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# Impact of electrolyte solvent and additive choices on high voltage Li-ion pouch cells

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# HIGHLIGHTS

• A LaPO<sub>4</sub>-coating showed benefits above 4.5 V but not at 4.3 V or 4.4 V.

• LaPO<sub>4</sub>-coated NMC442/graphite cells containing TAP performed best at 4.5 V.

• Uncoated NMC442/graphite cells with FEC:TFEC performed best at 4.5 V.

#### ARTICLE INFO

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## ABSTRACT

The effects that various electrolyte solvents and electrolyte additives had on both LaPO<sub>4</sub>-coated  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  and uncoated  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2/\text{graphite}$  pouch cells were studied using automated storage, electrochemical impedance spectroscopy, gas production and long-term cycling experiments. Storage experiments showed that the voltage drop during storage at 4.3 or 4.4 V for both coated and uncoated cells was very similar for the same electrolyte choice. At 4.5 V or above, the LaPO<sub>4</sub>-coated cells had a significantly smaller voltage drop than the uncoated cells except when fluorinated electrolytes were used. Automated charge discharge cycling/impedance spectroscopy testing of cells held at 4.5 V for 24 h every cycle showed that all cells containing ethylene carbonate:ethyl methyl carbonate electrolyte or sulfolane:ethyl methyl carbonate electrolyte exhibited severe capacity fade. By contrast, cells containing fluorinated electrolyte had the best cycling performance in the uncoated LiNi<sub>0.4</sub>Mn<sub>0.4</sub>Co<sub>0.2</sub>O<sub>2</sub>/graphite cells while cells containing sulfolane:ethyl methyl carbonate electrolyte had the best cycling performance in coated LiNi<sub>0.4</sub>Mn<sub>0.4</sub>Co<sub>0.2</sub>O<sub>2</sub>/graphite cells.

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# 1. Introduction

Since the first commercialization of  $LiCoO_2$ /graphite Li-ion batteries by Sony in 1991, intensive efforts have been aimed at developing new positive electrode materials with a higher operating voltage and higher discharge capacity [1,2]. Several high voltage electrode materials have been developed [3–8]. However, cycling performance of these materials is poor in conventional carbonate-based electrolytes due to increased electrolyte oxidation at high positive potentials, leading to cell failure stemming from gas generation and impedance growth [9–12].

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http://dx.doi.org/10.1016/j.jpowsour.2016.08.100 0378-7753/© 2016 Elsevier B.V. All rights reserved. It has been reported that electrolyte oxidation reactions can generate gaseous products, such as  $CO_2$  and/or  $C_2H_4$ , and cause swelling problems and cell failure [13–15]. Some oxidation products can directly accumulate into a surface film on the positive electrode and contribute to impedance growth on the positive electrode [16,17]. Others can dissolve in the bulk electrolyte, migrate to the negative electrode where reduction occurs and generate a film on the negative electrode and therefore contribute to impedance growth on the negative to impedance growth on the negative side [18–20].

Using an automated EIS/cycling measurement, Nelson et al. [12] measured the charge transfer resistance as a function of voltage during cycling of Li(Ni<sub>0.4</sub>Mn<sub>0.4</sub>Co<sub>0.2</sub>)O<sub>2</sub> (NMC442)/graphite cells. They demonstrated that impedance growth, especially at the positive electrode, was the main contributor to cell failure in high voltage NMC442 Li-ion cells. Based on ultra high precision





coulumetry (UHPC) and symmetric cell studies, Xia et al. [21] found that electrolyte oxidation at the positive electrode, rather than Li consumption in the solid electrolyte interface (SEI) at the negative electrode was the dominant contributor to reducing the coulombic efficiency (CE) and increasing cell impedance when the upper cutoff potential was increased.

Two approaches are commonly used to limit electrolyte oxidation in high-voltage Li-ion cells. The first approach involves surface modification of cathode materials either by providing physical protection layers through material coatings or by the incorporation of electrolyte additives to form a solid electrolyte interphase (SEI). Surface coatings create a physical layer that can slow the rate of parasitic reactions between the charged electrode materials and electrolyte and thus improve the cycle life, calendar life and safety of Li-ion cells [22,23]. Although numerous studies [24–33] have shown that surface coating materials can improve electrochemical performance, recent publications by Nelson et al. [34] and Xia et al. [35] clearly showed that the expected benefit of a LaPO<sub>4</sub> coating in NMC442/graphite pouch cells was not present at 4.4 or 4.45 V when advanced electrolytes were used. At 4.5 V, the LaPO<sub>4</sub> coating provided benefit only when used in cells containing control electrolyte without additives. The results also indicated that the benefits due to the additives at 4.5 V far outweighed the benefits due to the coating at 4.5 V. Similarly, the formation or modification of the SEI layers on the surface of the positive or negative electrode due to electrolyte additives has been shown to be effective in improving cycle life, calendar life and safety of Li-ion cells [36,37]. Numerous publications [38–49] have shown that electrolyte additives can increase the usable voltage range of electrolytes by stabilizing the electrode/electrolyte interface. However, recent work by Ma et al. [11] showed that the benefit provided by electrolyte additives in traditional carbonate electrolyte above 4.5 V is diminished.

The second approach used to limit electrolyte oxidation in high voltage Li-ion cells involves solvents that are difficult to oxidize. Some organic solvents with strong electron-withdrawing groups, such as sulfones [50,51], nitriles [52,53], ionic liquids [54–57] and fluorinated compounds [58–61] apparently limit oxidation at high potentials. By decreasing the energy of the highest occupied molecular orbital (HOMO) relative to the vacuum level, such solvents normally limit electrolyte oxidation [62–64].

Recently, some studies of the effect of alternative solvents on NMC442/graphite pouch cells have been performed. Xia et al. [65] showed that sulfolane (SL)-based electrolytes with vinylene carbonate (VC) as an SEI-forming electrolyte additive could provide comparable cycling and storage performance to state-of-the-art electrolytes in NMC442/graphite pouch cells tested to 4.4 and 4.5 V. Xia et al. [66] also showed that fluorinated electrolytes containing fluoroethylene carbonate (FEC) and bis(2,2,2trifluoroethyl) carbonate (TFEC) with prop-1-ene-1,3-sultone (PES) as an electrolyte additive outperformed all non-fluorinated electrolytes with all additives during continuous charge-discharge cycling tests to 4.5 V in NMC442/graphite pouch cells. Using isothermal electrochemical microcalorimetry, Downie et al. [67] showed that the parasitic heat flow from NMC442/graphite cells at high potential with FEC:TFEC electrolyte was much smaller than from cells with conventional electrolytes, suggesting that the fluorinated solvents limited electrolyte oxidation. Downie et al. [67] also observed that the separators extracted from NMC442 cells, tested to high voltage which contained FEC:TFEC electrolytes, were clean and white while those from extracted cells with conventional electrolytes were brown, suggesting electrolyte degradation.

Successfully operating Li-ion cells to high voltage may require the use of a combination of new electrolyte solvents, electrolyte additives as well as surface coatings. In this paper, the impact of different electrolyte solvents and electrolyte additives in high voltage coated and uncoated NMC442/graphite cells were carefully studied and compared head-to-head using an automatic storage system (up to 4.7 V) and automated EIS/cycling measurements (up to 4.5 V). The voltage drop measured during storage experiments, impedance growth during cycling experiments as well as gas evolution during both cycling and storage experiments were compared to make an overall evaluation in both coated and uncoated NMC442/ graphite Li-ion pouch cells. Long-term cycling experiments (to 4.5 V) were also performed to compare the charge-discharge cycling stability of cells containing these electrolyte systems.

# 2. Experimental

#### 2.1. Electrolyte and electrolyte additives

1 M LiPF<sub>6</sub> in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7 wt% ratio, BASF, 99.99%) was used as the control electrolyte. The other two electrolyte systems, 1 M LiPF<sub>6</sub> SL:EMC (3:7 wt % ratio) and 1 M LiPF<sub>6</sub> FEC:TFEC (1:1 wt% ratio), were used for comparison based on our previous publications [65]. Additives were included in the three electrolyte systems in a range of 0.5–2 wt%. These additives included vinylene carbonate (VC), prop-1-ene, 1,3sultone (PES), methane methylenedisulfonate (MMDS), propanediol cyclic sulfate (trimethylene sulfate - TMS), 1,3,2-dioxathiolan-2,2-oxide (ethylene sulfate - DTD), tris trimethylsilyl phosphite (TTSPi), lithium bis(oxalate)borate (LiBOB) as well as triallyl phosphate (TAP). The purities and the suppliers of the solvents and additives used are listed in Table S1 and the structural information of these additives are given in Fig. S1 (supporting information). Figs. S2 and S3 show the voltage (V) vs. capacity (Q) (Figs. S2a and S3a) as well as the dQ/dV vs. V curves (Figs. S2b and S3b) during formation step 1 (charge to 3.5 V). Figs. S2 and S3 show that the different electrolytes have different reduction potentials that are affected by the solvent and additive choices. Figs. S2 and S3 show that the V vs. Q and dQ/dV vs. V curves are similar for the same electrolyte in both types of cells, indicating that the coating does not have an obvious impact on the reaction of the additives with  $Li^+ + e^-$  at the graphite surface, which agrees with previous work [35].

The electrolyte solvents selected for this study are based on previous work [65,66,68]. The simple reason for choosing FEC-TFEC or SL-EMC:VC is to combine a high dielectric constant solvent with a low viscosity solvent. One component (FEC or SL:VC) can help to form the SEI on the negative electrode and dissolve the lithium salt due its high dielectric constant while the other component (TFEC or EMC) lowers the viscosity and the melting point.

The additives selected for this study are well-known in the literature and apparently improve the quality of the negative electrode SEI or reduce parasitic reactions at high voltage in NMC442/graphite cells. As examples, VC [69] and PES [70] are SEI forming additives and gas reducers during formation. MMDS [71], ES [72], TTSPi [73] have been shown to be effective impedance reducers. Both DTD [74] and TAP [48] can improve the coulombic efficiency (CE) and charge-discharge cycle life. The additive, TAP, can be polymerized through a cross-linked electro-polymerization of its three allyl groups at the surface of both graphite and coated NMC442 electrodes, leading to higher cell impedance [48]. The additive combination 2% PES + 1% DTD + 1% TTSPi, called PES211, was chosen based on previous work which showed cells with PES211 had the best cycling performance among the 110 additive blends studied [75].

# 2.2. Pouch cell construction

The 402035-size pouch cells used in this study were uncoated-NMC442/graphite cells with a capacity of 240 mAh and LaPO<sub>4</sub>- coated NMC442/graphite cells with a capacity of 180 mAh. The cells with coated NMC442 had lower capacity because the positive electrode coating was thinner in those cells. In the coated cells, the positive electrode material was coated with 3 wt% of LaPO<sub>4</sub> which appears as nanoparticles on the NMC particle surfaces. The LaPO<sub>4</sub> coating was performed at 3 M Company on the same NMC442 (provided by Umicore) that was used in the uncoated cells. Both types of cells were balanced for 4.7 V operation to avoid Li-plating at any potential below 4.7 V. The cells were made dry (without electrolyte) by Li-Fun Technology (Zhuzhou, Hunan Province, China).

The pouch cells were vacuum sealed without electrolyte in China and then shipped to our laboratory in Canada. Before filling with electrolyte, the cells were cut just below the heat seal and dried at 80 °C under vacuum for 14 h to remove most of the residual water. The cells were then transferred immediately to an argonfilled glove box for electrolyte filling and vacuum sealing. The NMC442/graphite pouch cells were filled with 0.75 mL of electrolyte (0.90 g for EC:EMC, 0.87 g for SL:EMC and 1.15 g for FEC:TFEC electrolyte because the density of EC:EMC electrolyte is 1.20 g/mL, compared to 1.17 g/mL for SL:EMC and 1.53 g/mL for FEC:TFEC). After filling, cells were vacuum-sealed with a compact vacuum sealer (MSK-115A, MTI Corp.). First, cells were placed in a temperature box at 40.0 °C where they were held at 1.5 V for 24 h, to allow for the completion of wetting. Then, cells were charged at C/20 to 3.5 V and were held at 3.5 V for 1 h. This step is called formation step 1. After formation step 1, cells were transferred into the glove box, cut open just below the seal to release any gas generated during the charge to 3.5 V and vacuum sealed again. These cells were then charged from 3.5 V at C/20 to 4.5 V (or to 4.7 V for the storage experiments). This step is called formation step 2. After formation step 2, the cells were transferred into the glove box, cut open to release gas generated and then vacuum sealed again. These degassing voltages were selected based on the in-situ gas evolution experiments that show that most of the gas evolves in the formation step at voltages below 3.5 V and above 4.3 V [76]. After the two degassing processes, cells were then discharged to 3.8 V where the cell volume and impedance spectra were measured.

#### 2.3. Storage experiments

It is extremely important to mention that all cells for the storage experiment were charged to 4.7 V for degassing. Downie et al. [67] show that exposure of cells with conventional electrolytes to high potential (e.g. 4.6 V) leads to excess parasitic heat, which slowly diminishes, when cells are returned to 4.1, 4.2 or 4.3 V [See Figure 10 in ref. [67]]. Therefore, the potential drops measured in this paper will be slightly different to those cells described in Refs. [44,46,49,66,67] which were never charged to 4.7 V.

For storage experiments, after formation cells were first charged and discharged twice between 2.8 V and the upper cut-off potential (between 4.3 and 4.7 V). Then the cells were held at the top of charge for 24 h. A Maccor series 4000 cycler was used for the preparation of the cells prior to storage. After the pre-cycling and 24 h hold process, cells were quickly (within 10 min) moved to the storage system where the open circuit voltage was measured every 6 h for a total storage time of 500 h [77]. Storage experiments were done at 40  $\pm$  0.1 °C. The voltage drops ( $V_{drop}$ ) after 30 h and after 500 h were measured and are considered in the results section. 160 cells were made and tested in the storage experiments.

# 2.4. Automated EIS/cycling system and frequency response analysis (FRA) measurement

Some cells were tested on a 32-channel automated EIS/cycling

system extremely aggressively to push the limits of the electrolyte [12]. The 32-channel EIS/cycling system consists of Neware (Shenzhen, China) cyclers connected to computers with Gamry frequency response analyzer (FRA) cards via appropriate computer controlled relays. The relay switching was controlled to connect the cells to the Neware charger or to the Gamry FRA cards as required. The FRA measurement allows one to measure the impedance spectra at different voltages as the cycle number increases without disturbing the cycling process. A special cycling protocol was designed for the FRA cycling, as is shown in Fig. 1c. Cells were cycled between 2.8 and 4.5 V at C/2.3 (100 mA for the uncoated cells and 80 mA for the coated cells) at 40  $\pm$  0.1 °C including a 24 h hold at 4.5 V. Every 5 charge-hold-discharge cycles, the cells underwent an "FRA cycle" consisting of a charge and discharge at C/10 between 2.8 and 4.5 V while the FRA measured the cell impedance every 0.1 V between 3.8 and 4.5 V. After the FRA cycle, the cells were cycled again between 2.8 and 4.5 V at C/2.5 for 5 cycles with a 24 h hold at 4.5 V every cycle, and the protocol was repeated.

# 2.5. Ex-situ gas measurement

Ex-situ gas measurements were made by suspending pouch cells from a fine wire "hook" attached under a Shimadzu balance (AUW200D) [78]. The pouch cells were immersed in a beaker of deionized "nanopure" water (18 MΩ) that was at 20  $\pm$ 1 °C for measurement. Before weighing, all cells were charged or discharged to 3.80 V. The changes in the weight of the cell suspended in fluid, before, during and after testing are directly related to the volume changes by the change in the buoyant force. The change in weight of a cell,  $\Delta w$ , suspended in a fluid of density,  $\rho$ , is related to the change in cell volume,  $\Delta v$ , in mL by

$$\Delta v = -\Delta w / (\rho g) \tag{1}$$

where the weight was measured in milliNewtons, the density in g/ mL and g is the acceleration due to gravity in  $m/sec^2$ . It is important to realize that w/g is what a balance reports as the mass in grams.

# 2.6. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were conducted on NMC442/graphite pouch cells after formation, after storage and also after FRA cycling. Cells were charged or discharged to 3.80 V before they were moved to a 10  $\pm$  0.1 °C temperature box. The potential of 3.8 V was chosen for the EIS measurements because at this voltage both graphite and NMC electrodes are at about 50% state of charge and are stable. The temperature 10 °C was chosen because a previous publication [79] showed the impedance at 10 °C is much larger than in the same cells tested at 30 °C. Therefore it is more effective to differentiate between additives when the impedance spectra are measured at 10 °C. Alternating current (AC) impedance spectra were collected with ten points per decade from 100 kHz to 10 mHz with a signal amplitude of 10.0 mV at 10  $\pm$  0.1 °C. A Biologic VMP-3 was used to collect these spectra. The experimental setup did not allow for reproducible solution resistance measurements due to cable and connector impedance. Therefore, all impedance spectra were manually shifted to zero on the real axis at the highest frequency measured.

# 3. Results and discussions

Fig. 1a and b shows typical data collected during some of these experiments for cells containing control electrolyte. Fig. 1a shows the open circuit voltage (OCV) vs. time during 500 h of storage at



**Fig. 1.** a) Open circuit voltage vs. time during 500 h storage at 40 °C b)  $V_{drop}$  during storage as a function of initial open circuit voltage. c) cycling protocol used during the automated cycling/EIS procedure. d) typical Nyquist representation of the impedance spectra collected during FRA cycle at 40 ± 0.1 °C. Fig. 1 gives example data showing the methods used in this paper.

40 ± 0.1 °C.  $V_{drop}$  was calculated by the change of cell voltage after 30 h of storage or after the entire 500 h storage period. The 30 h measurement was made because the cell potential changes initially very rapidly since the cell potential is highest.  $V_{drop}$  during storage corresponds to intercalation of lithium into the positive electrode material and is mainly caused by the parasitic reactions (mainly electrolyte oxidation) occurring at the positive electrode [68]. Fig. 1b shows  $V_{drop}$  during storage (after 500 h) as a function of initial open circuit voltage (OCV) in coated NMC442/graphite pouch cells filled with control electrolyte.

Fig. 1c shows the charge-hold-discharge protocol used during the automated cycling/EIS procedure and FRA measurements. Fig. 1d shows a typical Nyquist representation of the impedance spectra collected during a FRA cycle at  $40 \pm 0.1$  °C, measured during the charge from 3.8 V to 4.5 V and discharge from 4.5 V to 3.8 V, as indicated. The "diameter" of the "semi-circular" shape, also called R<sub>ct</sub>, is a combination of the charge transfer resistances from both the positive and negative electrodes as well as resistance due to the motion of ions through the SEI layers at both the positive and negative electrodes. Fig. 1d shows that R<sub>ct</sub> increases as the potential increases during charge and decreases again as the potential decreases during discharge. Since there is no potential hold before each EIS measurement, the potential during the EIS measurement is not exactly the same as the set potential.

Fig. 2 compares  $V_{drop}$  during storage as a function of the initial OCV with different electrolyte formulations for both coated and uncoated NMC442/graphite pouch cells. Each data point in Fig. 2 represents the average of two cells and the error bars are the

standard deviation of the results. Fig. 2a and b shows  $V_{drop}$ measured after 500 h and Fig. 2c and d shows V<sub>drop</sub> measured after 30 h. Fig. 2a and c shows V<sub>drop</sub> vs. initial OCV for coated NMC442/ graphite pouch cells with the different electrolytes as indicated while Fig. 2b and d shows similar results for the uncoated cells. The detailed OCV vs. time data for the coated NMC442/graphite pouch cells stored at different potentials are given in Figs. S4a, S5a, S6a, S7a and S8a while that for the uncoated cells is given in Figs. S4b–S8b. Fig. 2a and b shows that V<sub>drop</sub> increased approximately linearly with the initial OCV for all 8 electrolytes tested which was very surprising. Figs. S4-S8 show that the potential varies very rapidly at the beginning of the storage period and that when cells are stored at high potential, the cell potential spans a large range during the storage period. Fig. 2c and d shows that the potential change, V<sub>drop</sub>, during the first 30 h of storage increases in a supralinear fashion as the initial storage potential was increased as might be expected for a process which is exponentially activated based on overpotential.

Fig. 2 shows that cells containing 2% PES in EC:EMC have either the largest or almost the largest  $V_{drop}$ , even larger than control electrolyte under all conditions. This does not match the findings of Nelson et al. [80] who found that PES additions decreased the voltage drop compared to control cells at 4.2 V. This is believed to be because the cells studied by Nelson et al. were exposed to a maximum potential of 4.2 V during formation, while the cells tested here were exposed to 4.7 V during formation.

Fig. 2 shows that the cells with control, 2% PES and 2% VC in SL:EMC generally have larger  $V_{drop}$  than the other cells under most



Fig. 2. V<sub>drop</sub> during a, b) 500 h and c, d) first 30 h of storage at 40 °C as a function of initial OCV for a, c) coated and b, d) uncoated NMC442/graphite pouch cells with the electrolytes as indicated.

conditions. Fig. 2 shows that the trend of  $V_{drop}$  vs. initial storage potential is similar for the coated and uncoated cells below 4.5 V, but deviates significantly above 4.5 V, except for the cells which have FEC:TFEC-based electrolytes. The coating appears to be beneficial for the non-fluorinated electrolytes at 4.5 V and above. Coated and uncoated cells with FEC:TFEC based electrolytes have similar  $V_{drop}$  vs. initial storage potential curves. Fig. 2 also shows that cells which contain TAP (the red dashed and blue dashed curves) generally show small values of  $V_{drop}$  at each initial storage potential.

Fig. 3a and b shows R<sub>ct</sub> (diameter of the overlapping semicircles in the impedance spectrum (see Fig. 1d)) measured at 3.8 V and 10 °C after the storage tests for both coated and uncoated NMC442/ graphite pouch cells with the electrolytes as indicated. Fig. 3a and b shows that cells with FEC:TFEC-based electrolyte had much higher impedance than cells with EC:EMC-based or SL:EMC-based electrolytes in both coated and uncoated NMC442/graphite pouch cells, which agrees with previous results [68]. Fig. 3a and b shows that TAP-containing electrolytes had high impedance in coated NMC442/graphite pouch cells and lower impedance in uncoated cells. Fig. 3a and b shows that the impedance after storage increased perhaps more strongly with increasing initial OCV for uncoated cells than for coated cells. However, cells with fluorinated electrolytes did not show a strong variation in impedance with storage potential. This is because the large impedance of full cells with FEC:TFEC electrolyte has been shown to be dominated by the SEI at the negative electrode (See Fig. 4 in Ref. [67]). When PES and/ or MMDS were used as electrolyte additives in FEC:TFEC electrolyte, the impedance decreased slightly as the voltage increased. An impedance decrease in PES and/or MMDS-containing cells after cycling or storage for a period of time has been observed before [71,80,81]. However, we do not know why the impedance decreases with storage potential for cells treated the same way. We speculate that some components of the positive electrode SEI could be oxidized away by the exposure to high potential.

Fig. 3c and d shows the volume of gas evolved during the 500 h storage tests. Fig. 3c and d shows that the gas volume produced during storage increased with the initial OCV. Fig. 3c and d shows that FEC:TFEC-based electrolyte produced more gas than EC:EMC-based or SL:EMC-based electrolytes in both coated and uncoated NMC442/graphite pouch cells. Fig. 3c and d shows that the TAP-containing electrolytes produced the least amount of gas during storage in coated NMC442 cells while in the uncoated cells, the EC:EMC-based electrolyte generally produced less gas than SL:EMC or FEC:TFEC-based electrolytes. Understanding the reasons for all the trends in Figs. 2 and 3 could take many years. We encourage other researchers to assist.

Fig. 4 shows the charge transfer resistance, R<sub>ct</sub>, as a function of



Fig. 3. a, b) Impedance after storage and c,d) gas evolution during storage for a, c) coated and b, d) uncoated NMC442/graphite pouch cells with the electrolytes as indicated.

potential measured during the FRA cycles (See Fig. 1c) for both coated (Fig. 4a-h) and uncoated (Fig. 4i-p) NMC442/graphite pouch cells with the indicated electrolytes. These cells were cycled aggressively at 40 °C on an automated cycling/EIS system using the protocol shown in Fig. 1c. All cells were cycled with clamps to ensure firm pressure. Fig. 4 shows that the impedance increased significantly with both voltage and cycle number for all cells containing EC:EMC or SL:EMC electrolyte blends. Moreover, the impedance increased much faster at high voltages than at lower voltages. Fig. 4 shows that cells containing FEC:TFEC electrolyte had obviously slower impedance growth with voltage as well as cycle number, compared to cells containing EC:EMC or SL:EMC electrolytes. With proper additive combinations such as 2% PES + 0.5% MMDS + 1% TTSPi, cells containing FEC:TFEC electrolyte show no obvious impedance rise with both voltage (3.8 V-4.5 V) and cycle number during the first 68 cycles (about 2.5 months of cycling).

Fig. 5a shows the discharge capacity as a function of cycle number for both coated and uncoated NMC422/graphite pouch cells with the indicated electrolytes during FRA cycling. Fig. 5b shows the difference between average charge and discharge voltage ( $\Delta V$ ) *vs.* cycle number for the same cells shown in Fig. 5a. A

smaller value of  $\Delta V$  means smaller polarization and thus smaller overall cell impedance [82]. Despite the promising storage performance and long term cycling (Fig. 6) for the TAP containing electrolytes and FEC:TFEC electrolyte, the potential hold at 4.5 V led to severe discharge capacity fade and overall cell impedance growth in all cells. However, compared to cells containing EC:EMC or SL:EMC electrolytes, cells containing FEC:TFEC electrolyte had much better capacity retention and slower overall cell impedance growth during the aggressive charge-hold-discharge cycling.

Fig. 6a shows the capacity *vs.* cycle number for the coated NMC442/graphite pouch cells with the indicated electrolytes. Fig. 6c shows the measured  $\Delta V vs.$  cycle number for the same cells. Cells were cycled between 2.8 V and 4.5 V at 40  $\pm$  0.5 °C using currents corresponding to C/2.3 (80 mA). A low rate C/10 cycle was included every 50 cycles to help estimate what fraction of the capacity loss was due to impedance growth during the high rate cycling. All cells were cycled with clamps. Some of the cycling data (control and 2% PES in EC:EMC) are moved to Fig. S9 to avoid clutter. Fig. S9 shows cells containing control and 2% PES in EC:EMC electrolyte have much worse capacity retention than PES 211 in EC:EMC electrolyte. Fig. 6a and c clearly show that cells containing SL:EMC



Fig. 4. The charge transfer resistance,  $R_{ct}$ , as a function of potential measured every 5 cycles for coated (4a–4h) and uncoated (4i–4p) NMC442/graphite pouch cells with the indicated electrolytes. Cells were tested at 40 °C with the protocol shown in Fig. 1c.

electrolyte with VC and TAP as electrolyte additives had much better capacity retention and slower impedance growth than cells containing EC:EMC or FEC:TFEC electrolytes. The addition of some of the electrolyte additives such as TTSPi, TMS and LiBOB increased the discharge capacity possibly due to the reduction of cell impedance [83–85].

Fig. 6b and d shows the discharge capacity and  $\Delta V$  vs. cycle number, respectively, for the uncoated NMC442/graphite pouch cells containing the indicated electrolytes. Fig. 6b and d shows that cells containing 2% TAP in EC:EMC electrolyte had severe discharge capacity fade after 200 cycles. Fig. 6b and d shows that cells containing EC:EMC electrolyte with three additive combinations lost 20% of their initial capacity after about 400 cycles regardless of the additives used in the uncoated NMC442 cells. Fig. 6b and d shows that cells containing SL:EMC electrolyte with 2% VC + 2% TAP had low discharge capacity at the beginning due to high impedance and better capacity retention than EC:EMC electrolyte with the PES211 additive combination during the first 400 cycles. However, the capacity loss accelerated after 450 cycles for cells containing SL:EMC electrolyte with 2% VC + 2% TAP. Cells containing FEC:TFEC electrolytes had much better capacity retention as well as slower overall cell polarization growth than cells containing EC:EMC or SL:EMC electrolytes, although their initial polarization was larger.

Some of the data in Fig. 6 are extremely impressive. However, the reader is cautioned of the following facts:

1. Many of the cells that cycle extremely well in Fig. 6 have high initial impedance. For examples, cells containing SL:EMC with VC and TAP as electrolyte additives do not show good capacity retention during the initial 100 cycles when operated at room temperature (19 °C) at C/2.3 to 4.4 V using CCCV cycling protocols in NMC442/graphite pouch cells (See Fig. S10). This could be due to lithium plating on the negative electrode when kinetics (transport of Li<sup>+</sup> through the negative electrode SEI) are slower at room temperature. Cells containing FEC:TFEC electrolyte still show good capacity retention during the first 350 cycles at room temperature. Cells with 2% PES + 2% DTD + 2% TTSPi in EC:EMC show the best behavior of the cells tested at room temperature .

2. If cells are operated with a constant voltage hold at the top of charge (i.e. Fig. 5), instead of constant current charge followed immediately by discharge (i.e. Fig. 6), their capacity retention will be worse. This can be reasoned based on the poor performance in Fig. 5, where a constant potential hold (24 h) at the top of charge (4.5 V) was included, compared to Fig. 6. The performance in Fig. 5 is worse due to the extended time available for electrolyte oxidation at high potential on every cycle. Academic researchers should always present results like those shown in Fig. 5 (even though they look "bad") as well as results like those shown in Fig. 6.

Fig. 7a shows the volume of gas evolved and Fig. 7b shows  $R_{ct}$  both before and after the long term testing shown in Fig. 6 for the coated cells. For reference, with respect to Fig. 7b, the initial  $R_{ct}$  of a



**Fig. 5.** a, b) discharge capacity and c, d) ΔV as a function of time and cycle number for a, c) coated and b, d) uncoated NMC442/graphite pouch cells with the indicated electrolytes during FRA cycling. Cells were tested at 40 °C with the protocol shown in Fig. 1c.

cell with control electrolyte after formation is about 50  $\Omega$  cm<sup>2</sup>. For reference with respect to Fig. 7a, the initial volume of the pouch cells is about 2.5 mL. Thus, a volume increase of 0.1 mL represents a 4% volume change. Fig. 7a shows that cells with SL:EMC based electrolytes swelled very little (<0.1 mL) during the long term cycling while those with EC:EMC-based electrolytes swelled more. Cells with 2% PES and 2% TAP in EC:EMC swelled about 0.1 mL. Fig. 7b shows that the impedance of the cells with control, 2% PES or 2% TAP in EC:EMC electrolyte increased dramatically, while the impedance of cells containing PES 211 in EC:EMC electrolyte did not show this dramatic increase due to the better impedance control by these additive combinations [11]. Fig. 7b shows cells containing SL:EMC electrolyte with VC and TAP as electrolyte during long-term cycling experiments.

Fig. 7c and d shows analogous results as Fig. 7a and b except for the uncoated cells. Fig. 7c shows that gas generation is problematic for cells with control, 2% VC + 2% TAP in SL:EMC or with 2% PES in FEC:TFEC electrolyte for the uncoated cells. Gas generation is not overly problematic for the other electrolytes in this test. Fig. 7d

shows that  $R_{ct}$  is enormous for control cells (approx. 6000  $\Omega$ -cm<sup>2</sup>) and for cells with 2% VC + 2% TAP in SL:EMC after long-term cycling experiments. Fig. 7d shows that cells containing EC:EMC or SL:EMC electrolyte have a large increase in  $R_{ct}$  while cells containing FEC:TFEC electrolyte have a decrease in  $R_{ct}$  during long-term cycling experiments. Fig. 5 shows FEC:TFEC electrolyte has better impedance control than EC:EMC or SL:EMC electrolyte cycled to 4.5 V but that the charge-discharge polarization still increases with cycling number. A comparison of Figs. 5 and 7d suggests that other sources of impedance (not only  $R_{ct}$ ) are responsible for the increase in charge-discharge polarization seen in Fig. 5. However, it is important to mention that  $R_{ct}$  reported in Fig. 7d was measured at 10 °C, while the polarization in Fig. 5 was measured during cycling at 40 °C.

# 4. Summary and conclusions

Eight electrolyte blends containing different electrolyte solvents and additives were carefully studied in both LaPO<sub>4</sub>-coated and uncoated NMC442/graphite pouch cells. The results of voltage drop



Fig. 6. a, b) Discharge capacity and c, d)  $\Delta V$ , all plotted vs. cycle number for NMC442/graphite pouch cells containing different kinds of electrolytes with different additive sets as indicated. The cycling was between 2.8 and 4.5 V at C/2.4 (100 mA) and 40  $\pm$  0.1 °C using continuous cycling protocols.



Fig. 7. Summary of (a, c) gas evolution during long-term cycling and (b, d) R<sub>ct</sub> measured at 3.8 V and at 10 °C before and after long-term cycling for (a, b) coated and (c, d) uncoated NMC442/graphite pouch cells.

and gas evolution during storage,  $R_{ct}$  after storage,  $R_{ct}$  growth and capacity retention during FRA cycling, capacity retention and overall cell impedance growth during long-term cycling were considered and compared. It was found that the voltage drop increased with initial OCV in both coated and uncoated NMC442/ graphite pouch cells. The results clearly showed the benefit of a coating layer at 4.5 V or above while there was no obvious benefit at 4.3 V or 4.4 V. Electrolyte formulations also strongly impacted the storage performance. While TAP containing electrolytes gave the

smallest voltage drop and least amount of gas evolution during storage in the coated NMC442/graphite cells, FEC:TFEC based electrolytes generally showed the smallest voltage drop in uncoated NMC442/graphite cells at high potential.

The automated EIS/cycling results showed that FEC:TFEC based electrolytes were effective in controlling the impedance growth during aggressive charge-hold-discharge cycling to 4.5 V and at 40 °C in both coated and uncoated NMC442/graphite cells. By contrast, cells containing EC:EMC or SL:EMC electrolytes all

suffered from severe impedance growth at 4.5 V. Long-term cycling results further proved that the TAP containing electrolytes performed better in the coated NMC422 cells while the FEC:TFEC electrolyte generally performed better in the uncoated NMC422 cells.

This work also shows that different electrolytes have different behavior in different material systems (coated vs. uncoated). It is clear that coatings, electrolyte solvents and electrolyte additives all play a role in determining the final cell performance. Successfully operating Li-ion cells to high voltage may require a combination of all these strategies.

This work was mainly focussed on NMC442/graphite cells charged to high potentials. FEC:TFEC-based electrolytes show promise for cycling at high potential by limiting the impedance growth (although initial impedance is high). However gas evolution at high potentials was still a problem even when gas reducing additives like PES were added. The gassing problem of FEC:TFECbased electrolytes may be due to the use of large amounts of FEC which is apparently not stable at high temperature and/or high potentials [76]. Alternative solvents are required. We encourage other researchers to assist in the search.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jpowsour.2016.08.100.

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