K-ion batteries: role of K metal in half-cells and assembly of reliable full-cells

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1 IPREM
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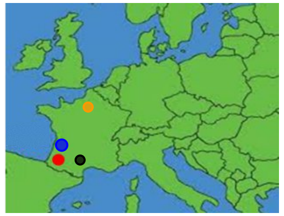


Fr-Jp, July 5, 2022

In collaboration with:

2 LRCS
3 ICG Montpellier
4 icmcb

Why K-ion batteries?

INTEREST

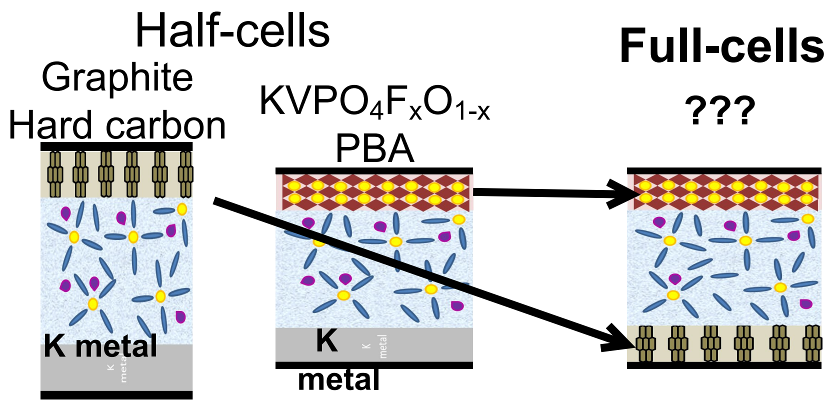
	Lithium	Sodium	Potassium
Abundance	0,002%	2,3%	1,5%
Ionic radii (Å)	0,6 Å	0,97 Å	1,33 Å
Stokes radii (Å)	4,8 Å	4,6 Å	3,6 Å
$E_{desolvation\ in\ PC}$ (kJ/mol)	~ 210	~ 155	~ 110
Cu → Al	x	✓	✓
Graphite	✓	x	✓

→ **Growing interest for K-ion**

- Low cost: high abundance / price (similar to Na)
- Power: low desolvation energy/ionic radii
- Negative electrode: use of graphite (KC_8) and Al

GOAL

What can be expected in term of energy/power for practical (high loading) full-cells?



Questions

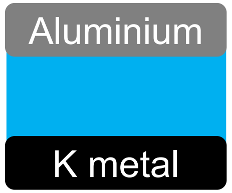
Impact/reactivity of K metal in half-cells?

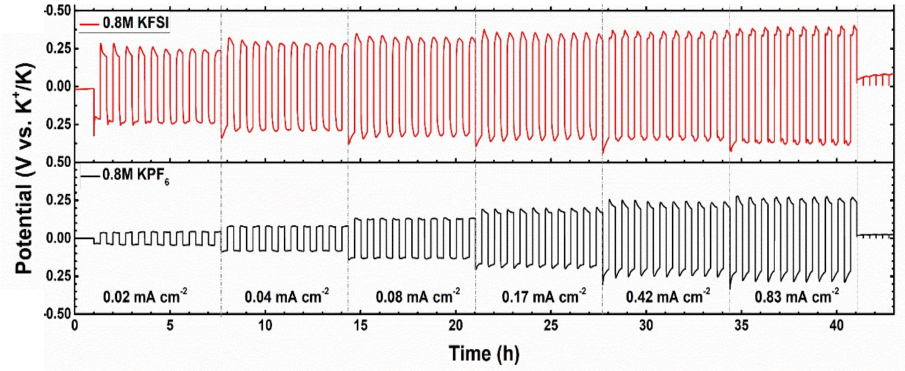
How to assemble full-cells?

K metal plating/stripping performance

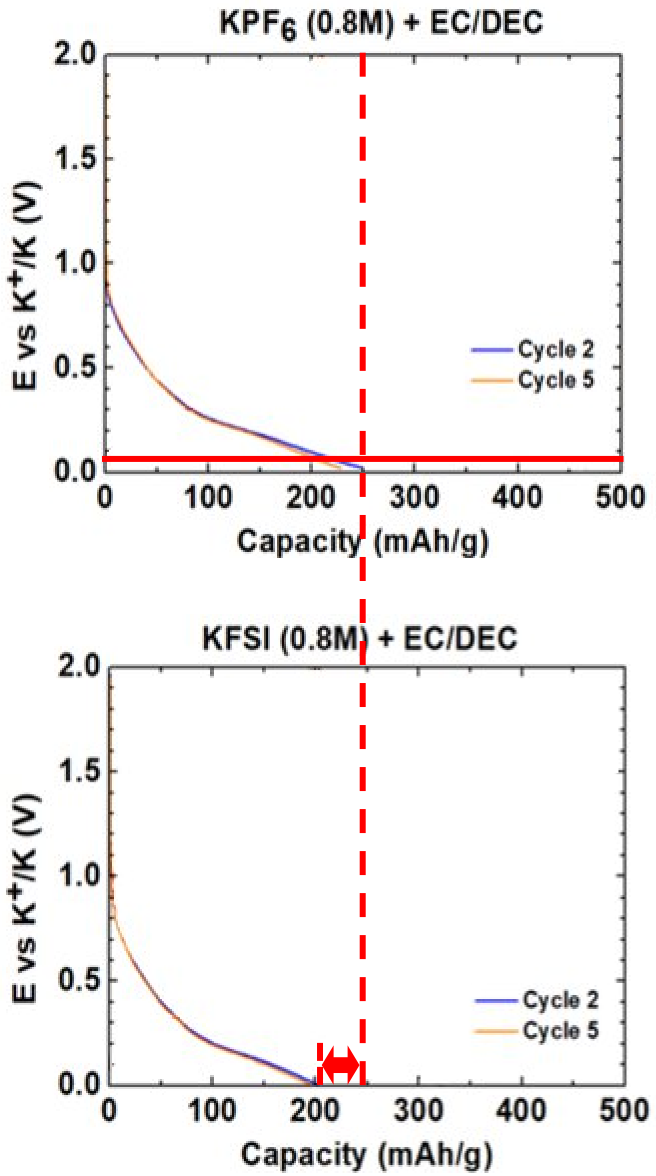
Coin cell

0.8M KFSI or KPF_6
EC:DEC





Polarization: KFSI > KPF_6
Explains why lower rate performance with KFSI



Coin cell

0.8M KFSI or KPF_6
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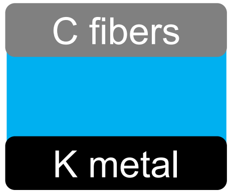


25 mA.g^{-1}
(~C/10)

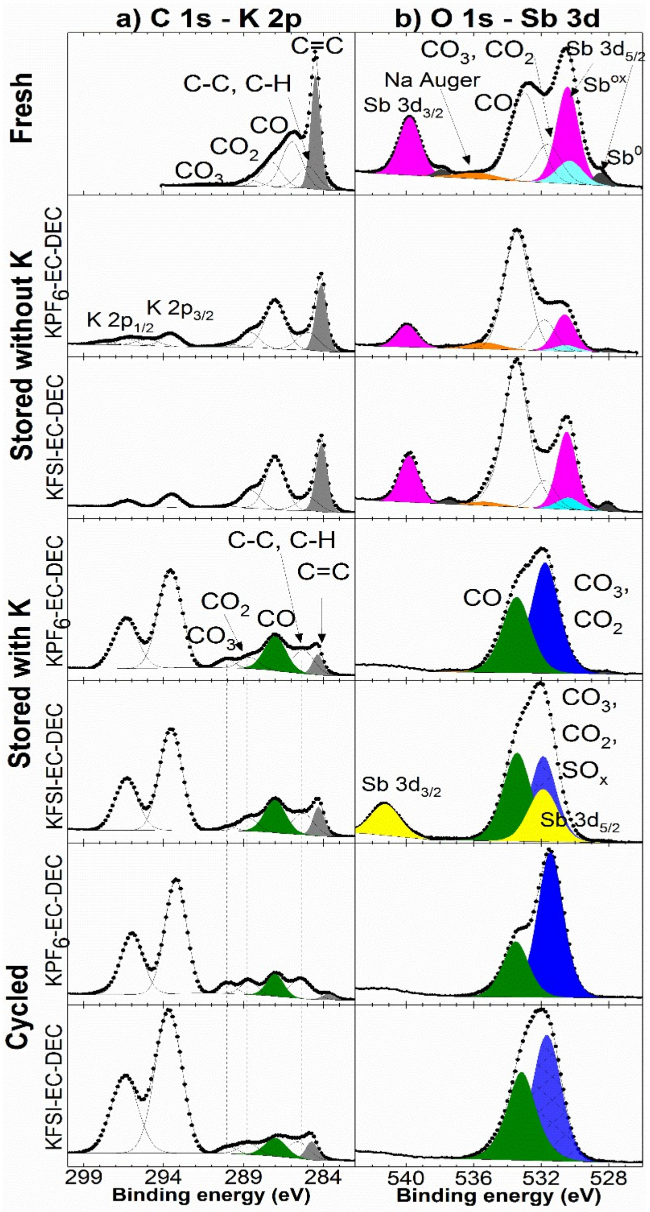
Take home

Potassiation
(even at moderate C/10)
limited by K metal polarization

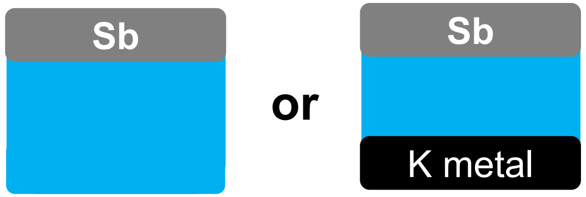
J. Touja *et al.* Electrochimica Acta, 362 (**2020**) 137125

Impact of K metal reactivity

SEI study at OCV (no cycling) after 3 weeks



1° Sb based electrodes



➔ *6 differents electrolytes*

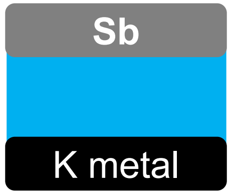
OCV without K metal:
Nearly no change
= no reactivity at Sb surface

OCV with K metal:
Significant changes
= reactivity at K surface + migration of species

CYCLING with K metal:
Similar changes
= no possible conclusion

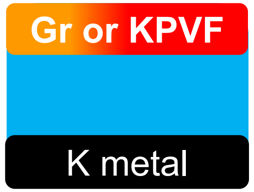
L. Madec *et al.* ACS Appl. Mater. Interfaces, 40 (**2018**)

Impact of K metal reactivity

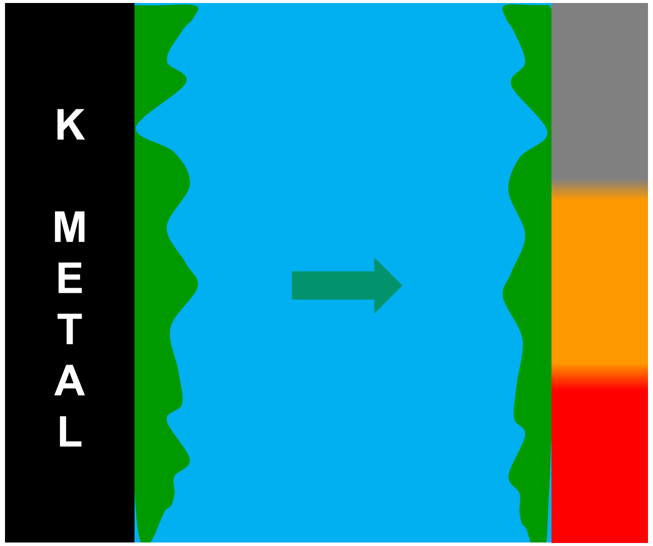


➔ *6 differents electrolytes*

or



➔ *0.8M KPF_6 EC:DEC*

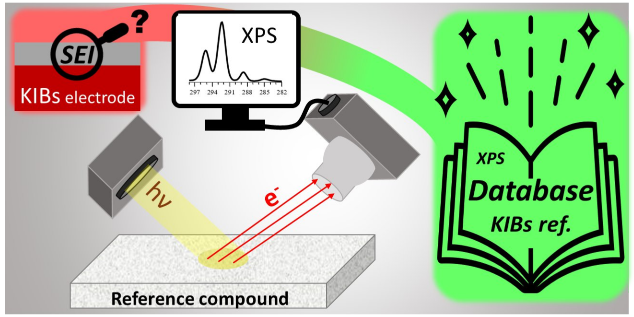


<u>Take home</u>

K metal forms SEI products that contaminate the studied electrodes whatever the electrolyte/electrode = full-cells needed to study SEI

What is the K metal reactivity?

REMARK:



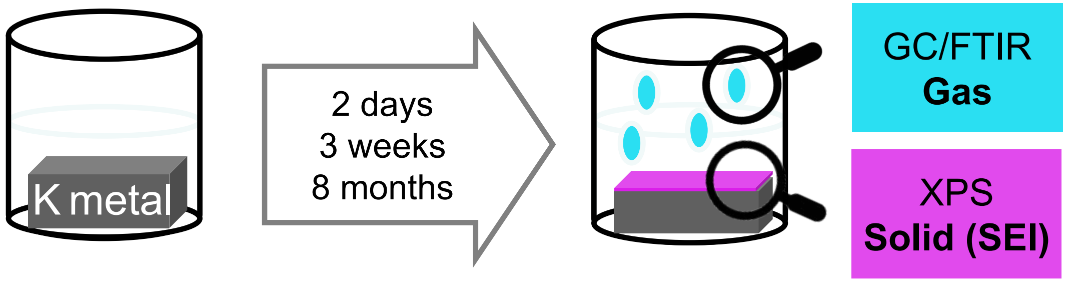
	K 2p or Na 1s or Li 1s		C 1s		O 1s		F 1s		P 2p		N 1s		S 2p		B 1s	
Compound	BE	FWHM	BE	FWHM	BE	FWHM	BE	FWHM	BE	FWHM	BE	FWHM	BE	FWHM	BE	FWHM
KPF_6	295	1.4					688.2	1.8	138.1	1.2						
$NaPF_6$	1073.2	2.5					688.1	1.8	138.2	1.3						
$LiPF_6$	58.4	1.6					688.1	1.8	138.3	1.4						
KBF4	294.5	1.5					687.7	1.9							196	1.4
NaBF4	1073.2	1.8					688	1.8							196.2	1.4
LiBF4	57.7	1.6					687.7	1.9							196.2	1.4
KFSI	293.7	1.5			533.4	1.6	688.1	2.1			400	1.5	170.3	1.3		
NaFSI	1072.3	1.7			533.3	1.6	688.2	2.1			400.1	1.5	170.4	1.3		
LiFSI	56.8	1.6			533.3	1.6	688	1.9			400	1.5	170.3	1.2		
KTFSI	294.2	1.4	293.5	1.2	533.4	1.4	689.2	1.7			400.2	1.3	169.8	1.1		
NaTFSI	1072.7	1.8	293.5	1.2	533.5	1.5	689.2	1.8			400.2	1.4	169.9	1.2		
LiTFSI	57	1.5	293.5	1.3	533.5	1.5	689.2	1.8			400.3	1.4	170	1.4		
KF	293.7	1.8					684.2	2								
NaF	1071.2	1.8					684.8	1.9								
LiF	56.2	1.8					685.1	1.6								
K_2CO_3	292.4	1.5	288.6	1.2	530.4	1.6										
Na_2CO_3	1071	1.9	289.4	1.3	531.1	1.5										
Li_2CO_3	55.3	1.4	290.1	1.3	531.8	1.6										
KOH	292.1	1.5			529.3	1.3										
NaOH	1070.1				529.8	1.3										
LiOH	54.8	1.5			531.1	1.5										
CH_3OK	292.6	1.5	286.1	1.4	531.4	1.7										
CH_3CH_2OK	292.7	1.4	286.1	1.4	531.3	1.6										
CH_3CH_2COOK	292.5	1.3	285.0 288.1	1.2 1	531	1.3										
$K_2C_2O_4$	292.5	1.3	288.1	1.2	531.2	1.4										
CH_3OCOOK	292.1	1.5	286.1 289.4	1.3 1.2	531.1 532.9	1.5 1.5										

➔ New XPS database of K-based SEI references
(comparison with Li and Na)

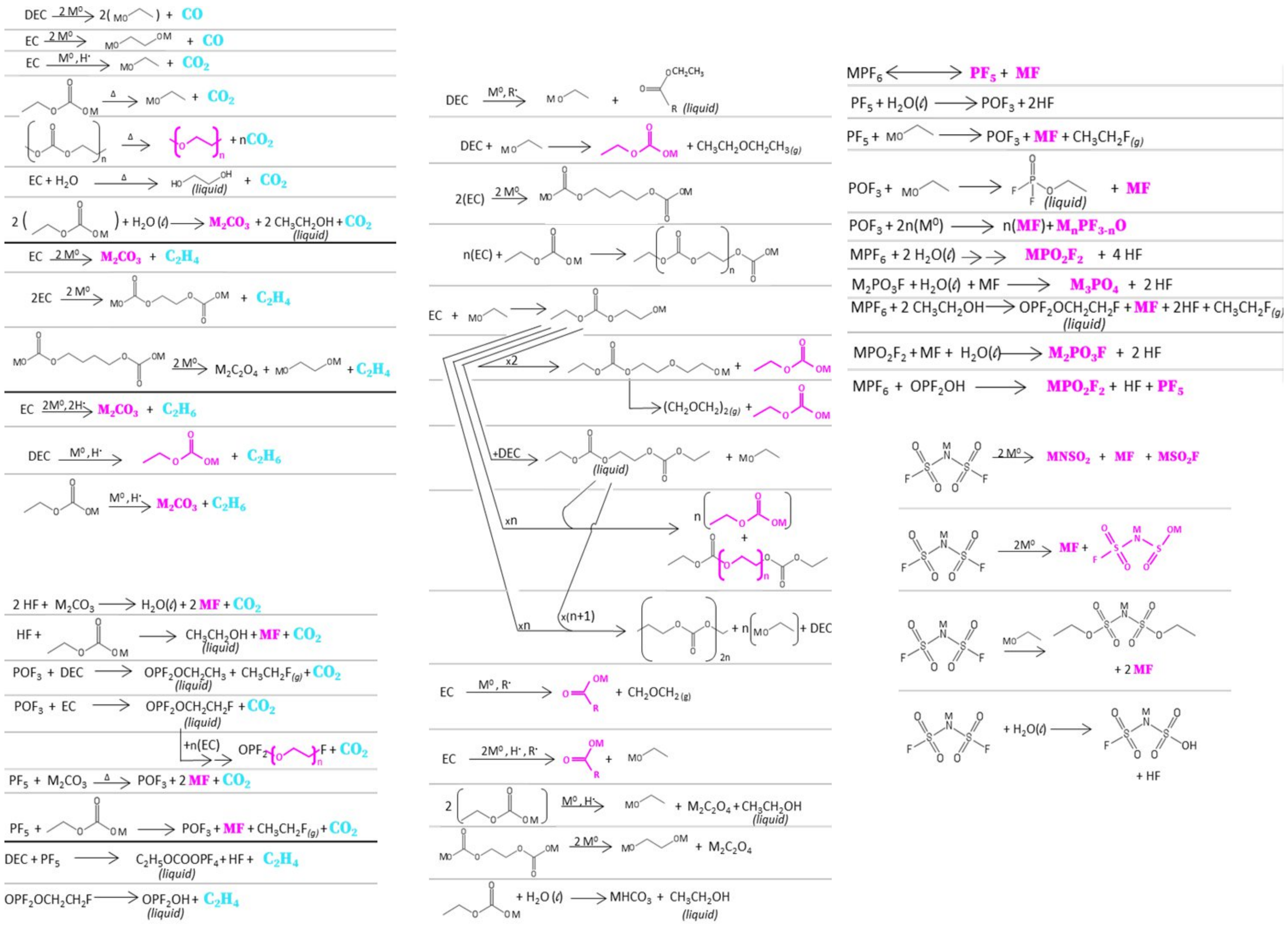
L. Caracciolo *et al*, ACS Applied Energy Materials 4 (**2021**) 11693

What is the K metal reactivity?

K metal storage in EC:DEC wo/w KPF_6 or KFSI salt



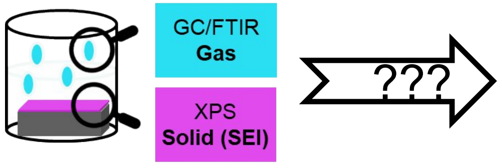
→ *Comparison with Li metal in EC:DEC wo/w $LiPF_6$*

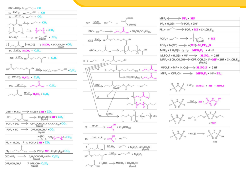


➔ Full electrolyte degradation pathways

L. Caracciolo *et al.*, ACS Applied Materials & Interfaces, 13 (**2021**), 57505.

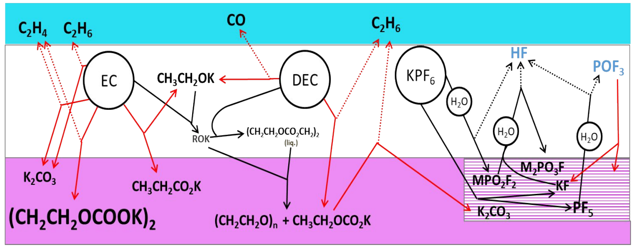
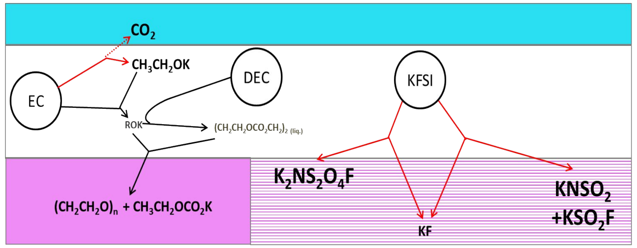
What is the K metal reactivity?





➔ **Full electrolyte degradation pathways**

Experimental (this study)

System	Reactivity driven by
Li or K in EC:DEC	**Solvent reduction**
Li in $LiPF_6$ EC:DEC → LiF 90%	**$LiPF_6$ dissociation**
K in KPF_6 EC:DEC  ***Organic 90%*** *Inorganic 10%*	➔ **Salt cation**
K in KFSI EC:DEC  *Organic 40%* ***Inorganic 60%***	➔ **Salt anion**

Theoretical studies

Stability

Li^+-solvent >> K^+-solvent (carbonate)

→ **Li^+** PF_6^- = **LiF SEI**

→ **K^+** PF_6^- = **organic SEI**

K^+-solvent-anion:

close anion to K^+ = more stable solvent

FSI^- closer to K^+ than PF_6^- (carbonate)

→ K^+ **FSI^-** = **inorganic SEI** (FSI^- reduction)

→ K^+ **PF_6^-** = **organic SEI**

=> Perfect agreement

L. Caracciolo *et al.*, ACS Applied Materials & Interfaces, 13 (**2021**), 57505.

How to assemble reliable full-cells

Half-cells

Coin cell

$KVPO_4F_{0.5}O_{0.5}$ or **graphite**

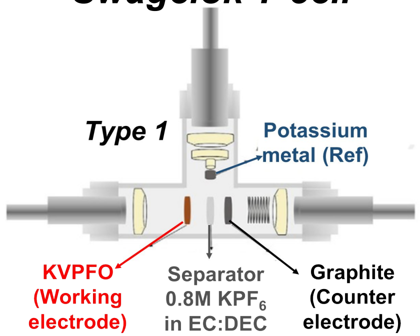
vs. K metal

Preliminary investigation

- *Material capacity*
- *Electrolyte amount*

3-electrodes full-cells

Swagelok T-cell

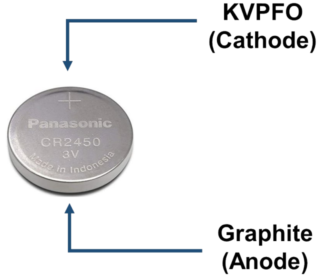


Determination of full-cells parameters

- *N/P diameter ratio*
- *N/P areal capacity ratio*

Practical full-cells

Coin cell



Reliable full-cells performance investigation

- *Capacity retention*
- *Power rate*
- *CEI/SEI study*

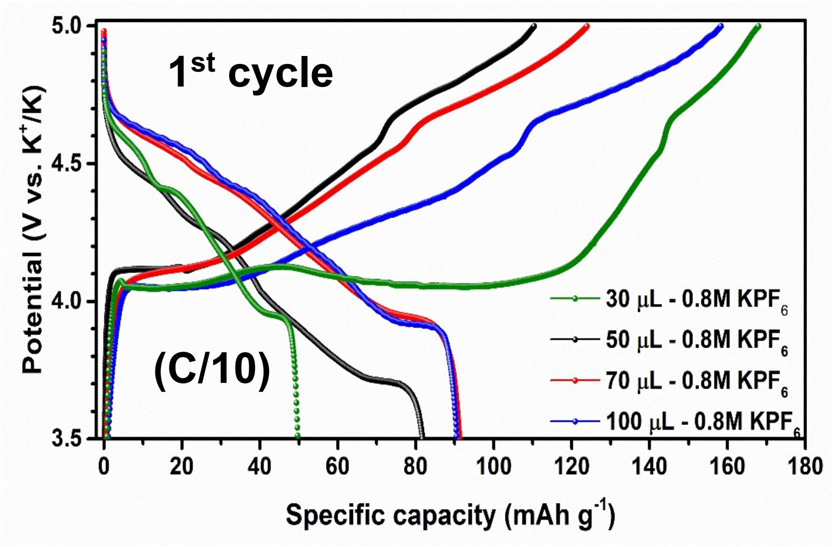
vs. voltage window

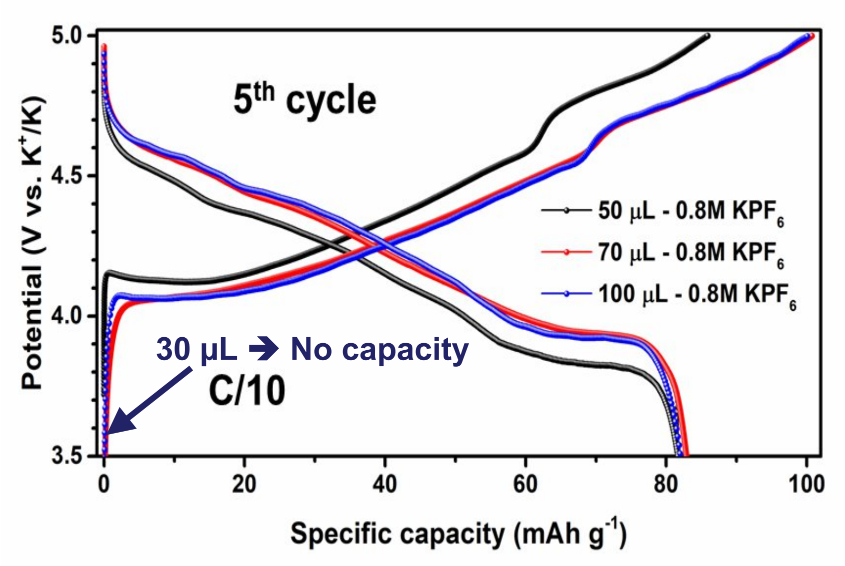
Graphite electrodes **(optimized)** → 85/5/8/2 graphite/CB/CMC/$SBR_{Synthomer}$

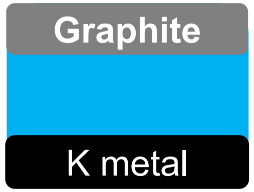
KVPFO electrodes **(non optimized)** → 70/20/10 KVPFO/CB/PVDF

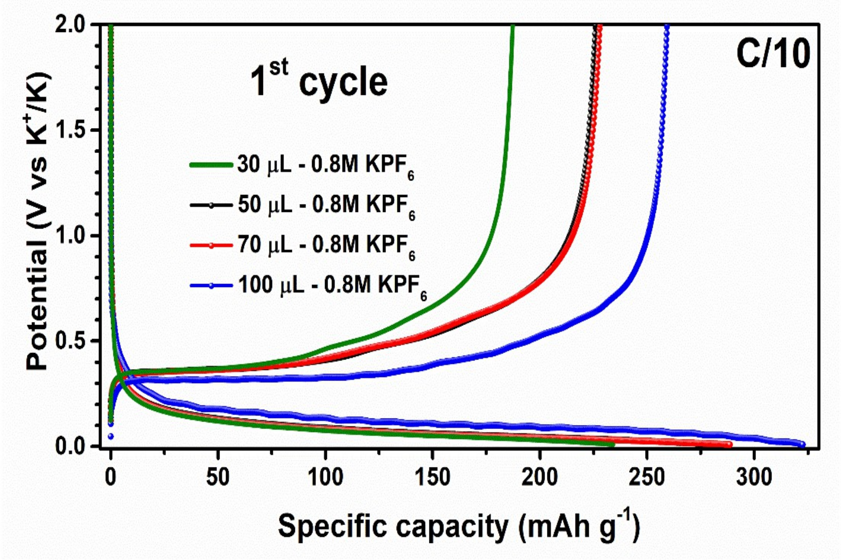
Electrolyte amount

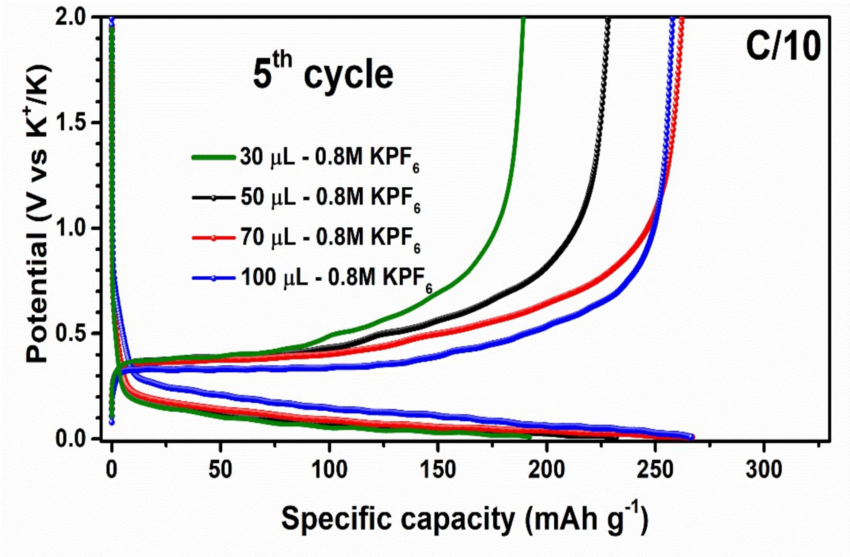
0.8M KPF_6
EC:DEC











Best
electrolyte amount
70 μL

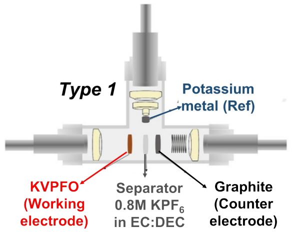
With
separator / electrode
porosity

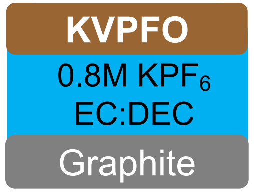
100 μL for 3-E cells

50 μL for full cells

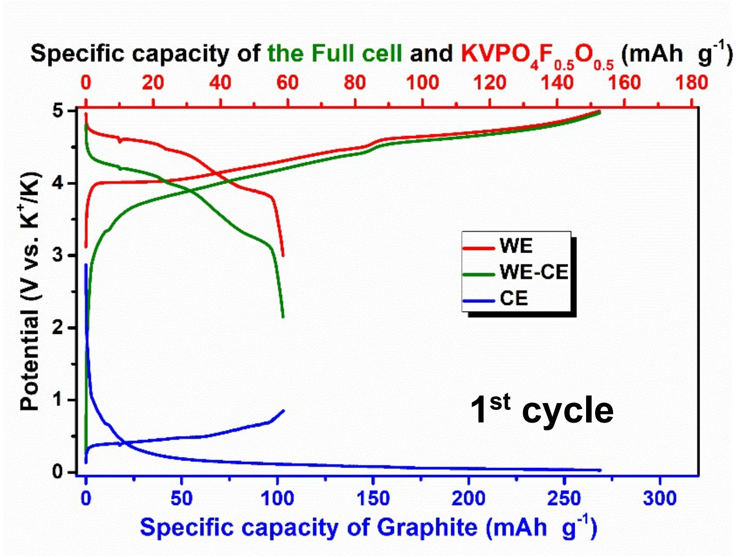
N/P diameter ratio impact

➔ *N/P areal capacity ratio = 1.2*
➔ *cycling at C/10 (2-5V)*

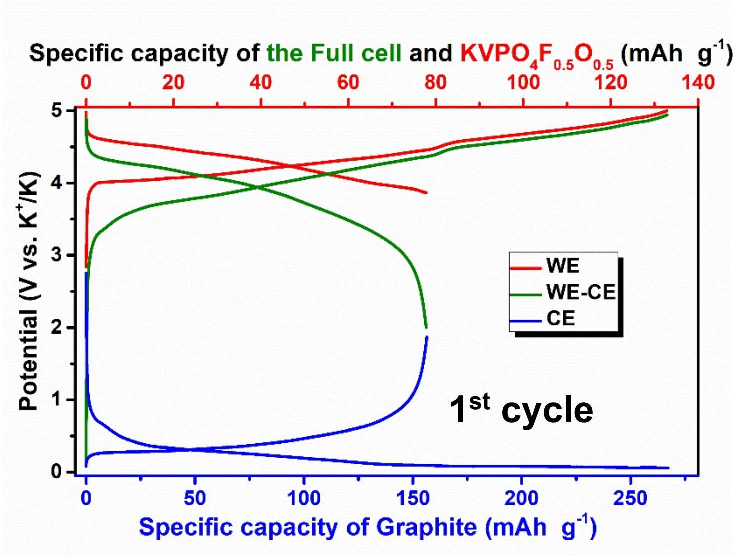


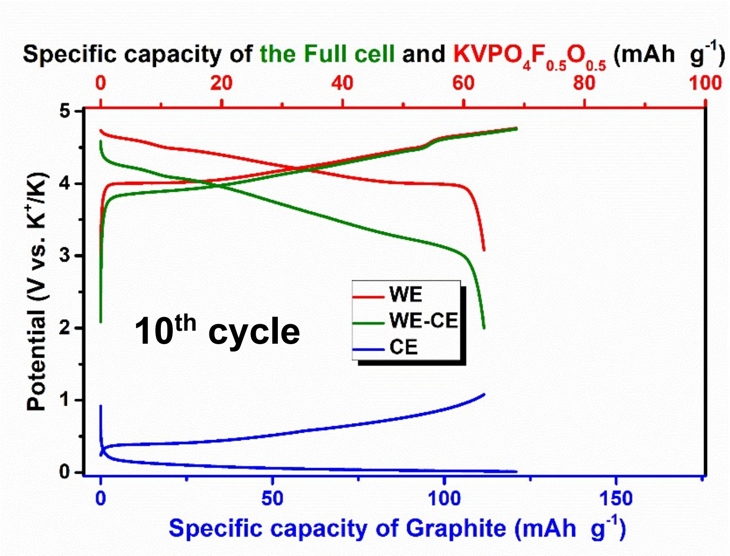


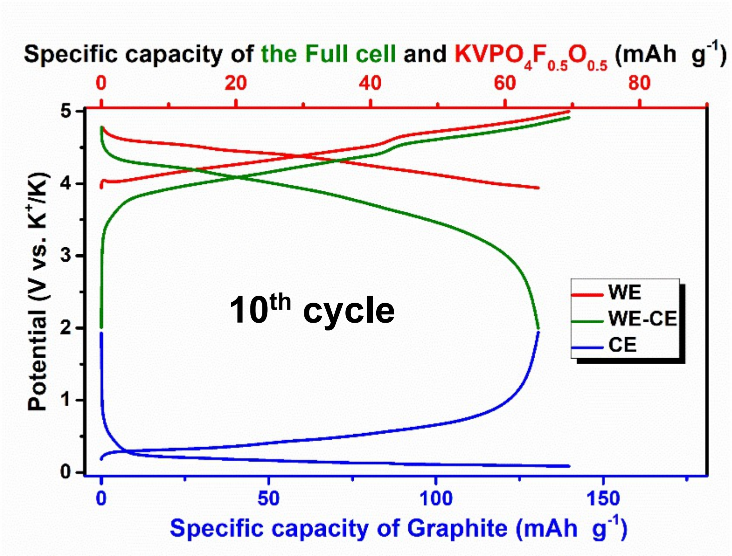
N/P diameter ratio = 1.33



N/P diameter ratio = 1.16



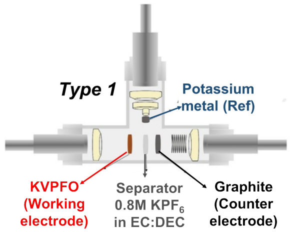




Best
N/P diameter ratio = 1.16

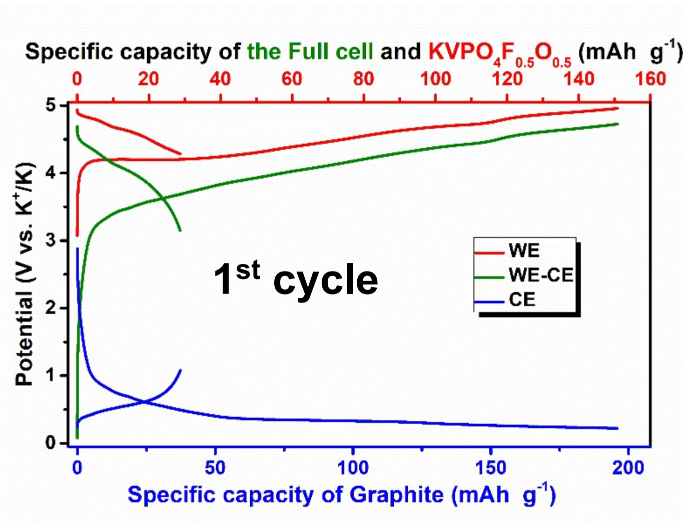
N/P areal capacity ratio impact

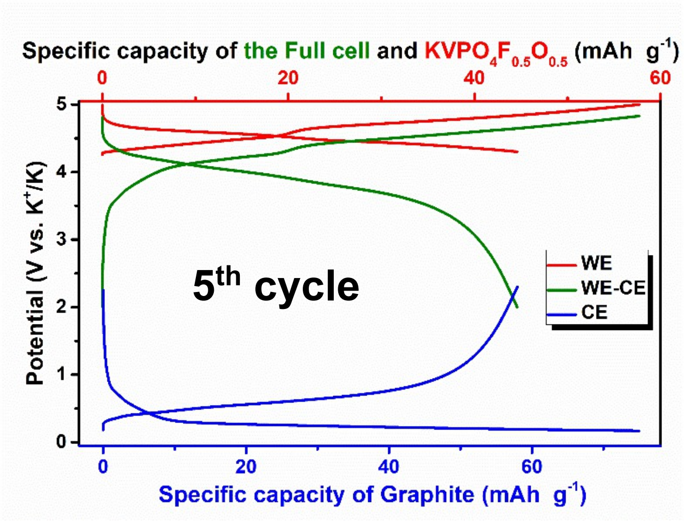
➔ *N/P diameter ratio = 1.16*
➔ *cycling at C/10 (1.2-5V)*



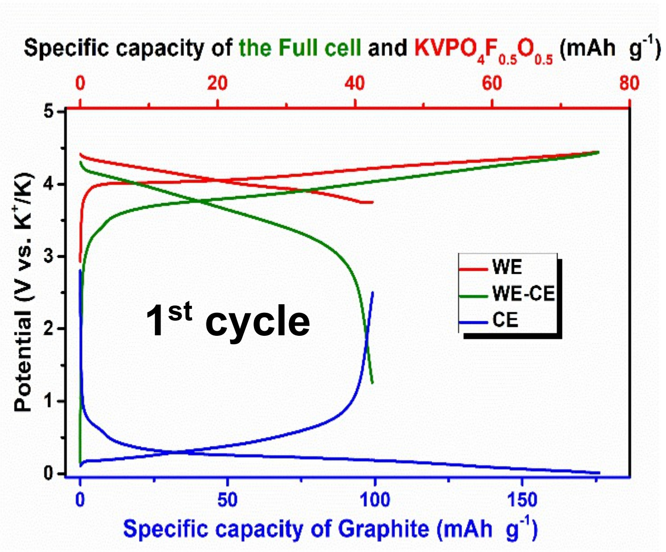
KVPFO
0.8M KPF_6
EC:DEC
Graphite

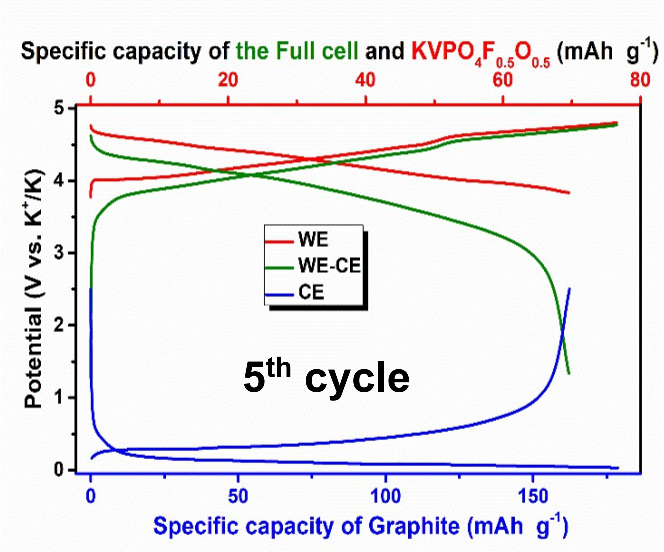
N/P capacity ratio = 1.35





N/P capacity ratio = 1.06



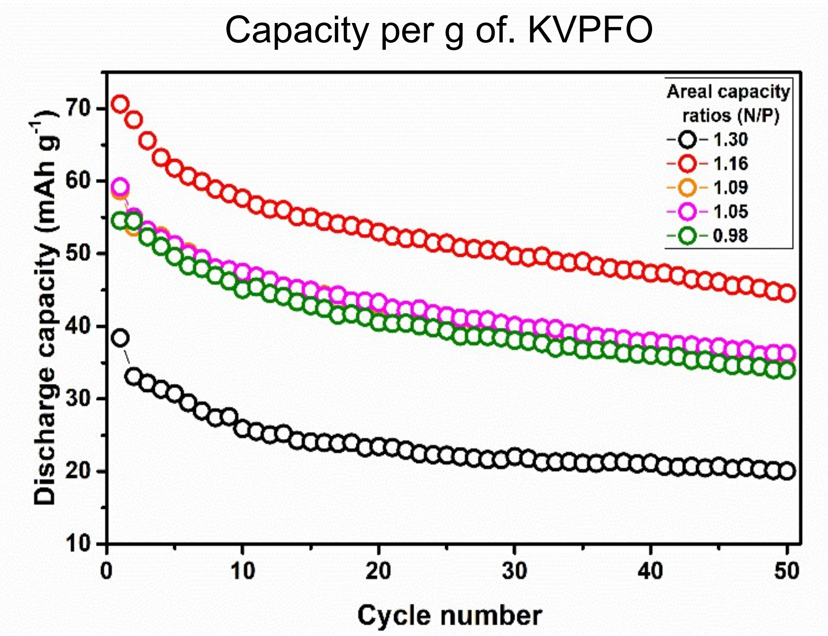


Optimal
N/P areal capacity ratio between 1.06 and 1.35

N/P areal capacity ratio impact

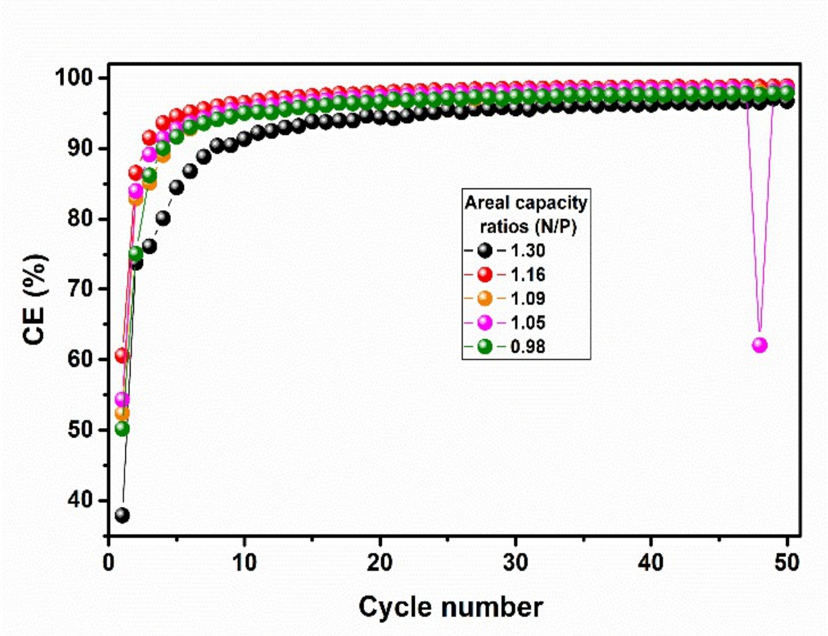
➔ N/P diameter ratio = 1.16
➔ cycling at C/10 (1.2-5V)

KVPFO
0.8M KPF_6
EC:DEC
Graphite



N/P areal capacity ratio = 1.16
➔ Optimal delivered capacity

Best
N/P areal capacity ratio
= 1.16

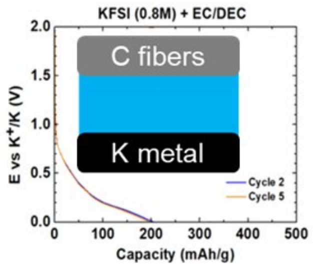


N/P areal capacity ratio = 1.16
➔ Best coulombic efficiency

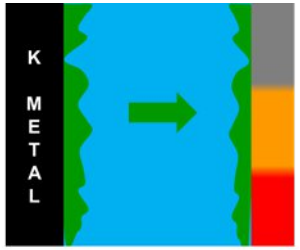
Conclusions and perspectives

Take home
K metal governs

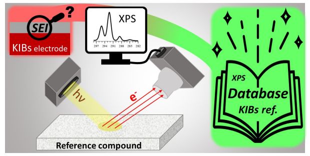
Potassiation capacities
(K metal polarization)



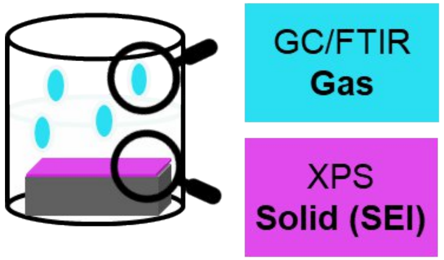
SEI formation
(interaction between electrodes)



Take home
K metal reactivity

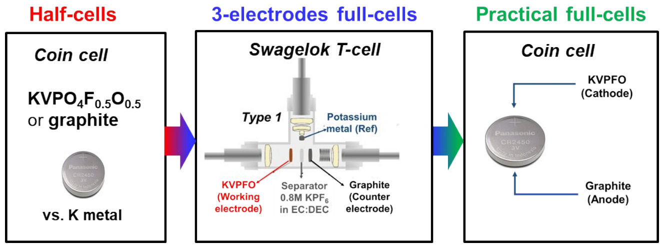


XPS database of K-based SEI references



Impact of salt cation: higher solvent reduction for K^+ vs. Li^+
Impact of salt anion: lower solvent reduction for FSI^- vs. PF_6^-

Take home
assembly of reliable full-cells



Electrolyte amount = 50 µl
N/P diameter ratio = 1.16
N/P areal capacity ratio = 1.16

Full-cells vs. potential, additives…

Thanks

K reactivity
Laure Caracciolo
Previous PhD at IPREM/UPPA

Assembly of full-cells
Badre Larhrib
(PhD at IPREM/UPPA)

Toward practical graphite electrodes for high performance K-ion batteries
(O27 at 17h50)

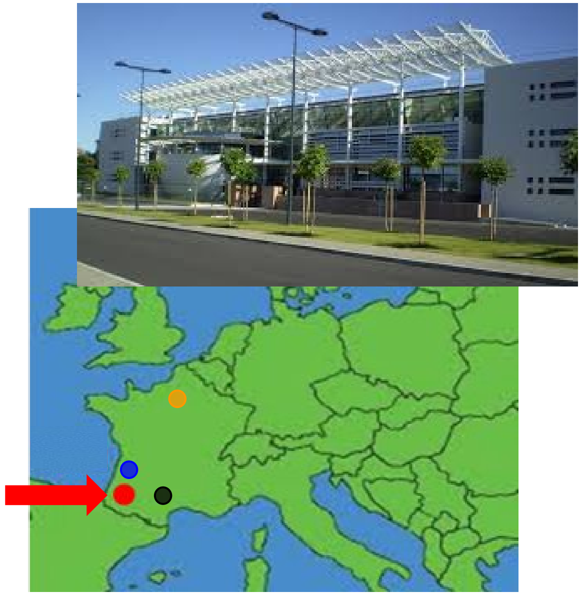
Collaborations

2 LRCS

3 ICG Montpellier

4 icmcb

IPREM - UPPA/CNRS



And thank you for your attention

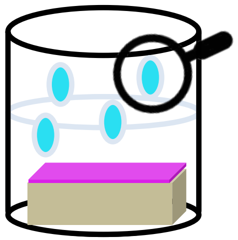
Funding

anr

TROPIC Project

Contact: lenaic.madec@univ-pau.fr

What is the K metal reactivity?



GC/FTIR
Gas

	EC:DEC				EC:DEC + 0.8M MPF_6						EC:DEC + 0.8M KFSI		
	Lithium		**Potassium**		**Lithium**			**Potassium**			**Potassium**		
	2 days	22 days	2 days	22 days	2 days	22 days	8 months	2 days	22 days	8 mois	2 days	22 days	8 months
CO						✔	✔	✔	✔	✔			
CO_2	✔	✔	✔	✔	✔	✔	✔			✔		✔	✔
C_2H_4	✔	✔	✔	✔		✔	✔	✔	✔	✔			
C_2H_6									✔	✔			
CH_3-CH=O													✔

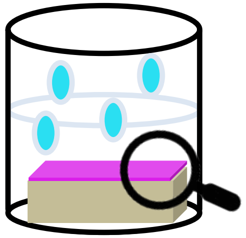
Without salt:
Only CO_2 / C_2H_4
= Same reactivity

With MPF_6 salt:
C_2H_6 only with K
= Higher/faster reactivity with K
= Salt cation impact

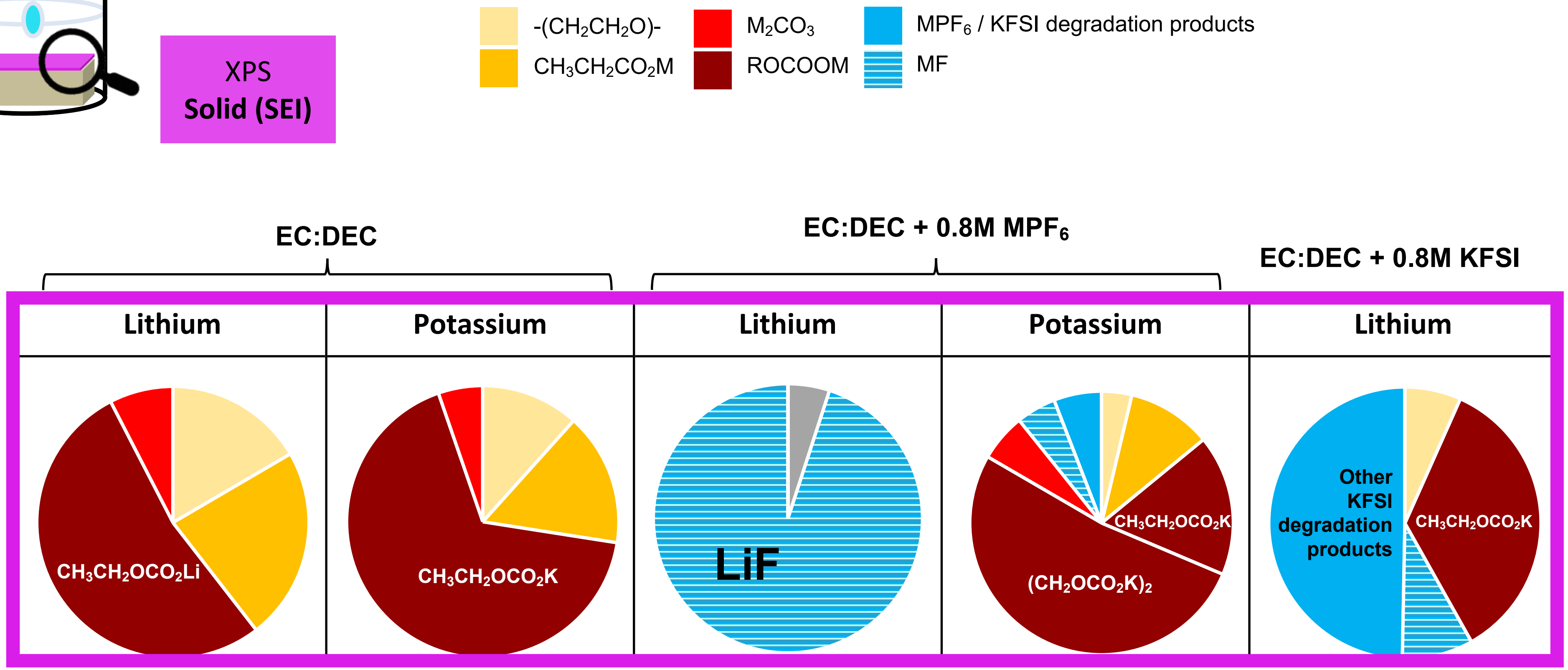
With KFSI:
Much less gas
= Salt anion impact

L. Caracciolo *et al.*, ACS Applied Materials & Interfaces, 13 (**2021**), 57505.

What is the K metal reactivity?



XPS
Solid (SEI)



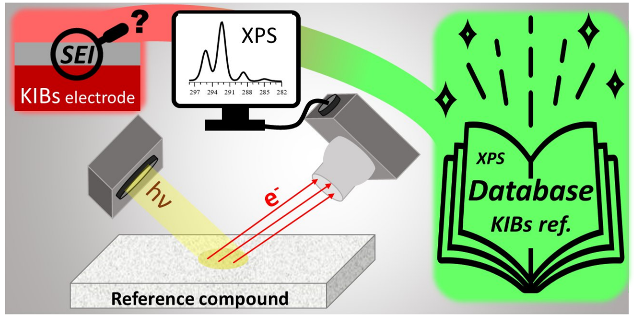
Without salt:
Similar SEI but thicker with K
= Same reactivity

With MPF_6 salt:
Mostly LiF with Li
Mostly organic with K
= Salt cation impact

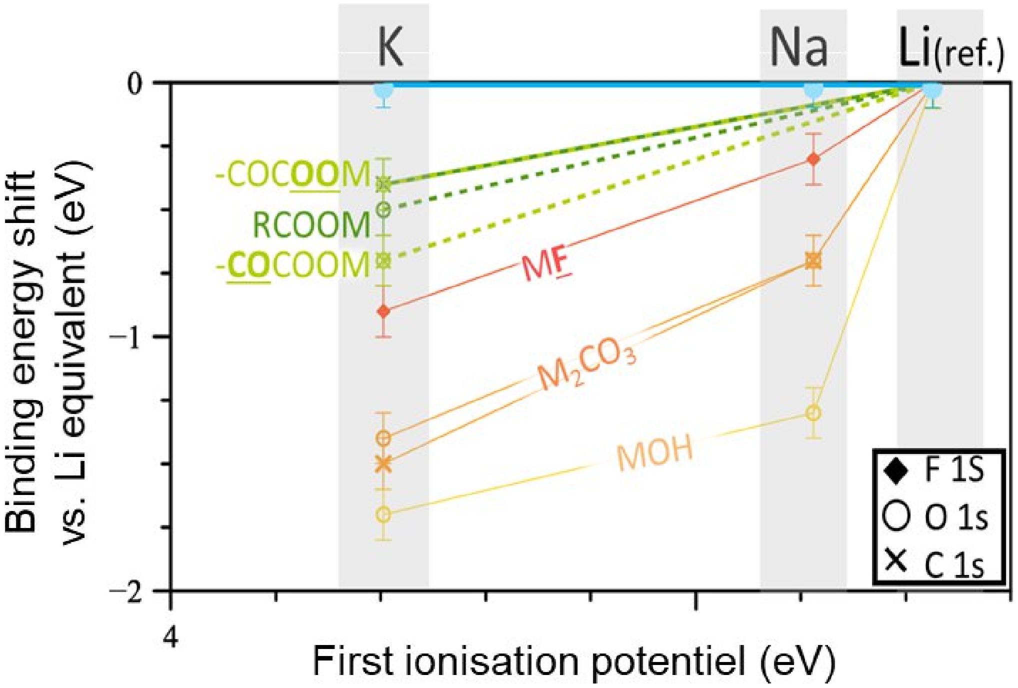
With KFSI:
Mostly inorganic
= Salt anion impact

L. Caracciolo *et al.*, ACS Applied Materials & Interfaces, 13 (**2021**), 57505.

What is the K metal reactivity?



Peak at 288.5 eV = $R\underline{\mathbf{C}}O_2Li$ / $K_2\underline{\mathbf{C}}O_3$



➔ ***New XPS database of K-based SEI references***
(comparison with Li and Na)

L. Caracciolo *et al*, ACS Applied Energy Materials 4 (**2021**) 11693

Voltage limit impact

➔ *N/P diameter ratio and capacity ratio = 1.16 - cycling at C/5*

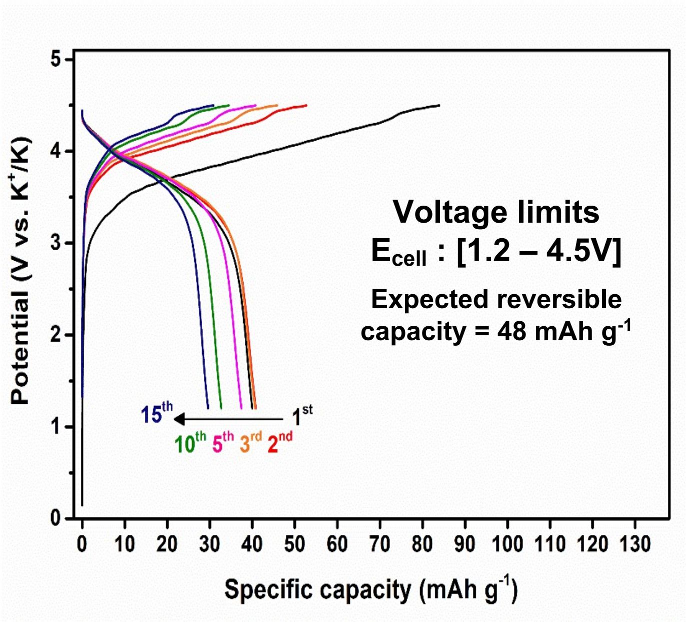
Loadings: (+): 4.92 mg cm^{-2} / (-): 1.94 mg cm^{-2}

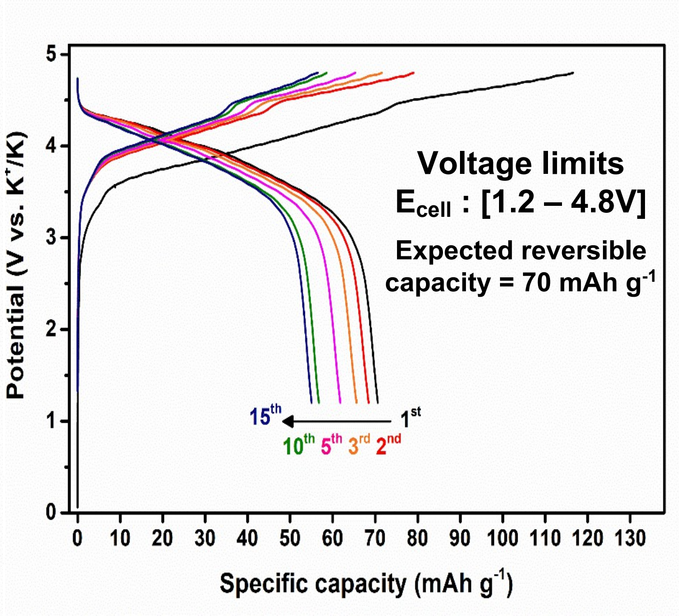
KVPFO

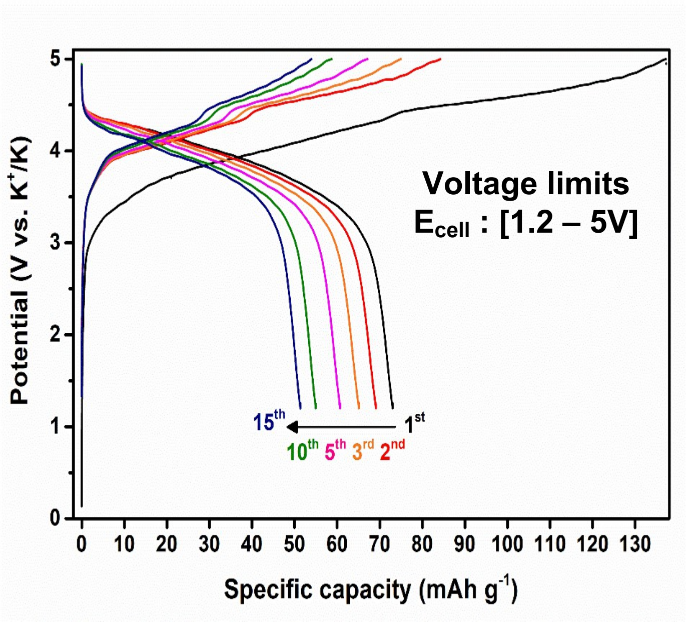
0.8M KPF_6
EC:DEC

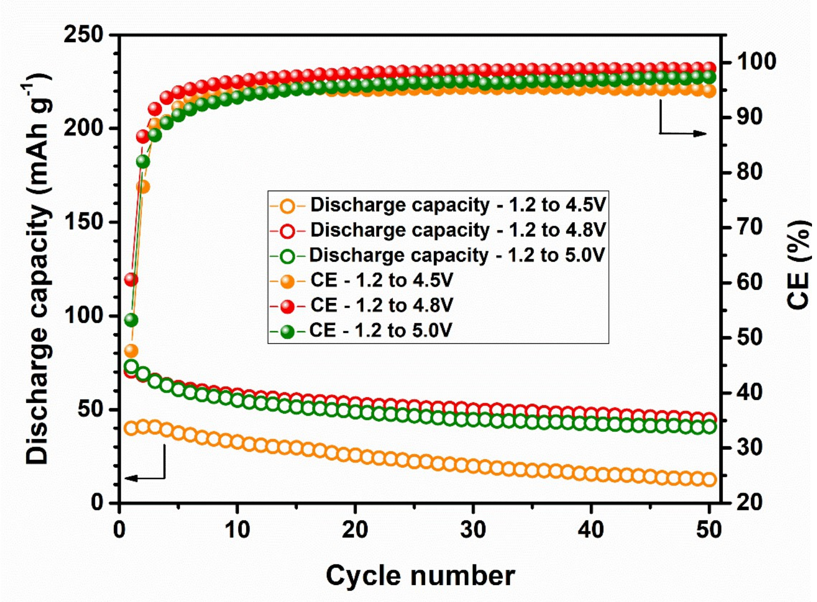
Graphite

Capacity per g of. KVPFO









5 V ➔ High electrolyte degradation
4.8 V ➔ Lower capacity decrease
4.5 V ➔ Poor delivered capacity

4.8 V = Best capacity retention and coulombic efficiency
➔ Selected after