The effects of a ternary electrolyte additive system on Li[Ni_{0.42}Mn_{0.42}Co_{0.16}]O_{2} (NMC442)/graphite pouch cells balanced for a factor of 3 after 150 cycles at 60 °C compared to cells using VC.24

Methylene methane disulfonate (MMDS, Figure 1) has also been recently proposed as an efficient sulfur-containing additive for high voltage Li-ion cells. Zuo et al.28 showed that MMDS dramatically improved the capacity retention of LiCoO_{2}/graphite cells with 1 M LiPF_{6} in EC:EMC (1:2 by weight) at 4.5 V. Zuo et al.29 also showed a significant improvement of the capacity retention of LiNi_{0.5}Co_{0.2}Mn_{0.3}O_{2}/graphite cells using MMDS in 1 M LiPF_{6} in EC:EMC (1:2 by weight) but only when cycled at 4.4 V, while they observed little difference at 4.2 V compared to cells without MMDS. In both studies, they ascribed the enhanced cycling performance of the cells to the modification of the positive electrode SEI films by MMDS which hindered solvent decomposition and led to lower impedance compared to control cells. Later, MMDS was shown to improve the capacity retention of LiMn_{2}O_{4} electrodes cycled at elevated temperature in 1 M LiPF_{6} in EC:EMC:dimethyl carbonate (DMC) (1:1:1 by weight) due to reduction of both the decomposition of the electrolyte and the dissolution of Mn ions in the electrolyte. Xia et al.30 also studied the use of MMDS in NMC/graphite pouch cells with 1 M LiPF_{6} in EC:EMC (3:7 by weight) at 4.2 V. They showed that MMDS reduced the rate of parasitic reactions (i.e. MMDS increased the coulombic efficiency and lowered the charge end point capacity slippage), decreased the impedance measured after storage and after cycling and reduced the amount of gas produced during formation compared to cells without MMDS.

Silyl substituted electrolyte additives such as tris-(trimethylsilyl)-phosphosphate (TTSPi, Figure 1) were recently developed by Wildcat Discovery Technologies (California, USA) to improve the cycling performance of various positive electrode materials at high voltage and/or elevated temperature.33 Sinha et al.34 studied the effect of TTSPi in NMC/graphite pouch cells with 1 M LiPF_{6} in EC:EMC (3:7 by weight) at 4.2 V and showed that TTSPi not only increased the coulombic efficiency but also reduced the cell impedance significantly. Mai et al.35 also showed that adding only 0.5 wt% of TTSPi in 1 M LiPF_{6} EC:DMC (1:2 by volume) significantly improved the impedance and capacity retention of NMC/Li half cells at 4.5 V which they ascribed to a preferential oxidation of TTSPi that formed a protective SEI on the NMC. Song et al.36 also used TTSPi as a multifunctional additive to improve the electrochemical performance of LiNi_{0.5}Mn_{1.5}O_{4} at 5 V. They showed that TTSPi hindered the decomposition of LiPF_{6} by hydrolysis, scavenged HF and therefore limited Mn/Ni dissolution and
formed a protective positive electrode SEI to limit electrolyte decomposition at high voltages. Similarly, Yim et al.37 used TTSPi to improve the cycling stability of 0.5 Li2MnO3 • 0.5 Li(Ni0.42Mn0.42Co0.16)O2 positive electrode material. They proposed that the trivalent phosphorus in TTSPi can scavenge oxygen gas in the cell, that the electrophilic phosphorus and silicon can remove nucleophilic lithium oxide species by a chemical scavenging reaction and that the silyl ether component can prevent transition metal dissolution through a fluoride scavenging reaction.

Recently, Ma et al.38 showed that the combination of the three additives PES, MMDS and TTSPi (2:1:1 wt%, referred to as “PES211”) stabilized the impedance and improved the capacity retention of NMC442/graphite pouch cells cycled at constant current up to 4.4 V or to 4.5 V and also increased the safety of the cells.39 Later, Nelson et al.40 showed that NMC442/graphite pouch cells cycled aggressively at 40 °C with a 20 h hold at the top of each charge displayed a dramatic capacity loss and large impedance increase which was mitigated to some extent by the use of “PES211”. Here, the effects of the ternary additive system, “PES211”, on the electrode/electrolyte interphases was investigated by correlating the electrochemical performance of NMC442/graphite pouch cells with thorough X-ray photoelectron spectroscopy (XPS) analysis of the SEI films formed at the surfaces of both graphite and NMC442 electrodes during formation and after different cycling protocols.

**Experimental**

**Cell preparation.**—1 M LiPF6 (BASF, purity 99.94, water content < 20 ppm) in EC:EMC (3:7 by weight, BASF, water content < 20 ppm) was used as the control electrolyte. To this electrolyte, either 2 wt% vinylene carbonate (VC from BASF, 99.97%), 2 wt% PES (Lianchuang Medicinal Chemistry Co., 98.2%) or 1 wt% MMDS (Tinci Materials Technology, 98.7%) or 1 wt% TTSPi (Sigma-Aldrich, > 95%) were added as single additives. The combination of 2% PES + 1% MMD + 1% TTSPi (by weight, referred to as “PES211”) was also used as ternary additive system. Machine-made 240 mAh LiNi0.42Mn0.42Co0.16O2 (NMC442)/graphite pouch cells balanced for 4.7 V operation were obtained dry (vacuum sealed) in an argon-filled glove box then vacuum-sealed at -94 kPa (relative to atmospheric pressure) using a compact vacuum sealer (MSK-115A, MTI Corp.). For each of the following electrochemical experiments, two identical pouch cells were prepared for reproducibility.

**Cell formation and cycling protocols.**—After filling, formation was performed using a Maccor 4000 series cycler. Cells were placed in a home-made temperature-controlled box at 40. ± 0.1 °C and held at 1.5 V for 24 h (for completion of wetting) then charged to 3.8 V at 12 mA (C/20). Cells were then cut open in an argon-filled glove box to release any gas generated and vacuum sealed again. Cells were then charged either to 4.4 V or 4.5 V at 12 mA (C/20) and the degassing procedure was repeated. For the XPS study, some selected cells were further charged to 4.7 V at 12 mA (C/20). Then, cells were discharged to 2.8 V at 12 mA (C/20). For all pouch cells dedicated to the XPS study, at each charge/discharge step during the formation process, the potential was held until the measured current decreased to 0.005C so that electrodes were in electrochemical equilibrium.

**Constant current cycling (CC) for XPS.**—Cells were cycling using a Maccor 4000 series battery cycler between 4.4 or 4.5 V and 2.8 V at 40. ± 0.1 °C and 12 mA (C/20) for 24 cycles and stopped either fully charged at 4.4 or 4.5 V or fully discharged at 2.8 V.

**Constant current-constant voltage cycling (CC-CV) for XPS.**—Cells were cycled using a Maccor 4000 series battery cycler at 40. ± 0.1 °C. One cycle of charge-hold-discharge protocol consisted of a constant current charge to 4.4 or 4.5 V at 48 mA (C/5) followed by a constant voltage step at the top of charge (4.4 or 4.5 V) for 24 h, then a constant current discharge to 2.8 V at 48 mA (C/5).

**CC and CC-CV procedures coupled with impedance measurements.**—Additional cells were subjected to either CC or CC-CV cycling while their impedance spectra measured every 12 cycles or 4 cycles, respectively. A system built in house41 consisting of a Neware Battery Testing System connected to a computer equipped with a Gamry frequency response analyzer (FRA) card was used for these experiments. During impedance measurements, relays disconnected the cells from the Neware cycler and connected them to the FRA card to have their impedance spectra measured. To accommodate the impedance measurement, the CC-CV protocol described above was slightly altered. Every 12 (CC) or 4 (CC-CV) cycles, cells underwent a slow C/20 constant current cycle while impedance spectra were measured every 0.1 V from 3.6 V to the top of charge (4.4 or 4.5 V) during both charge and discharge.
Gas measurements.—Gas evolution measurements employing Archimedes’ principle were performed before and after each formation step and after the constant current (CC) or the charge-hold-discharge (CC-CV) cycling by weighing cells submerged in deionized nanopure water (18 M) at 20 ± 1°C. This procedure is fully described in reference 42.

X-ray Photoelectron Spectroscopy (XPS).—Sample preparation.—After formation, CC and CC-CV cycling, pouch cells were disassembled in an argon-filled glove box within the first 12 h following the end of the electrochemical process. Graphite and NMC442 electrodes were cut from the pouch cell electrodes with a precision punch and washed twice by immersion into 0.8 mL of EMC solvent (BASF) in a clean and dry glass vial with a mild manual agitation for 10 s to remove the majority of the LiPF6 salt. Air sensitive samples were then mounted onto a molybdenum holder using a copper conductive tape (3M) under argon and placed into a special transfer system. The latter was then put under vacuum at approx. 10−3 mbar for 1 h and then connected to the spectrometer where samples were loaded under a pressure of ~10−3 mbar. All samples were kept at 10−8 mbar for one night before analysis to ensure a strictly identical vacuum procedure.

Data acquisition and treatment.—XPS was performed on a SPECS spectrometer equipped with a Phoibos 100 hemispherical energy analyzer and using Mg Kα radiation (hν = 1253.6 eV). The analyzed sample area was ~2 × 3 mm2 which gave results representative of the whole electrode. Core spectra were recorded in the fixed analyzer transmission (FAT) mode with a 20 eV pass energy at an operating pressure <2 × 10−9 mbar. Short acquisition time spectra were first recorded as a reference to follow any possible sample degradation during the analysis. Data treatment was performed using CasaXPS software. The binding energy scale was calibrated from the C1s peak at 285 eV (C-C/C-H) and the O1s peak at 529.6 eV (O2− anion from the NMC442) for the graphite and NMC442 electrodes, respectively. A nonlinear Shirley-type background was used for core spectra analysis while 70% Gaussian - 30% Lorentzian Voigt peak shapes and full width at half-maximum (fwhm) constraint ranges were selected to optimize areas and peak positions.

Results and Discussion

Long term cycling and impedance.—Figure 2 shows the discharge capacity and the total resistance, Rtotal, (measured at 4.4 V), as function of cycle number for the NMC442/graphite pouch cells that underwent either the CC or the charge-hold-discharge (CC-CV) cycling coupled with impedance measurements. Here, Rtotal is the diameter of the “semicircle” or overlapping semicircles of the Nyquist plot and represents the sum of the charge transfer resistance, the resistance associated with the motion of the Li ion through the SEI and any current collector/electrode resistance for both electrodes. Results from cells with 2 wt% VC are also shown for comparison as VC is well known to improve the capacity retention of Li-ion cells. Note that control cells (no additive) are not presented here but showed very poor capacity retention with ~70% (~160 mAh) of the initial capacity after only 20 cycles (see Figure 5b). Compared to control cells, the use of 2% VC may appear useful up to 20 cycles, however, beyond that point, 2% VC cells showed dramatic capacity fade due to resistive (see Rtotal, Figure 2b) and unstable SEI layers. During CC cycling at only 4.4 V, the use of 2% PES outperformed 2% VC electrolyte which shows the benefit of using PES rather than VC for cells destined for high potential. When the upper cutoff potential was increased to 4.5 V, however, cells with 2% PES immediately showed a lower capacity retention followed by a severe capacity fade after 115 cycles. These phenomena were associated to an increase of the impedance as soon as the voltage range was increased to 4.5 V indicating an increase of the parasitic reactions and the formation of resistive SEI films upon exposure to potentials above 4.4 V. Cells with “PES211” had the best capacity retention (about 87% after 285 cycles) during constant current cycling to 4.5 V which suggests more stable SEI films with low impedance as shown in Figure 2b. Cells with “PES211” were also subjected to the charge-hold-discharge (CC-CV) protocol to an upper cutoff potential of 4.4 V. Figure 2 shows that those cells failed rapidly due to extensive impedance increase. Figure 2 demonstrates that the CC-CV protocol is much more challenging than the CC protocol. This is a good lesson for researchers who may promote CC cycling results as indicative of commercially relevant results.

Combination of the charge transfer resistance and the resistance due to motion of Li-ions through the SEI layers for the full cell, Rrotal, measured at 4.4 V as a function of cycle number for the same cells.

Figure 2. a) Discharge capacity as a function of cycle number for NMC442/graphite pouch cells undergoing CC cycling between 2.8 and 4.4 V then 4.5 V at C/5 (48 mA) and 40. ± 0.1°C for selected electrolyte blends. The dotted line indicates when the upper cutoff voltage was increased from 4.4 V to 4.5 V. For PES 211 electrolyte, data for cells undergoing the charge-hold-discharge (CC-CV) procedure between 2.8 and 4.4 V (48 mA, C/5 – 20 h, see Experimental section) at 40. ± 0.1°C are also presented for comparison. b) Combination of the charge transfer resistance and the resistance due to motion of ions through the SEI layers for the full cell, Rrotal, measured at 4.4 V as a function of cycle number for the same cells.

dQ/dV vs. V measured during the initial stages of the formation cycle.—Figure 3b shows the differential capacity (dQ/dV) versus V curves of the NMC442/graphite pouch cells between 1.6 and 3.5 V during the formation cycle. The voltage versus capacity during the first 14 mAh of the formation cycle is also showed (Figure 3a) so that readers can have a better understanding of the dQ/dV versus V curves. Control cells showed a pronounced peak at 2.9 V (graphite at ~0.8 V vs. Li/Li+ due to the reduction of EC at the graphite surface44,45. When 1% TTSPi was added, the reduction peak of EC was unaffected and no additional peak was detected indicating that TTSPi may not undergo an electrochemical reduction during
Figure 3. a) Voltage versus capacity during the first 14 mAh of the formation cycle and b) differential capacity (dQ/dV) versus potential (V) during the early stages of the formation cycle of NMC442/graphite pouch cells at C/20 and 40 °C for the different electrolyte blends studied here.

The formation as expected from previous studies.34,36 To validate this hypothesis, the consumption/reaction of TTSPi was probed using liquid electrolyte analysis by gas chromatography/mass spectrometry (GC-MS), following the procedure described by Petibon et al.46,47 The total consumption of TTSPi was found after formation at 3.5 V and more interestingly TTSPi was also totally consumed when a cell was simply filled with 1% TTSPi electrolyte and put in a freezer for 24 h without any charging at all (Figure S1). This result suggests that TTSPi reacts chemically in NMC442/graphite pouch cell. Figure 3 shows that the use of 1% MMDS partially decreased the EC reduction at 2.9 V due to the preferential reduction of MMDS at 2.4 V (graphite at ~1.35 V vs. Li/Li+).16 For 2% PES electrolyte, the EC reduction was almost suppressed due to the preferential reduction of PES at 2.45 V (graphite at ~1.35 V vs. Li/Li+).25 Finally, when “PES211” was used, the EC reduction was nearly eliminated due to the combined reduction of both MMDS and PES at 2.4 V and 2.5 V, respectively.

Gas analysis.—Figure 4 shows the volume of gas evolved in the NMC442/graphite pouch cells at 40 °C during (a) formation and (b) during the CC and charge-hold-discharge (CC-CV) cycling at 4.4 and 4.5 V. The data in Figure 4 is for the cells used for the XPS studies. For reference, the initial volumes of the pouch cells is 2.2 mL. During the formation process (Figure 4a), control cells produced about 0.8 mL of gas while the use of 1% MMDS slightly increased the gas production to 0.6 mL. For 1% TTSPi and 2% PES electrolytes, however, the gas generated during formation decreased to 0.35 mL and 0.15 mL, respectively. TTSPi and especially PES are therefore very efficient gas reducing agents during formation. When “PES211” was used, the EC reduction was nearly eliminated due to the combined reduction of both MMDS and PES at 2.4 V and 2.5 V, respectively.

Figure 4. Volume of gas evolved in NMC442/graphite pouch cells for the different electrolytes a) during the formation process at C/20 (12 mA) and 40 °C and b) during the CC and charge-hold-discharge (CC-CV) cycling (see Experimental section) at 40 °C.

Figure 5 shows the discharge capacity for the short term CC and charge-hold-discharge (CC-CV) cycling between 2.8 and 4.4 or used to 4.5 V suggesting that extensive electrolyte degradation occurs as soon as the cells are exposed for too much time at potentials above 4.4 V.

Figure 5. Discharge capacity as function of cycle number for NMC442/graphite pouch cells with control and “PES211” electrolytes undergoing a) the 12 mA (C/20) CC cycling and b) the charge-hold-discharge (48 mA, (C/5) CC- 20 h CV) cycling between 2.8-4.4 V and 2.8-4.5 V at 40 °C.
Figure 6. Carbon 1s (a) and Oxygen 1s (b) XPS core spectra of graphite electrodes as well as Oxygen 1s XPS core spectra of NMC442 electrodes (c) for control and “PES211” electrolytes, as taken from NMC442/graphite pouch cells during formation at 3.8 V, 4.4 V and 4.7 V during charge and at 2.8 V during the discharge following the charges to 4.4 V and 4.7 V.

Figure 6.—Figure 6 shows the Carbon 1s (a) and Oxygen 1s (b) XPS core spectra of graphite electrodes as well as Oxygen 1s XPS core spectra of NMC442 electrodes (c) for control and “PES211” electrolytes taken from NMC442/graphite pouch cells during formation at 3.8 V, 4.4 V and 4.7 V during charge and at 2.8 V during the discharge following the charges to 4.4 V and 4.7 V.

Formation of the cells.—Figure 6 shows the Carbon 1s (a) and Oxygen 1s (b) XPS core spectra of graphite electrodes as well as Oxygen 1s XPS core spectra of NMC442 electrodes (c) for control and “PES211” electrolytes as taken from NMC442/graphite pouch cells during formation at 3.8 V, 4.4 V and 4.7 V during charge and 2.8 V during the discharge following the charge at 4.4 V and 4.7 V. The C 1s core spectrum of the fresh graphite electrode showed five components at 284.1, 285.0, 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 During formation to 3.8 V and higher potentials, the intensity of the graphite peak at ∼282.7 eV significantly decreased for control electrolyte indicating the continuous formation of a SEI film on the graphite surface. For “PES211” electrolytes, however, the graphite peak was barely visible even at 3.8 V which indicates the rapid formation of a relatively thick SEI film compared to control electrolyte possibly due to the preferential reduction of both PES and MMDS at the graphite surface (Figure 3). This suggestion is supported by a similar evolution of the graphite peak during formation for 2% PES and 1% MMDS electrolytes compared to “PES211” cells while the graphite peak evolution for 1% TTSPi electrolyte was close to control cells (Figure S2 in the supporting information). Figure 6a also shows that when formed at 4.7 V, the carbon content of the SEI on the graphite electrode decreased significantly for control electrolyte indicating a large change of the composition of the SEI most likely due to the products of electrolyte oxidation at the positive electrode migrating to the negative. When “PES211” was used, however, almost no change of carbon content was observed at 4.7 V most likely due to a more stable SEI film at the positive electrode, limiting oxidation products. After discharge, no significant change of the graphite peak intensity and carbon content was observed for both control and “PES211” electrolytes.
In the O 1s spectra of the graphite electrodes (Figure 6b), the two components of the fresh electrode were replaced by two new main components at 532 and 533.8 eV due to the simultaneous covering of the graphite and CMC binder by the SEI. The peak at 533.8 eV is assigned to -C=O-bonds from ROCO₂Li and/or ether derivatives. For control electrolyte, the peak at 532 eV was more intense compared to control electrolyte due to the additional O contribution of sulfite species (RSO₃) formed from PES and MMDS as discussed later when the S spectra are considered. This result is in agreement with the higher contribution of the 532 eV components for 2% PES and 1% MMDS electrolytes while the use of "PES211" led to a similar contribution of the 532 eV peak compared to control electrolyte (Figure S3 in the supporting information). For control electrolyte, two additional peaks were observed at ~530.7 and ~528.3 eV and attributed to the formation of lithium alkoxide (ROLi) more likely from EMC and lithium carbonate (Li₂CO₃) and/or other ROCO₂Li compounds formed by the reduction of EC and EMC. However, for "PES211" electrolyte, the peak at 532 eV was more intense compared to control electrolyte due to the additional O contribution of sulfite species (RSO₃) formed from PES and MMDS as discussed later when the S spectra are considered. This conclusion was confirmed when the cells were discharged to 4.7 V after a charge at 4.7 V indicating a partial recovering of the initial NMC442 peak at 529.5 eV significantly increased after discharge at 4.7 V, the intensity of the NMC442 peak at 529.5 eV was further decreased for control electrolyte while it remained almost unchanged for "PES211" electrolyte. Also, the contribution of the -C=O- peak at 533.5 eV continuously increased from 4.4 V to 4.7 V for control electrolyte while with almost no change was found for "PES211". These results indicate that PES 211 forms a relatively stable and passivating SEI film at the NMC442 surface compared to control electrolyte from a thickness perspective anyway (peak at 529.5 eV). This conclusion was confirmed when the cells were discharged to 2.8 V after formation at 4.4 and 4.7 V. Indeed, when PES 211 was used, almost no change in the O 1s spectra of the NMC442 electrode was observed. For control electrolyte, however, the intensity of the NMC442 peak at 529.5 eV significantly increased after discharge at a charge at 4.7 V indicating a partial recovering of the initial SEI film, suggesting instability of the control SEI at high potential. It is therefore concluded that during formation, the use of "PES211" rapidly creates a more stable and passivating SEI film at the NMC442 surface compared to control electrolyte.

Figure 7a shows the sulfur 2p XPS core spectra of graphite and NMC442 electrodes as taken from NMC442/graphite pouch cells with the fresh electrode while it was significantly decreased with the use of "PES211" electrolyte. These results suggest that, similarly to the graphite electrode, "PES211" electrolyte rapidly forms a relatively thick SEI film at the NMC442 surface with a large contribution of oxygen from sulfite species (RSO₃) due to the preferential reaction of both PES and MMDS. This is supported by the lower intensity of the NMC442 peak at 529.5 eV and the higher contribution of the oxygen peak at 531.7 eV for both 2% PES and 1% MMDS electrolytes at 3.8 V while the use of TTSPi led to a similar O 1s spectrum compared to control electrolyte (Figure S4 in the supporting information). At 4.7 V, the intensity of the NMC442 peak at 529.5 eV was further decreased for control electrolyte while it remained almost unchanged for "PES211" electrolyte. Also, the contribution of the -C=O- peak at 533.5 eV continuously increased from 4.4 V to 4.7 V for control electrolyte while with almost no change was found for "PES211". These results indicate that PES 211 forms a relatively stable and passivating SEI film at the NMC442 surface compared to control electrolyte from a thickness perspective anyway (peak at 529.5 eV). This conclusion was confirmed when the cells were discharged to 2.8 V after formation at 4.4 and 4.7 V. Indeed, when PES 211 was used, almost no change in the O 1s spectra of the NMC442 electrode was observed. For control electrolyte, however, the intensity of the NMC442 peak at 529.5 eV significantly increased after discharge at a charge at 4.7 V indicating a partial recovering of the initial SEI film, suggesting instability of the control SEI at high potential. It is therefore concluded that during formation, the use of "PES211" rapidly creates a more stable and passivating SEI film at the NMC442 surface compared to control electrolyte.

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Figure 8. Oxygen 1s XPS core spectra of graphite (a) and NMC442 (b) electrodes for control and “PES211” electrolytes as taken from NMC442/graphite pouch cells after the 25 cycles of CC and charge-hold-discharge (CC-CV) cycling (see Figure 5) at 4.4 and 4.5 V. The cells were stopped at 2.8 V before the XPS spectra were measured.

Constant current and charge-hold-discharge (CC-CV) cycling.—Figure 8 shows the oxygen 1s XPS core spectra of graphite (a) and NMC442 (b) electrodes for control and “PES211” electrolytes as taken from NMC442/graphite pouch cells after the 25 cycles of CC and charge-hold-discharge (CC-CV) cycling at 4.4 and 4.5 V. These spectra were taken after discharge to 2.8 V. Figure 8 shows that the chemical nature of the oxygen-containing compounds at both graphite and NMC442 surfaces changes with the upper cutoff potential and the cycling conditions. The ratio of oxygen in a -C-O- environment at 533.8–533.5 eV to a -CO2 environment at 532–531.7 eV increased from 4.4 V to 4.5 V as well as between the CC and charge-hold-discharge (CC-CV) cycling. Finally, the CC-CV cycling at 4.5 V led to the higher -C-O- / -CO2 ratio. These results suggest that further parasitic reactions take place between 4.4 and 4.5 V and/or during long term exposure at 4.4 and 4.5 V. The increase of the relative amount of -C-O- containing compounds could be explained by further reaction of carbonate degradation species such as ROCO2Li and/or by direct degradation of the solvent at the positive electrode through a new reaction pathway at the higher potential. When “PES211” was used, however, the increase of the -C-O- / -CO2 ratio was lowered except during the charge-hold-discharge of the initially formed sulfite species by other SEI compounds generated at high potential. Also, at 4.7 V, two new S 2p peaks appeared at the NMC442 surface at about 166 and 164.2 eV and could be assigned to inorganic Li2SO3 and RSSO3 (S-like) such as Li2S2O3 and/or -S- species, respectively. These new sulfur compounds are likely generated by further reaction of relatively unstable sulfite species formed from MMDS as the same phenomenon was observed for 1% MMDS electrolyte and not with the use of PES (Figure S5).
Figure 9. Sulfur 2p (a) XPS core spectra of graphite and NMC442 electrodes for “PES211” electrolyte after the 25 cycles of CC cycling at 4.4 V and the 25 cycles of charge-hold-discharge (CC-CV) cycling at 4.5 V. The cells were discharged to 2.8 V before XPS spectra were taken. Fluorine 1s (b) XPS core spectra of graphite electrodes for control and “PES211” electrolyte taken from the same NMC442/graphite pouch cells as in Figure 9a.

Conclusions

The effects of a ternary additive system 2% PES + 1% MMDS + 1% TTSPi (“PES211”) in NMC442/graphite pouch cells balanced for 4.7 V was thoroughly investigated. The use of “PES211” electrolyte significantly improved the capacity retention, impedance and gas formation of NMC442/graphite pouch cells cycled at constant current (CC) up to 4.4 or 4.5 V compared to control electrolyte. When cycled using a charge-hold-discharge (CC-CV, with a 20 h hold at top of charge) protocol, however, the NMC442/graphite pouch cells filled with “PES211” electrolyte displayed capacity loss, impedance increase and gas formation, especially at 4.5 V, which indicates that extensive electrolyte degradation occurs as soon as the cells are exposed for long periods of time at potentials above 4.4 V.

XPS analysis of the SEI films showed that during formation, “PES211” electrolyte rapidly creates more stable and passivating SEI films at both the graphite and NMC442 surfaces compared to control electrolyte, apparently due to the preferential reaction of PES and MMDS. It was found that TTSPi also reacts at the graphite surface through a chemical reaction even before the cells are charged for the first time. The use of “PES211” also modifies the reactivity of the LiPF<sub>6</sub> salt at the NMC surface and hinders its degradation during formation at high voltage (4.7 V) and after long time exposure at high potential (CC-CV). Additionally, “PES211” almost eliminated changes to the chemical nature of the oxygen-containing compounds observed at both graphite and NMC442 surfaces (i.e. the increase of the -C-O-/ -CO<sub>2</sub>- ratio) except for the case of long time exposure (CC-CV) at 4.5 V. These results indicated the passivating effect of the SEI films formed with “PES211” electrolyte at both the graphite and NMC442 surfaces which led to better capacity retention and lower gas production. However, a relatively poor stability of the sulfite species and the resulting SEI films was observed with “PES211” electrolyte when exposed for long times at 4.5 V.
