⁻¹ (150 cycle)	7
NPDC-600 NPDC-700 NPDC-800	600 700 800	n.a 0.395 n.a	0.80 0.99 1.02	6.5 10.5 7.6	70:20:20 AM:CB:PVDF ----- 0.8 M KPF ₆ in (EC:DEC)	500	44.4 40.5 39.4	286/644 369/911 255/647	n.a 80 % at 100 mA g ⁻¹ (500 cycles) n.a	8

Carbon dot @rGO	1000	n.a	1.61	n.a	Film ----- 0.8 M KPF ₆ in (EC/DMC) + 5 wt% of fluoroethylene carbonate	100	44.4	310/698	~95 at 100 mA g ⁻¹ (100 cycles)	9
Graphite (SLP50)	Commercial (>2500)	0.335	n.a	n.a	90:10 AM:PVDF ----- 0.8 M KPF ₆ in (EC:DEC)	6.97	57.4	273/475	n.a	10
Polynanocrystalline graphite	1100	0.345	0.81	91	80:10:10 AM:CB:CMC ----- 0.8 M KPF ₆ in (EC:DEC)	139.5	54.1	224/414	~26 at 100 mA g ⁻¹ (300 cycles)	11
Activated graphite AC-2	800	0.335	0.43	6.17	80:10:10 AM: CB: PVDF ----- 0.8 M KPF ₆ in (EC:DEC)	50	~70%	~260/356	n.a	12
HCS1500 HCS1700 HCS1900 Gr-SLP30	1500 1700 1900 >2500	0.369 0.364 0.359 0.335	1.46 1.32 1.27 0.31	3.6 1.4 1.0 6.5	90:5:5 AM:CB:PVDF ----- 0.8 M KPF ₆ in (EC:DEC)	At 11.5 (5 first cycles) then at 23 (rest of cycles)	54 62 51 43	254/470 247/398 247/484 219/509	88 83 79 87 at 23 mA g ⁻¹ (50 cycles) ----- HCS1500: 125 mAh g ⁻¹ at 115 mA g ⁻¹ (50 cycles) ----- HCS1500: 230 mAh g ⁻¹ HCS1700: 228 mAh g ⁻¹ HCS1900: 214 mAh g ⁻¹ Gr-SLP30: 147 mAh g ⁻¹ At 2300 mA g ⁻¹ (after 32 cycles in depotassiation)	This work

AM: Active material

CB: Carbon black

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