



Understanding the Role of Prop-1-ene-1,3-Sultone and Vinylene Carbonate in $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ /Graphite Pouch Cells: Electrochemical, GC-MS and XPS Analysis

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The role of prop-1-ene-1,3-sultone (PES) used alone or in combination with vinylene carbonate (VC) in $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC)/graphite pouch cells was studied by correlating data from differential capacity (dQ/dV) analysis, gas chromatography/mass spectroscopy (GC-MS), ultrahigh precision coulometry, storage experiments and X-ray photoelectron spectroscopy. VC formed more stable and protective SEI films at both graphite and NMC surfaces due to the formation of a polymer of VC. For PES-containing electrolytes, the preferential reaction of PES led to the formation of SEI films with higher oxygen content at both graphite and NMC surfaces due to the additional oxygen contribution of sulfite species and substantially less LiF compared to control and VC electrolytes. PES also led to thicker SEI films at the NMC surface. When VC was combined with PES, features of the SEI films from both VC and PES were observed. The SEI film features for VC and PES used alone or in combination can explain the improved electrochemical performance as well as the lower production of gas observed with these additives compared to control electrolyte.

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Extending the lifetime of Li-ion cells to several decades is one of the most challenging problems especially for high voltage applications. To meet this target, the use of electrolyte additives is one of the most simple, economical and effective approaches to improve both cycle and calendar life as well as the rate capability of Li-ion batteries.^{1,2} The main role of electrolyte additives is to prevent or hinder unwanted parasitic reactions of electrolyte solvents and/or salts that occur during cycling/storage at the electrolyte/electrode interfaces by modifying the Solid Electrolyte Interphase (SEI) films.³ Although literature reports increasingly study electrolyte additives, their exact impact on the chemistry and morphology of the SEI still remains poorly understood.

Vinylene carbonate or 1,3-Dioxol-2-one (VC, Figure 1) is perhaps the most well-known additive for Li-ion cells⁴⁻⁷ since the time it was proposed by SAFT.⁸ It has been shown to improve both cycle and calendar life as well as thermal stability of different Li-ion systems.⁹⁻¹³ While VC was often reported to have a major impact at the negative electrode, recent works showed that the main beneficial effects could be derived from impact at the positive electrode.^{5,7,10,12} For instance, storage experiments¹⁴ and high precision coulometry¹⁵ showed that VC decreases the rate of electrolyte oxidation at the positive LiCoO_2 electrode. However, the performance and/or gas evolution of cells containing VC degrade at high voltage¹⁶ and high temperatures¹⁷ due to extensive electrolyte degradation. The benefit of using VC as an SEI film forming additive arises from its polymerizable vinyl group. Among the various reaction mechanisms of VC that lead to different polymerization products as well as nonpolymeric species,^{5,18,19} recent XPS analysis combined with theoretical simulations showed that VC more likely polymerizes via a radical mechanism at the surface of both electrodes of a LiCoO_2 /graphite cell.²⁰ Also, it has been shown that no interaction occurred between the negative and positive electrodes during the reaction of VC as no polymeric product of VC was found at the LiFePO_4 surface after the first charge of a LiFePO_4 /graphite cell.²¹

Sulfur-containing electrolyte additives have also shown promising performance.²²⁻²⁶ Prop-1-ene-1,3-sultone or 5H-1,2-Oxathiole, 2,2-dioxide (PES, Figure 1) was first proposed as a SEI film forming additive by Li et al.²⁷ They found that in PC-based electrolyte, PES

can successfully suppress the exfoliation of the graphite which resulted in lower initial capacity loss and better capacity retention of LiCoO_2 /graphite cells even compared to cells with propane sultone (PS), a similar molecule. The beneficial effect of PES was attributed to its preferential reduction and the formation of a more protective SEI film at the graphite surface due to a higher sulfur content in the SEI.²⁸ Later, they showed that for LiMn_2O_4 /graphite cells using ethylene carbonate (EC):ethyl methyl carbonate (EMC) (1:2 by weight) electrolyte, the use of PES increased the capacity retention at elevated temperature (60°C) compared to cells using VC.²⁹ Based on molecular energy level calculations, they assigned the formation of more stable SEI films at the surface of both graphite and LiMn_2O_4 electrodes surface to the preferential reaction of PES. A beneficial impact on the gas production during cycling was also observed with a three times lower volume of gas formed after 150 cycles at 60°C with the addition of PES compared to VC. From XPS analysis, sulfite compounds such as organic RSO_3Li and inorganic Li_2SO_3 were detected as main degradation compounds of PES at the surfaces of both graphite and LiMn_2O_4 electrodes. An additional but unidentified reduced sulfur species was observed at the graphite surface when PES was used in both PC-²⁸ and EC-based electrolyte.²⁹ Li et al.³⁰ also showed that 1 wt% PES in EC:EMC (1:2 by weight) greatly improved the capacity retention of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /Li half cells to about 90% of initial capacity after 400 cycles at 1C rate compared to 49% for control cells. They attributed this result to the preferential oxidation of PES and the formation of a thin SEI film at the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ surface which hinders both the degradation of the active material and the electrolyte oxidation.

Recently, Xia et al.³¹ extended the use of PES as single additive and in combination with VC in EC:EMC (3:7 by weight) for more practical $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC)/graphite pouch cells balanced for 4.2 V. They found that at 40°C and for a concentration of 2%, PES and VC showed similar improvements in the coulombic efficiency, charge endpoint capacity slippage, voltage drop during storage and volume of gas produced during formation, cycling and storage compared to control cells. At 60°C, however, cells containing 2% PES produced virtually no gas during 500 h of storage while cells with 2% VC generated a small amount of gas which corresponds to a significant improvement and a major advantage for pouch cell applications for instance. The combination of 2% VC with PES led to slightly higher coulombic efficiency (CE), lower charge endpoint capacity slippage and smaller voltage drop during storage than the additives alone with, however, a higher impedance. Nelson et al.³² showed that

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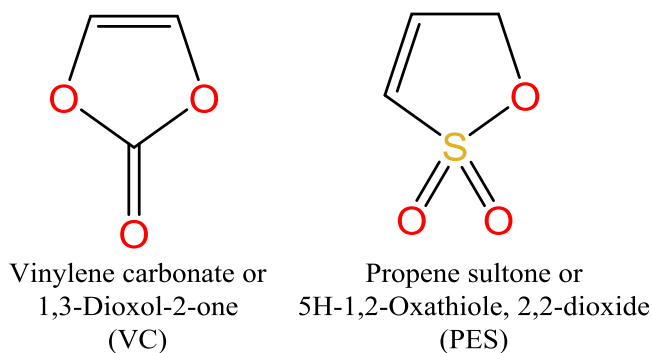


Figure 1. Molecular formula and structural information for VC and PES.

increasing the PES content to 4% or 6% also slightly improved the CE, charge endpoint capacity slippage, voltage drop during storage and gas production at the expense of a large impedance rise.

In this work, the role of 2% PES alone or in combination with 2% VC was investigated by correlating the electrochemical performance of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC)/graphite pouch cells with thorough gas chromatography mass spectroscopy (GC-MS) and X-ray photoelectron spectroscopy (XPS) analysis. The initial reactivity and consumption of the additives was studied using the dQ/dV vs. V plots recorded during the early stages of the formation cycle combined with GC-MS experiments. A careful analysis of the different gas species generated during the formation of the pouch cells was performed by GC-MS to highlight the reactivity of the different electrolytes. Ultra high precision coulometry and storage experiments were used to emphasize the electrochemical differences between the different electrolytes. XPS analysis of the SEI films formed at the surfaces of both graphite and NMC electrodes during formation and after cycling was performed to understand the exact role of the additive on the observed electrochemical performance.

Experimental

The materials and methods used in this study are fully described and identical to those reported by Madec et al.³³ For the analysis of the gaseous compounds by gas chromatography coupled with electron impact mass spectroscopy (GC-MS), the detailed extraction procedure follows the one fully described by Petibon et al.³⁴

For the schematic representations of the SEI films, the SEI thicknesses were estimated using the relative intensity of the active material features, i.e. the lithiated graphite C 1s and the NMC O 1s features at ~ 282.6 eV and 529.5 eV, respectively. The relative intensity was defined as:

$$I_{\text{rel}} = \text{at. \% (sample)} / \text{at. \% (fresh)} \quad [1]$$

where at. % (sample) and at. % (fresh) are the atomic percentages for the active material feature of a given sample and for the fresh electrode, respectively, as determined from XPS quantification. Assuming a simple model where the SEI layer was considered as homogenous in thickness (d) with no porosity and with an average composition, the SEI thickness was then calculated as:

$$I = e^{-d/\lambda} \quad [2]$$

where the inelastic mean free path (IMFP), λ , was calculated by averaging values of the polyacetylene, LiF and polyethylene.^{35,36} This procedure yields $\lambda = 2.7$ nm and 2.1 nm for photoelectron kinetic energies of ~ 1000 eV (C 1s) and ~ 700 eV (O 1s) used in this study.

Results and Discussion

Reactivity of the additives.— In this section, the reactivity of VC and PES alone or in combination during the early stage of the formation cycle was investigated by combining dQ/dV vs. V and GC-MS

analysis. Figure 2a shows the differential capacity (dQ/dV) versus V curves of the NMC/graphite pouch cells between 1.6 and 3.2 V of the formation cycle for the different electrolytes. Figure 2b shows the corresponding cell terminal voltage (V) versus specific charge capacity (Q) of the same cells. Control cells showed a pronounced peak corresponding to a plateau at 2.75 V (graphite at ~ 0.8 V vs. Li/Li^+) which is attributed to the preferential reduction of EC at the graphite surface.^{37,38} When VC and PES were used either alone or in combination, the EC peak at 2.75 V was almost suppressed which means that both VC and PES nearly eliminate the reduction of EC at this voltage.³³ For VC, however, a peak/plateau appeared at ~ 2.65 V (graphite at ~ 0.9 V vs. Li/Li^+) due to the preferential reduction of VC, in agreement with the consumption of about 9% of the initially added VC at 2.4 V and 55% at 3.5 V measured by GC-MS (Figure 2c).^{20,33,39} In the case of PES, a peak/plateau was observed at a lower voltage of 2.4 V (graphite at ~ 1.1 V vs. Li/Li^+) and is assigned to lower reduction potential of PES at the graphite surface compared to VC. Indeed, a three times more PES (27%) was consumed at 2.4 V according to GC-MS (Figure 2d) indicating a higher reactivity than VC below 2.4 V. At 3.5 V, the consumption of PES was similar to that of VC (about 55%). When VC was combined with PES (Figures 2a and 2b), the VC feature at 2.6 V was almost suppressed while the intensity of the PES feature at 2.4 V was also decreased suggesting a different reactivity of the additives when used together. The weaker intensity of the PES feature at 2.4 V corresponded to 2.5 times less consumption of PES at 2.4 V (Figure 2d). Although a decrease in the VC consumption was expected based on the electrochemical data (Figures 2a and 2b), an increase from 9% to 30% was instead found (Figure 2c). At 3.5 V, however, similar consumptions of the additives were measured in the cells where they were combined compared to when the additives were used alone (Figures 2c and 2d).

The use of VC totally suppressed the transesterification of EMC into DEC and DMC that used up about 40% of the EMC in control electrolyte at 3.5 V.^{33,39} For PES, however, 7% of the EMC was involved in transesterification reactions. This conversion reaction has been attributed to the catalytic effect of the lithium alkoxide (ROLi) species that can be formed by carbonate solvent reduction during the formation of a Li-ion cell.^{40–43} It has been proposed that the use VC, for instance, can dramatically decrease the formation of ROLi species due to the passivating role of VC at the graphite surface and/or that VC can trap the free alkoxide anion (RO^-) in the electrolyte through nucleophilic addition reactions. Therefore, PES more likely forms a less passivating SEI film at the graphite surface that does not prevent the formation of ROLi and/or PES does not efficiently trap the ROLi. Note that the dimerization of EC with EMC, DEC and DMC that accounted for 1–3% of the total electrolyte weight with control electrolyte was nearly suppressed ($<0.1\%$) when VC or PES were used either alone or in combination.

Gas analysis.— In this section, the gas volume generated during both formation, cycling and storage as well as the nature of the gaseous species produced during the formation cycle were studied to compare and understand the impact of the different electrolytes on the gas production.

Figures 3a–3c show the volume of gas evolved at 40°C in the NMC/graphite pouch cells for the different electrolytes during formation, UHPC cycling and storage, respectively. Control cells produced about 0.6 mL of gas during the formation process. For VC or PES, less than 0.1 mL of gas was generated which therefore means that both VC and PES act as very efficient gas reducing agents during formation most likely due to the suppression of the EC reduction (Figure 2). When VC was combined with PES, virtually no gas was produced suggesting a cooperative role of the additives when used together. During cycling (Figure 4b), VC cells produced less than half the volume of gas compared to control electrolyte while PES further decreased the production of gas. Considering the initial 2.2 mL volume of the pouch cells, cells cycled or stored with VC and PES alone

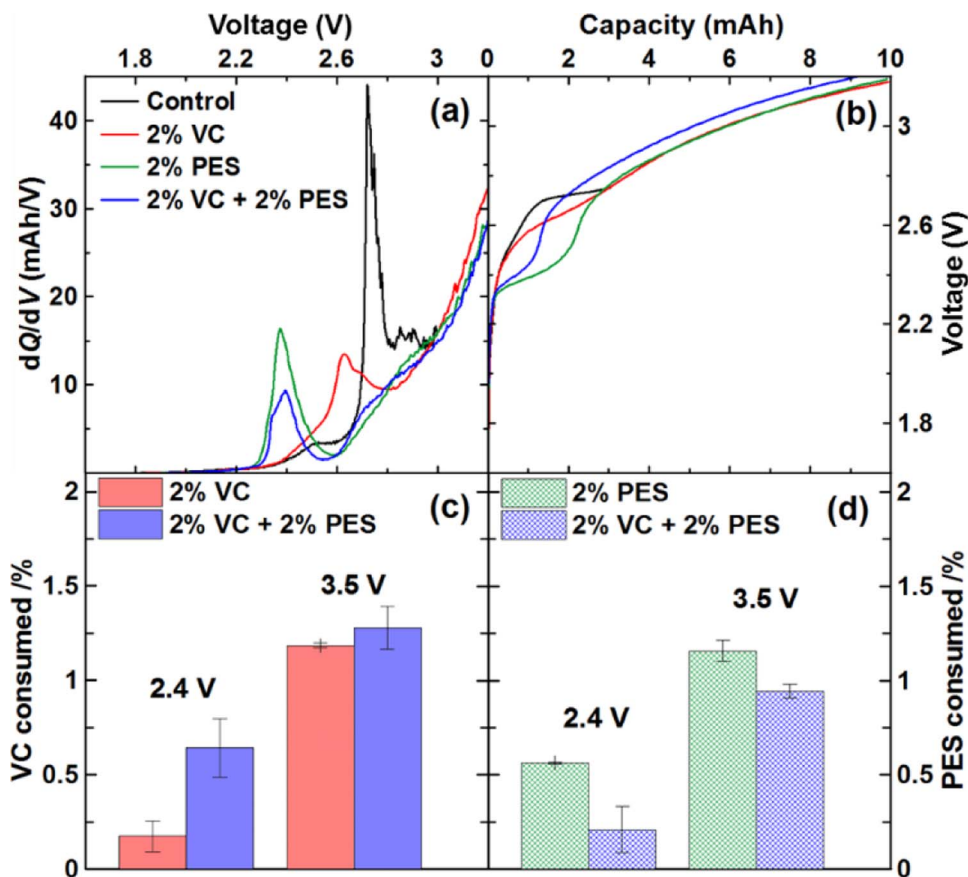


Figure 2. (a) Differential capacity (dQ/dV) versus voltage (V) during the early stages of the formation cycle of the 220 mAh NMC/graphite pouch cells at C/20 and 40°C for the different electrolytes; (b) corresponding cell voltage versus capacity during the first 25 mAh of the formation cycle. Amount of (c) VC and (d) PES consumed in NMC/graphite pouch cells after formation at 2.4 V and 3.5 V.

or in combination (about 0.02 to 0.04 mL of gas) do not have any swelling problem.

Figure 4 shows the GC-MS peak areas for the gaseous species extracted at room temperature from the NMC/graphite pouch cells after formation at 2.4 V and 3.5 V. Details about the reaction pathways followed to create these species can be found in reference.⁴⁴ For the different electrolytes, CO_2 was the more abundant gas at 2.4 V and small amounts of ethene and CO were found. At 3.5 V ethene became the most abundant gas and small amounts of ethane and CH_4 were observed. For control electrolyte at 3.5 V, in addition to the large formation of ethene from the reduction of EC,^{37,45,46} small amounts of methyl formate, ethyl formate, 1-propene, ethanol and ethyl acetate from the reduction of EMC⁴⁴ as well as acetaldehyde and methoxymethane originating from either EC⁵⁴ and EMC⁴⁴ were found. For VC and PES alone, the amount of ethene decreased compared to control electrolyte due to their preferential reduction (Figure 2a). This result indicates that both VC and PES form passivating SEI films at the graphite surface that suppress the reduction of EC (Figure 2a) and significantly lower the volume of gas produced during formation (Figure 3). Compared to control electrolyte, the larger amounts of CO_2 and 1-propene for VC and PES, respectively, are attributed to their specific reactivity.^{18,47} When VC was combined with PES, the formation of CO_2 was further increased due to the higher consumption of VC (Figure 2c) while 1-propene formed from the reduction of PES was found. PES alone also showed additional gaseous compounds, methyl formate, ethyl formate, ethanol and acetaldehyde, some at 2.4 V, probably due to the reaction of EMC.⁴⁴ The formation of these additional gases was suppressed when VC was combined with PES indicating a beneficial effect of VC against parasitic reactions of the solvents at the graphite surface.

Electrochemical performance.— Figure 5 shows a summary of the coulombic inefficiency ($1 - \text{CE}$), charge endpoint capacity slippage rate (in mAh/cycle) during cycling and voltage drop during storage of the NMC/graphite pouch cells for the different electrolytes. Cells with VC and PES alone had greatly improved performance compared to cells with control electrolyte. Cells with both VC and PES had further improved CIE and voltage drop. From these results, it is expected that both VC and PES form relatively stable and efficient SEI films at both the graphite and NMC surfaces that hinder parasitic reactions.

Figure 6a shows the discharge capacity for the short term cycling between 2.8 and 4.2 V at C/20 and 40°C for NMC/graphite pouch cells with different electrolytes. Although the discharge capacity over the short term cycling was well maintained for all cells (Figure 6a), some trends were observed. Cells with control electrolyte clearly showed higher capacity fade than cells with 2% VC, 2% PES or 2% VC + 2% PES as expected from on Figure 5. Figure 6b shows the discharge capacity for long term cycling between 2.8 and 4.2 V at C/2.5 and 55°C. Cells with 2% VC or 2% PES showed similar cycle life and much longer cycle life than cells with control electrolyte.

XPS analysis.— The role of PES used either alone or in addition with VC on the electrode/electrolyte interfaces was investigated by XPS in order to understand how those interfaces are correlated to the electrochemical performance. For control and VC electrolytes, the results described hereafter follow our previous study on NMC/graphite pouch cells.³³ For the different electrolytes, the SEI films were analyzed both during formation at 2.4 V, 3.8 V, 4.2 V during charge and 2.8 V during discharge as well as after 25 cycles at both 4.2 V during charge and 2.8 V during discharge (referred to as C4.2 V and D2.8 V, respectively).

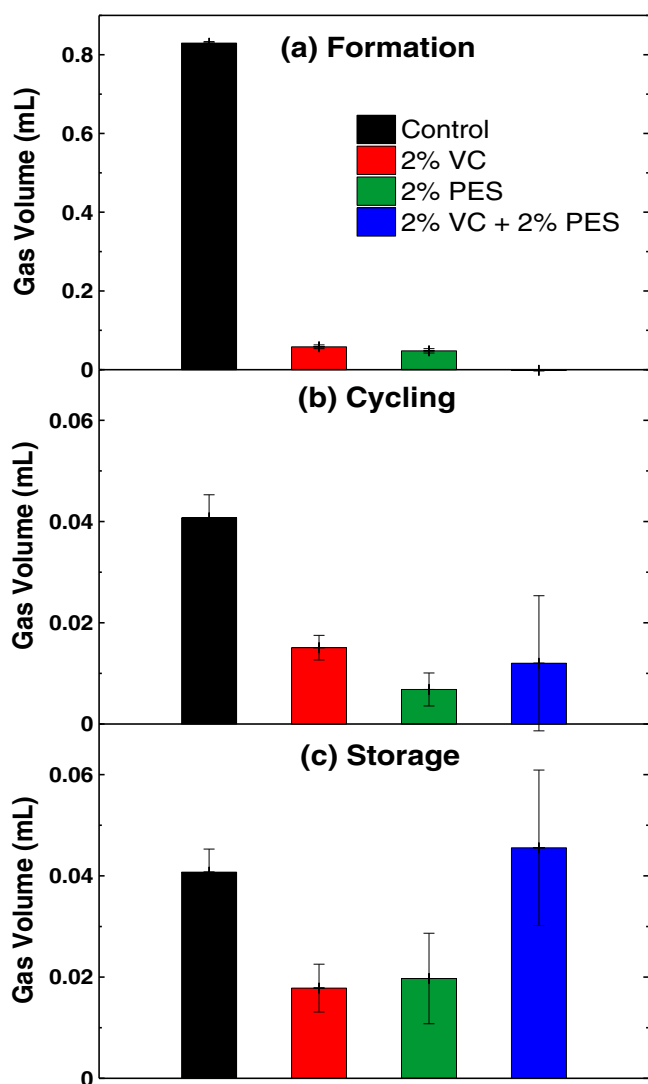


Figure 3. Volume of gas evolved for NMC/graphite pouch cells (220 mAh) containing different additives (a) during the formation cycle, (b) during UHPC cycling at 11 mA (C/20) and $40 \pm 0.1^\circ\text{C}$ between 2.8 and 4.2 V and (c) during 500 h of storage at 4.2 V and $40 \pm 0.1^\circ\text{C}$.

Graphite negative electrodes.—Figure 7 shows the C 1s and O 1s core spectra of the graphite electrodes from cells with 2% PES and 2% VC + 2% PES electrolytes compared to control and 2% VC electrolytes during formation and after 24 cycles. The C 1s core spectrum of the fresh electrode showed five C 1s core components at 284.1, 285, 286.9, 288.6 and 290.8 eV attributed to the C=C bonds from the graphite, C-C/C-H from the SBR binder, C=O and COOR carbons as well as the “shake up” satellite from the graphite, respectively.^{48,49} In the O 1s spectra, the fresh electrode showed two peaks at 531.6 and 533.4 eV that correspond to the oxygen environment of the CMC binder.²⁰

After the early stages of formation (i.e. 2.4 V), control and 2% VC electrolytes showed very similar C 1s spectra compared to the fresh electrode as expected from the absence of peaks below 2.4 V in the dQ/dV vs. V curves (Figure 2a). The formation of the SEI at the graphite surface is therefore not initiated at this voltage. On the other hand, for PES containing electrolyte, a decrease of the graphite peak at 284.1 eV as well as an increase of other components, for instance at 285 eV, was observed which indicates the beginning of the SEI film formation. This phenomenon was more important when PES was combined with VC. These results are consistent with the dQ/dV and GC-MS analysis (Figure 2) that showed electrochemical

activities below 2.4 V corresponding to the consumption of the additives. Similarly, the O 1s core spectra at 2.4 V showed no apparent change for control and 2% VC electrolytes compared to the fresh electrolyte while for PES-containing electrolytes, two new main components were observed at 532 and 533.7 eV due to the reactivity of PES as discussed later. When VC was added to PES, the evolution of the O 1s core spectrum was more pronounced and a third O 1s peak was observed at a very high binding energy of 534.5 eV. This peak is attributed to the formation of an oligomer of VC (Oligo-VC) at the graphite surface.^{18,20,33} Considering the relatively low intensity of this O 1s peak from Oligo-VC, the expected C 1s counterparts were not observed. Also, no Oligo-VC component was observed for VC alone which is consistent with its smaller consumption at 2.4 V compared to 2% VC + 2% PES electrolyte (Figure 2c).

After formation at 3.8 V then 4.2 V, a significant decrease of the intensity of the graphite peak at ~ 282.7 eV was observed for every electrolyte blend, indicating the continuous formation of a SEI film at the graphite surface. The graphite peak shifted from 284.1 eV to ~ 282.7 eV during charge compared to the fresh electrode due to the continuous lithiation of the graphite and it remained shifted at ~ 282.7 eV after discharge due to some remaining intercalated lithium. At 4.2 V, based on the graphite peak relative intensity, the SEI thickness followed control > 2% VC + 2% PES > 2% PES > 2% VC. After discharge to 2.8 V, the electrode tested with control electrolyte showed a decrease in SEI thickness as the graphite peak was partially recovered possibly due to the dissolution/consumption of the SEI species. When 2% PES was used, less change in the graphite peak was observed while the electrode tested with VC-containing electrolyte showed no apparent change after discharge which suggests that during formation, PES forms more stable SEI films than control electrolyte and VC creates an even more stable SEI (from a thickness perspective anyway). After cycling, the graphite peak was not visible for control electrolyte which indicates a thick SEI due to the continuous degradation of the solvents while for VC- and PES-containing electrolytes, thinner SEI films were found based on the graphite peak relative intensity.

In the 286–292 eV range, the C 1s core spectra showed the appearance at 286.9, 289.2 and 290.3 eV of CO-, CO₂- and CO₃-like carbon environments in agreement with the formation of carbonaceous species from the solvents at the graphite surface. The intensity of the peaks at 286.9 and 289.2 eV increased significantly between 3.8 and 4.2 V during formation and further increased after cycling due to the continuous formation/deposition of SEI species at the graphite surface. More importantly, for VC-containing electrolytes, two new C 1s components appeared at 287.9 and 291.3 eV with a 2:1 ratio due to the formation of an oligomer of VC (Oligo-VC) at the graphite surface.^{20,33}

In the O 1s core spectra, after formation at 3.8 V, the two O 1s components of the fresh electrode were replaced by two new main components at 532 and 533.8 eV which can be explained by the simultaneous covering of the CMC binder and the graphite by the SEI.²⁰ For VC-containing electrolytes, the second peak was slightly shifted to 533.5 eV more likely due to a specific reactivity of VC at the graphite surface.²⁰ The peak at 532 eV is attributed to CO₂-like oxygen from carbonate compounds such as lithium ethylene dicarbonate (CH₂OCO₂Li)₂ (LEDC)^{50,51} formed by reduction of EC and/or other lithium alkyl carbonates (ROCO₂Li) including lithium carbonate formed for instance by the reduction of EC and/or EMC. The second peak at 533.5–533.8 eV is assigned to -C-O- bonds from ROCO₂Li and/or other derivatives.^{52,53} At 3.8 V, PES-containing electrolytes showed a significantly higher relative intensity of the 532 eV component compared to the second peak at 533.5–533.8 eV. This result is attributed to the additional O contribution of sulfite species (RSO₃) formed from PES as discussed later when the S spectra are considered, in agreement with the appearance of this feature as soon as 2.4 V. This result is also supported by the higher total oxygen content at the graphite surface for PES-containing electrolytes whatever the state of charge. For instance, at 3.8 V, the total oxygen content was about 28 at% of the SEI for both PES-containing electrolytes while it was only 18 at. % for control and VC electrolytes. This feature is therefore attributed to the reactivity of PES at the graphite surface during

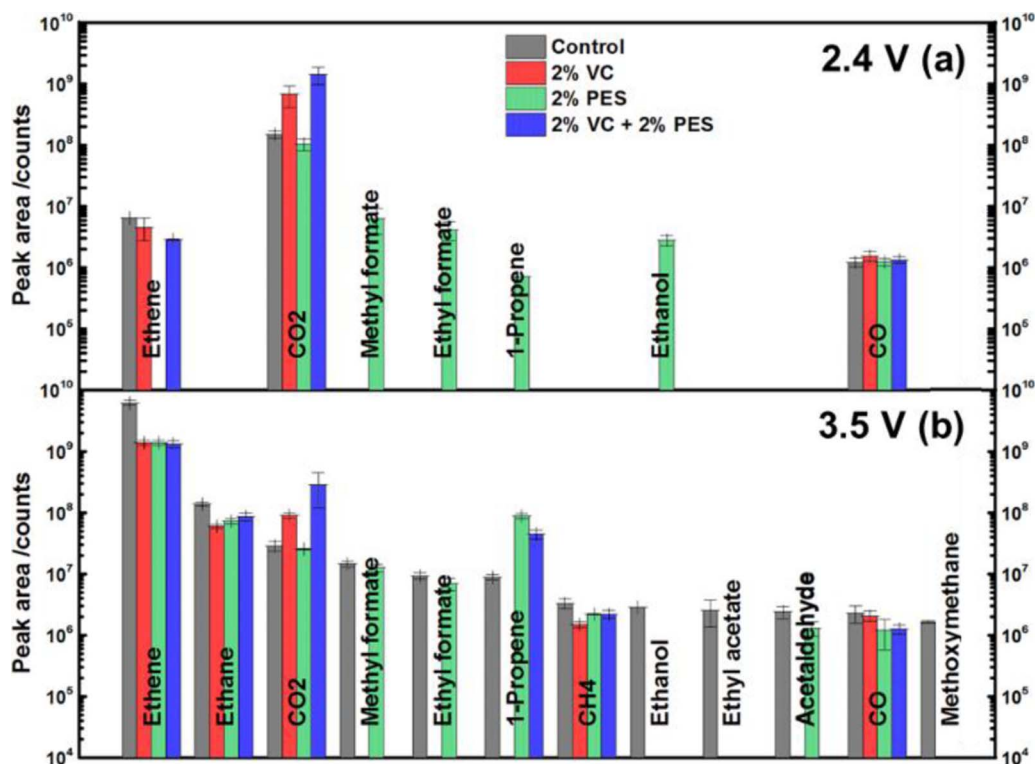


Figure 4. GC-MS data for gases extracted from NMC/graphite pouch cells for the different electrolytes after formation at (a) 2.4 V and (b) 3.5 V. The data presented here shows the peak area for compounds that are gaseous at room temperature.

formation. Moreover, for graphite electrodes from cells with VC-containing electrolytes, an additional O 1s component was observed at 534.5 eV due to the formation of Oligo-VC at the graphite surface.^{18,20,33} Also, graphite electrodes from cells with VC-containing electrolytes showed a higher carbon content at the graphite surface whatever the state of charge. For instance, at 3.8 V, the total carbon content was about 38 at. % of the SEI for both VC-containing electrolytes compared to about 33 at. % for control and PES electrolytes. The O 1s peak at 534.5 eV as well as the higher carbon content found for VC-containing electrolytes are therefore due to the reactivity of VC at the graphite surface during formation. When VC was combined with PES, features arising from the additives alone were observed which indicates a combined effect of VC and PES when added together. For control electrolyte, two additional peaks were observed at 530.7 and 528.6 eV due to the formation of lithium alkoxide (ROLi) (from EMC for instance) and lithium oxide (Li₂O), respectively.^{54,55} The formation of Li₂O from water through $\text{H}_2\text{O} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}_2\text{O} (\text{s}) + \text{H}_2 (\text{g})$ is unlikely here.³³ Instead, Li₂O is more likely formed from further reduction of carbonate degradation compounds^{53,56} as Li₂O was formed during charge both during formation and after cycling. Moreover, as the SEI thickness increased during charge, it suggests that Li₂O is located at the outermost surface of the SEI and that compounds formed at the NMC electrode during charge may migrate to the graphite surface where they react to form Li₂O. When 2% VC was used, the amount of Li₂O was almost suppressed while for PES-containing electrolytes, the formation of Li₂O was totally eliminated.

Positive LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ electrodes.—Figure 8 shows the O 1s XPS core spectra of the NMC electrodes from cells with 2% PES or 2% VC + 2% PES electrolytes compared to those from cells with control and 2% VC electrolytes during formation and after 24 cycles. The fresh electrode showed two components, the first one at 529.5 eV being attributed to O²⁻ anions from the lattice oxygen of the NMC active material while the second peak at 531.5 eV is assigned to oxygen anions with deficient coordination at the NMC

surface (“surface oxygens”)²⁰ and/or CO_x-like oxygen from the carbon black.^{48,49}

After formation at 2.4 V, similarly to the graphite electrode, control and 2% VC electrolyte showed no significant difference compared to the fresh electrode which indicates that almost no SEI is formed at the NMC surface at 2.4 V. Similarly to the graphite electrodes, PES-containing electrolytes showed, however, a decrease of the NMC peak at 529.5 eV as well as an increase of two peaks at 531.7 and 533.5–533.1 eV which indicates the beginning of the SEI film formation at the NMC surface as soon as cells reached 2.4 V (NMC at ~3.5 V vs. Li/Li⁺). This phenomenon was more important when PES was used alone probably due to its higher consumption observed by GC-MS (Figure 2d). Also, when VC was combined with PES, a third O 1s peak was observed at a very high binding energy of 534.2 eV attributed to the formation of Oligo-VC at the NMC surface.^{18,20,33} Similarly to the graphite electrode, no Oligo-VC component was observed for VC alone due to its small consumption at 2.4 V compared to 2% VC + 2% PES electrolyte (Figure 2c).

After further formation to 4.2 V, the intensity of the O 1s peak from the NMC at 529.5 eV significantly decreased indicating the continuous formation of a SEI film at the NMC surface. Based on the NMC peak intensity, the SEI thickness at 4.2 V followed 2% PES > VC-containing electrolyte > control. After 25 cycles to 4.2 V, 2% PES still showed the thickest SEI while 2% VC became the thinnest SEI. These results suggest that compared to control electrolyte, PES produces a relatively thick SEI at the NMC surface during formation that continues to slightly increase during cycling probably due to its further consumption. For VC electrolyte, a more stable and/or more protective SEI film is formed at the NMC surface compared to control electrolyte. When VC was combined to PES, an intermediate SEI thickness was observed compared to the additives used alone which indicates a combination of VC and PES when added together.

After formation at 3.8 V, whatever the electrolyte blend, the second O 1s component of the fresh electrode at 531.5 eV was replaced by two peaks at 531.7 and 533.5 eV in agreement with the

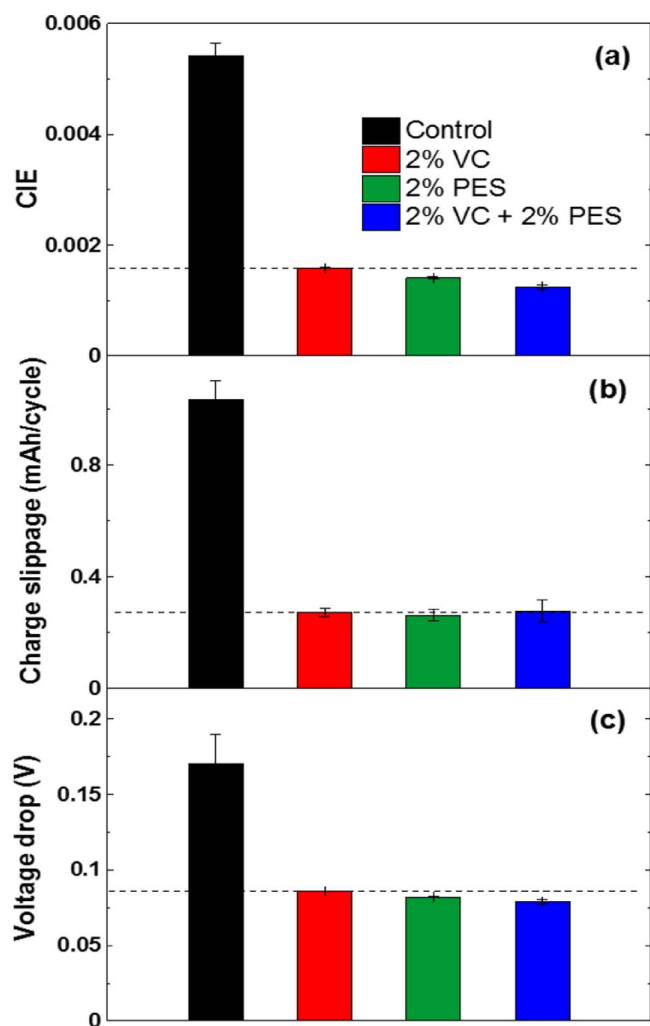


Figure 5. Summary of the high precision cycling and storage data for the NMC/graphite pouch cells studied here: (a) coulombic inefficiency (CIE) and (b) charge endpoint capacity slippage during cycling between 2.8 and 4.2 V at C/20 and 40. $\pm 0.1^\circ\text{C}$ and (c) voltage drop during OCV storage for 500 h at 4.2 V and 40. $\pm 0.1^\circ\text{C}$.

formation of carbonaceous species from the solvents at the NMC surface. Similarly to the graphite electrodes, for VC-containing electrolytes, the second peak was shifted to 533.1 eV due to the specific reactivity of VC at the NMC surface. The peak at 531.7 is attributed

to CO_2 -like oxygen from carbonate compounds (ROCO_2Li) in addition to any remaining contribution of the “surface oxygens” from the NMC material²⁰ and/or the CO_x -like oxygen from the carbon black.^{48,49} The peak at 533.5–533.1 eV is assigned to $-\text{C}-\text{O}-$ bonds from ether derivatives^{52,53} and/or ROCO_2Li . Similarly to the graphite electrode, PES-containing electrolytes showed a significantly higher relative intensity of the 531.7 eV component compared to the second peak at 533.1–533.5 eV especially at 3.8 V. This is again attributed to the additional O contribution of sulfite species (RSO_3) formed from PES at the NMC surface and in agreement with the appearance of this feature as soon as 2.4 V. NMC electrodes from cells with PES-containing electrolyte also showed a higher oxygen content of about 3 at. % at the NMC surface whatever the state of charge compared to control and VC electrolytes. Moreover, VC containing electrolytes showed an additional peak at 534.2 eV due to the formation of Oligo-VC at the NMC surface.^{18,20,33} This is supported by the appearance of two C 1s components from Oligo-VC at 287.9 and 290.9 eV with a 2:1 ratio on the difference spectrum between VC containing electrolytes and the corresponding control electrolytes (not shown), in agreement with our previous study.³³ When VC was combined with PES, intermediate features of the additives alone were observed at the NMC surface which indicates a combine effect of VC and PES when added together.

Further studies on F-, P-, and S-containing species.—Figure 9 shows the typical S 2p core spectra for graphite and NMC electrodes from cells with PES-containing electrolytes as well as the evolution of the S content for the different sulfur species as determined from XPS quantification. As soon as 2.4 V, graphite electrodes showed two S 2p components at 168.7 and 167.0 eV while one peak at 168.1 eV was observed for NMC electrodes. The peak at high binding energy is assigned to organic sulfite species (RSO_3) such as RSO_3Li and/or ROSO_2Li ⁵⁷ for both graphite and NMC electrodes considering the relatively small binding energy difference. For graphite electrodes, the second peak at 167 eV can be attributed to inorganic Li_2SO_3 .⁵⁷

At 2.4 V, PES-containing cells showed a similar content of S species at the graphite surface. At the NMC surface, however, 2% PES electrolyte showed twice the S content found for 2% VC + 2% PES electrolyte. This result indicates a lower consumption of PES when VC was combined to PES in agreement with the GC-MS results (Figure 2d). During further formation and after cycling, the amount of S remained always lower for PES used in combination with VC probably due to the contribution of VC in the SEI films. For instance, at the NMC surface during formation, the S content in the SEI film continuously increased for PES alone while it remained stable for 2% VC + 2% PES electrolyte. After cycling, however, PES alone showed only a slight increase of the S content while when PES was combined with VC, the S content was almost double. This result indicates that VC slows the reaction of PES at the NMC

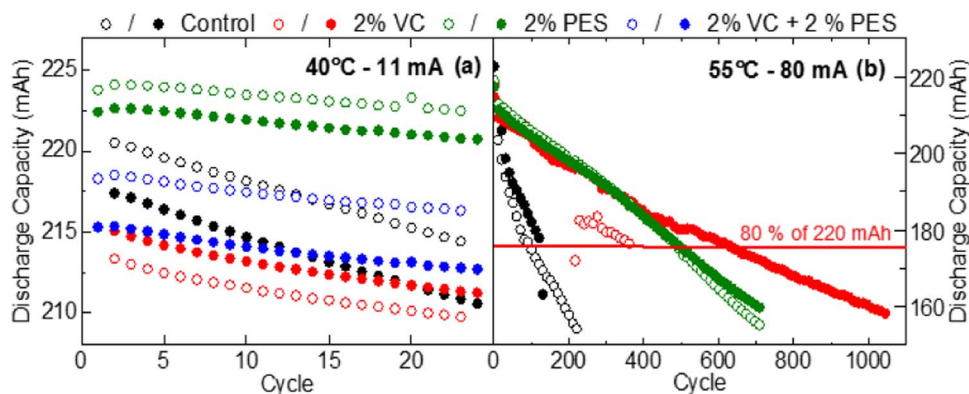


Figure 6. Discharge capacity versus cycle number for NMC/graphite pouch cells (220 mAh) with different electrolyte additives as indicated when cycled between 2.8 and 4.2 V at (a) 40.0 $\pm 0.1^\circ\text{C}$ with a current of 11 mA (C/20) and (b) 55 $\pm 0.1^\circ\text{C}$ with a current of 80 mA (C/2.5). Discharge capacity is shown for a pair of nominally identical cells in each panel (open and closed symbols of the same color).

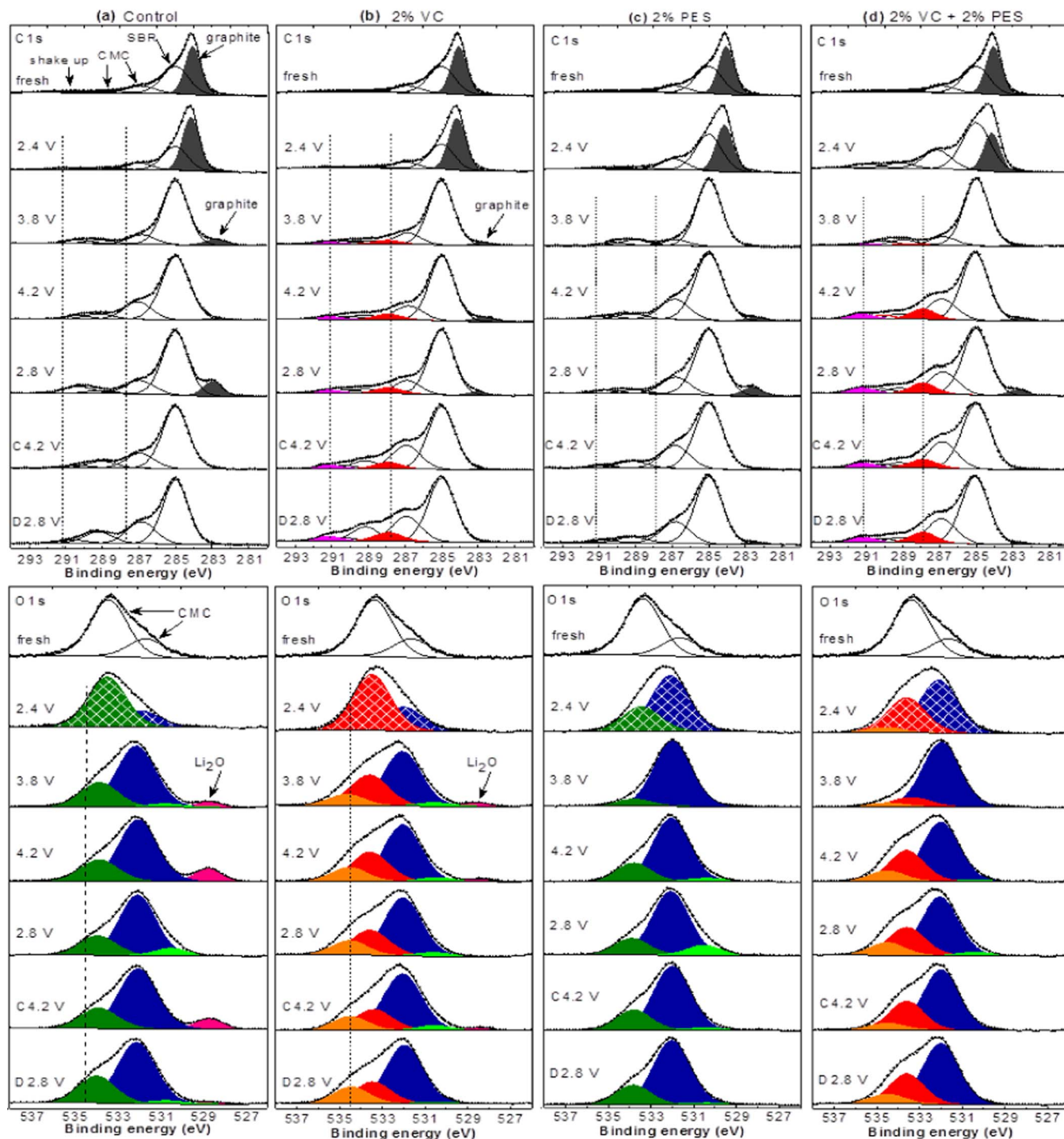


Figure 7. C 1s and O 1s XPS core spectra for graphite electrodes with (a) control, (b) 2% VC, (c) 2% ES, and (d) 2% VC + 2% ES electrolytes taken from cells during formation at 2.4 V, 3.8 V and 4.2 V during charge as well as after cycling at 4.2 V during charge (C4.2 V) and at 2.8 V during discharge (D2.8 V) at C/20 and 40. $\pm 0.1^\circ\text{C}$. On the C 1s core spectrum of the fresh electrode, the five components at 284.1, 285, 286.9, 288.6 and 290.8 eV are attributed to the C=C bonds from the graphite, the C-C/C-H from the SBR binder, the C=O and COOR carbons as well as the “shake up” satellite from the graphite. On the O 1s core spectrum of the fresh electrode, the two peaks at 531.6 and 533.4 eV are assigned to the two oxygen atoms of the CMC binder.

electrodes which continues to occur during cycling, while for PES alone, PES reacts rapidly and almost fully during formation. For graphite electrodes, the two S 2p components followed a similar evolution during formation although the S content was lowered for 2% VC + 2% PES electrolyte. Again, once formed at 4.2 V, the S content for PES alone at the graphite surface remained almost stable after cycling.

Table I shows the atomic percentage (at. %) of the F 1s peak attributed to LiF at the surface of both graphite and NMC electrodes. The exact F 1s and P 2p core components assignment can be found in our previous study.³³ Generally, the LiF content increased during the first charge then decreased during discharge while the SEI thickness decreased indicating a formation of LiF throughout the entire SEI thickness. As this phenomenon was still observed after cycling for

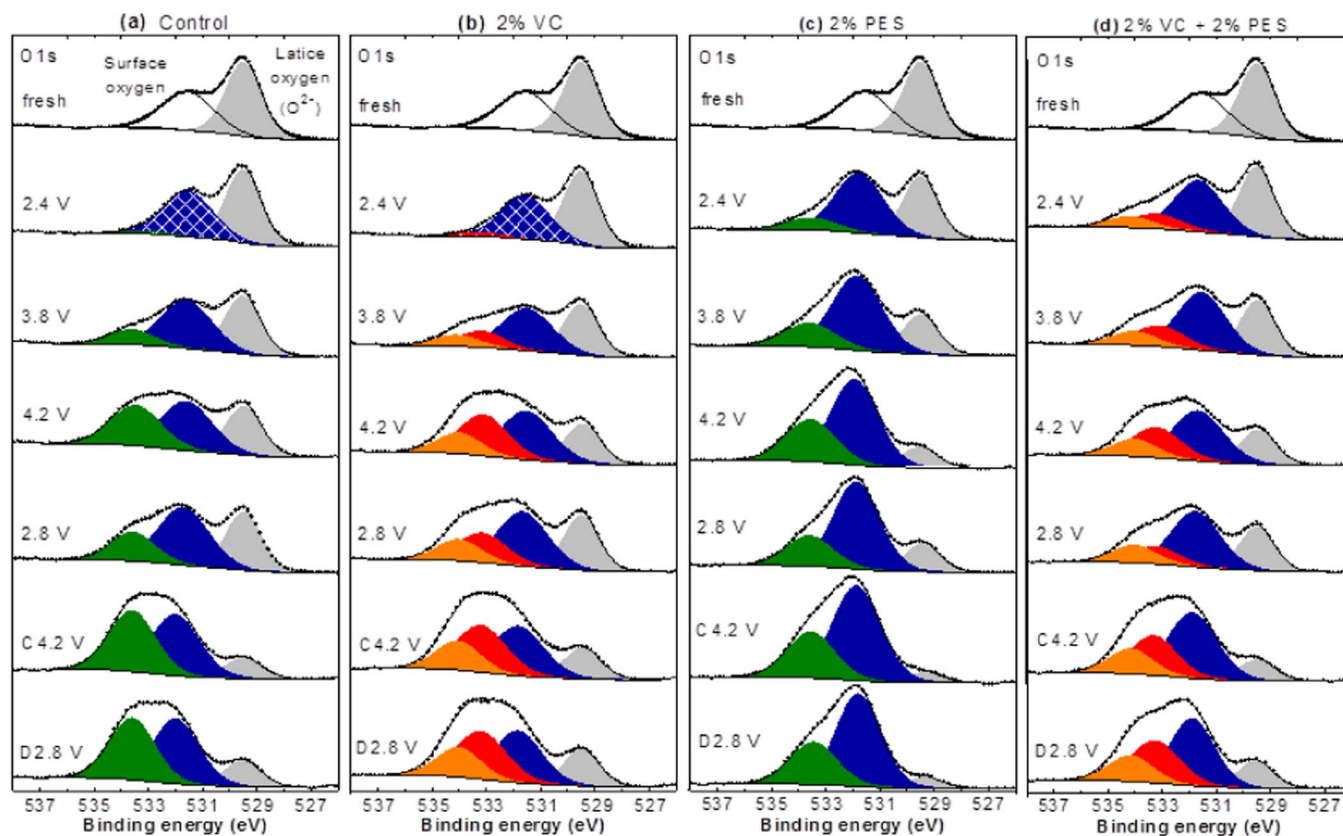


Figure 8. O 1s XPS core spectra for NMC electrodes with (a) control, (b) 2% VC, (c) 2% PES, and (d) 2% VC + 2% PES electrolytes taken from cells during formation at 2.4 V, 3.8 V and 4.2 V during charge and 2.8 V during discharge as well as after cycling at 4.2 V during charge (C4.2 V) and at 2.8 V during discharge (D2.8 V) at C/20 and $40. \pm 0.1^\circ\text{C}$.

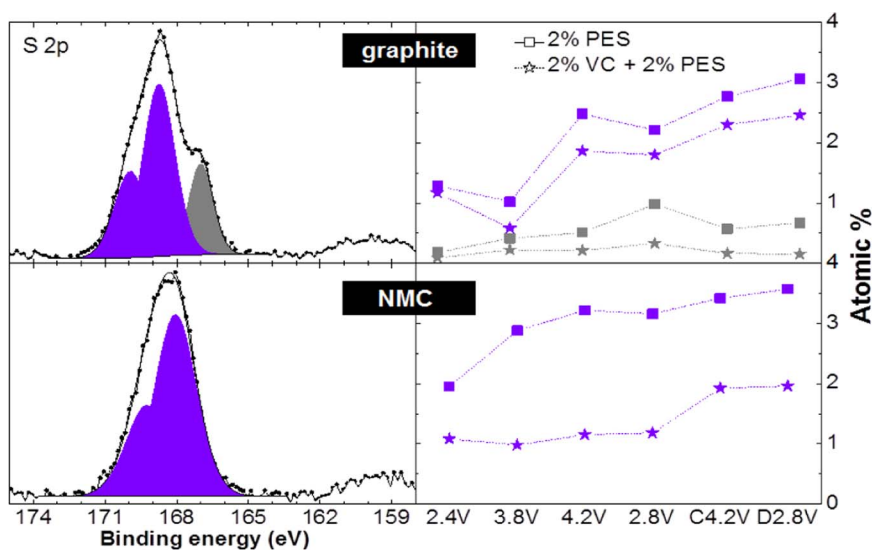


Figure 9. Typical S 2p XPS core spectra for graphite and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ from cells with PES containing electrolytes as well as the evolution of the S content of the different sulfur species as determined from XPS quantification.

Table I. Atomic percentage (at. %) of the F 1s peak associated with LiF as measured from the XPS quantification at the surface of graphite and NMC electrodes as function of the voltage of the cell during formation and after cycling.

Sample	Graphite						$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$					
	2.4V	3.8V	4.2V	2.8V	C4.2V	D2.8V	2.4V	3.8V	4.2V	2.8V	C4.2V	D2.8V
Control	1.1	15.4	16.3	12.3	11.6	9.2	1.4	1.3	2.5	2.0	2.6	2.8
2% VC	2.5	5.4	6.0	5.4	12.8	12.3	2.1	2.2	4.8	1.9	2.4	3.5
2% PES	2.0	4.7	2.1	2.8	1.9	0.9	2.8	1.5	3.5	2.2	3.2	3.6
2% VC + 2% PES	2.2	5.3	0.7	0.5	2.8	0.4	2.3	1.4	4.6	3.1	3.6	3.4

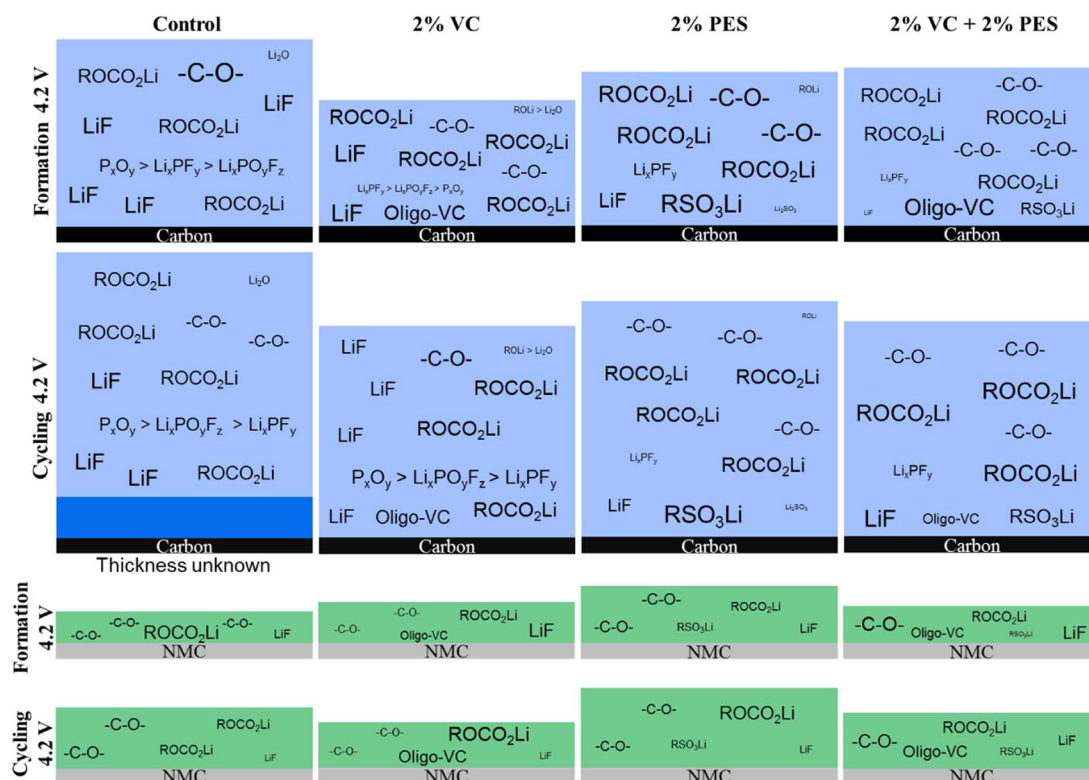


Figure 10. Schematic representations of the SEI films on the lithiated graphite and delithiated NMC electrodes taken from NMC/graphite pouch cells during formation and after cycling at 4.2 V for the different electrolytes, as deduced from the XPS experiments. The heights of the SEI films in Figure 10 are proportional to their estimated heights, except for one case where the thickness is so great the underlying graphite feature at about 282.5 eV cannot be observed. For NMC electrodes, small amounts of Li_xPF_y , $\text{Li}_x\text{PO}_y\text{F}_z$ and P_xO_y (less than 5 at. % in total) were also found in the SEI films (see Table S2) but are not represented in the schematic diagrams for better clarity.

graphite electrodes, LiF is more likely formed via an electrochemical reduction of PF_6^- anion during charge rather than via an impurity from hydrolysis. For NMC electrodes after cycling, the LiF content slightly increased during discharge while the SEI thickness slightly decreased indicating that LiF is more likely formed close to the NMC surface during formation and that no further formation/consumption of LiF occurs during cycling. Also, except for PES containing electrolytes, the LiF content was 2–5 times higher at the graphite surface in agreement with the higher amount of phosphates (P_xO_y) and fluorophosphates ($\text{Li}_x\text{PO}_y\text{F}_z$) compounds at the graphite surface (not shown). For VC alone, a lower LiF content was observed during formation at the graphite surface compared to control electrolyte while similar amount was found after cycling. However, slightly higher LiF amount were observed at the NMC surface indicating that VC has no beneficial impact on the degradation of LiPF_6 . For PES containing electrolytes, significantly lower amounts of LiF (about 5–10 times lower, Table I) as well as phosphates and fluorophosphates (not shown) were observed at the graphite surface compared to control and VC electrolyte while at the NMC surface, however, slightly higher amounts were observed. PES therefore almost suppresses the LiPF_6 degradation at the graphite surface which partially explains the much more oxygen content previously observed. The SEI films formed at the graphite surface by PES containing electrolytes are then more organic compared to control and VC electrolytes.

Summary of the XPS data.—A summary of the SEI composition (at. % for all elements) during formation at 4.2 V for both graphite and NMC electrodes is shown in the supporting information (Table S1 and S2) so that readers can have more details about the XPS quantification. Figure 10 shows the schematic representations of the SEI films highlighting the differences between the graphite and NMC SEI films as observed from the XPS data. Figure 10 focuses on the results obtained during formation and after cycling at 4.2 V during charge. The

heights of the SEI films in Figure 10 are proportional to their estimated heights, except for one case where the thickness is so great the underlying graphite feature at about 282.5 eV cannot be observed. For instance, SEI thicknesses were estimated to be about 12 nanometers at the graphite surface and 2 nanometers at the NMC surface for control electrolyte during formation at 4.2 V (see Experimental section for details), in good agreement with a similar study by Malmgren et al.⁵³ In each panel of Figure 10, the distribution of the species is based on the evolution of their content between the different states of charge while the number of times a species appears and the font size are proportional to the relative amount of the associated core level peak in atomic percentage (at. %) as measured from the XPS quantification. For instance, at the graphite surface during formation at 4.2 V, electrodes with control electrolyte showed about 44 at. % of fluorine from LiF, 30 at. % of oxygen from $-\text{CO}_2$ (ROCO_2Li), 12 at. % of oxygen from $-\text{C}-\text{O}-$, 5 at. % of oxygen from Li_2O and 9 at. % of phosphorus from P_xO_y , $\text{Li}_x\text{PO}_y\text{F}_z$ and Li_xPF_y . The sum of the different species in one panel is equal to 100% which allows a direct comparison between samples.

At the graphite surface, at 4.2 V during formation, electrodes with control electrolyte showed a large fraction of inorganic compounds, mostly LiF and some Li_2O as well as organic species like alkyl carbonates (ROCO_2Li) formed by the degradation of both LiPF_6 salt and the solvent (EC and EMC). After cycling, electrodes tested in control electrolyte showed a more organic concentration in the outermost SEI and the presence of Li_2O due to an unstable SEI film that led to the continuous degradation of the solvents and a thick SEI film. When VC and PES were used alone or in combination, thinner SEI films were observed during both formation and after cycling compared to control electrolyte. Also, more organic SEI films were initially formed at the graphite surface compared to control electrolyte due to the formation of a polymer of VC (Oligo-VC) and sulfite species (RSOLi

and Li_2SO_3) from VC and PES, respectively. VC and PES therefore stabilize the reactivity of LiPF_6 during formation. After cycling, however, VC alone showed an increase of the LiF content while no change was observed for PES-containing electrolytes. Small amounts of Li_2O were also found with VC while the Li_2O was totally suppressed for PES-containing electrolytes.

At the NMC surface, thinner and more organic SEI films were observed for all electrolytes compared to those found at the graphite surfaces. NMC electrodes tested with control electrolyte showed larger relative amounts of ether derivatives -C-O- and alkyl carbonates (ROCO_2Li) during both formation and after cycling. Cells using control electrolyte also showed a larger SEI thickness increase at the NMC surface during cycling due to an unstable SEI film. For VC and PES used alone or in combination, thicker SEI films were found during formation while smaller SEI thickness increases were observed during cycling compared to control electrolyte. Also, fewer organic species, especially ether derivatives -C-O- were found for VC- and PES-containing electrolytes due to the formation of a polymer of VC (Oligo-VC) and sulfite species (RSOLi) from VC and PES, respectively. These results that will be now presented in detail therefore highlight the passivating role of VC and PES when used alone as well as a combined effect when used together.

Conclusions

The role of propene sultone used alone or in combination with VC in NMC/graphite pouch cells was thoroughly investigated. Liquid GC/MS was used to precisely interpret the dQ/dV vs. V plots recorded during the early stages of the formation cycle. GC-MS analysis of the gaseous products formed during formation showed that VC produced CO_2 due to its reduction while it significantly decreased the formation of ethene by suppressing the reduction of EC at the graphite surface. For PES alone, the production of ethene from the EC reduction was also almost eliminated while the formation of 1-propene was increased due to the reduction of PES. When VC was added to PES, both these phenomena were observed due to the combined impact of the two additives. Similarly to control electrolyte, PES alone produced additional gases probably due to the reactivity of EMC that were suppressed by the combination of VC.

Ultrahigh precision coulometry and storage experiments were then correlated to thorough XPS analysis of the SEI films formed at both graphite and NMC electrodes during formation and after cycling. VC was shown to form a polymer (Oligo-VC) at both graphite and NMC surfaces that resulted in stable and passivating SEI films compared to control electrolyte. VC containing electrolytes also showed a higher carbon content at the graphite surface due to the specific reactivity of VC. For PES containing electrolytes, a significantly higher oxygen content was observed at both the graphite and NMC surface due to the additional oxygen contribution of sulfite species (RSO_3) formed from PES and due to the lower formation of LiF compared to control and VC electrolytes. These SEI film features were attributed to the preferential reaction of PES at both electrode surfaces. When VC was combined to PES, both features of the additives alone were observed in the SEI films. For instance, intermediate contribution of the additives alone on the SEI film was observed at the NMC surface. The different SEI films features for VC and PES used alone or in combination can explained the better electrochemical performance as well as the lower production of gas during cycling.

Acknowledgments

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