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The effect of electrolyte additives on both $LaPO_4$-coated $Li(Ni_{0.4}Mn_{0.4}Co_{0.2})O_2$ and uncoated $Li(Ni_{0.4}Mn_{0.4}Co_{0.2})O_2$ in Li-ion pouch cells

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HIGHLIGHTS

- Electrolyte additives are more effective than a $LaPO_4$ coating for improving lifetime.
- A $LaPO_4$ coating is more valuable at 4.5 V.
- State-of-the-art electrolyte additives that improve high voltage lifetime are discussed.

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ABSTRACT

The effectiveness of some selected electrolyte additive blends were systematically studied in Li $[Ni_{0.4}Mn_{0.4}Co_{0.2}]O_2$/graphite and 3 wt% $LaPO_4$-coated $Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O_2$/graphite pouch cells using *ex-situ* gas measurements, ultra high precision coulometry, automated storage experiments, long-term cycling and electrochemical impedance spectroscopy. For cells tested to an upper cutoff potential of 4.4 V the $LaPO_4$-coating provided no benefit when state-of-the-art electrolyte additives were used. For cells tested to 4.5 V, the $LaPO_4$ coating appeared to limit electrolyte oxidation slightly and resulted in better capacity retention compared to uncoated cells for cells with state-of-the-art electrolyte additives. However, even for cells tested to 4.5 V, the benefits of the additives far outweighed the benefits of the coating. This suggests literature papers that compare the impact of coatings on positive electrode materials in cells that contain electrolytes without electrolyte additives have limited value.

1. Introduction

The development of high voltage Li-ion batteries is one of the best ways to increase their energy density. State-of-the-art electrolytes include cyclic and linear carbonates which are prone to failure at high voltages [1]. A main contributor to this failure is the electrochemical oxidation reactions between the charged positive electrode and electrolyte at high potentials [2,3]. Surface coatings on the positive electrode, as well as the use of electrolyte additives, have been shown to lead to longer life time, higher energy density and improved safety [4–8]. Surface coatings can form a physical protective layer between the electrolyte and positive electrode material [9–11], however, many apparently effective coatings have been shown to consist of an incomplete layer of nanoparticles [12,13]. Minimizing cathode/electrolyte interactions reduces undesired side-reactions during charge–discharge cycling that diminish cell lifetime. In a similar way, electrolyte additives are believed to function by forming or modifying a solid electrolyte interface (SEI) layer on the surface of the positive or negative electrode thus impacting the cycle life, calendar life and safety of Li-ion batteries [9,10].

Despite numerous efforts devoted to finding the best coating materials or the best electrolyte additives, no comparative studies of the effects of electrolyte additives upon the charge–discharge cycling behavior of the commercial-type Li-ion cells with coated and uncoated cathodes have been reported. Such studies would bring the battery community one step closer to understanding how

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surface coatings work and whether electrolyte additives can further improve the performance of the Li-ion cells with a coated positive electrode. In addition, it is very important to determine whether the "best electrolyte additives" used in cells with uncoated positive electrodes can have equal or better performance and lifetime to cells with coated positive electrodes containing electrolyte additives. This would help researchers decide whether to focus on electrolyte additives, on coatings or on both.

Tarnopolskiy et al. [14] studied the impact of over 40 electrolyte additives in cells with 4.7 V $LiNi_{0.5}Mn_{1.5}O_4$ positive electrodes. Of all the electrolyte additives studied, only two, succinic anhydride and methyl succinic anhydride were found to provide a benefit in limiting electrolyte oxidation at the positive electrode, but even so, the coulombic efficiencies (CE) measured at C/2 and room temperature were at most 99.5%. The CE would be approximately 95% measured at C/20 at room temperature and far worse at elevated temperature based on the work of Smith et al. [15]. It is suggested that the potential of $LiNi_{0.5}Mn_{1.5}O_4$ is simply too high for known electrolytes to function.

Recently, $Li(Ni_{0.4}Mn_{0.4}Co_{0.2})O_2$ (NMC442) has been used as a canonical trial material in studies of problems one encounters in high voltage Li-ion cells. This is because NMC442 has a voltage, V, vs. capacity, Q, relation where V varies almost linearly with Q between 4.1 and 4.7 V so that the dependence of CE and other properties can be measured as the upper cutoff potential is sequentially increased. Nelson et al. [16] and Ma et al. [7] showed that impedance growth in NMC442/graphite pouch cells charged to 4.4 V and above is perhaps the major obstacle to high voltage NMC cells and that this can be mitigated by the use of electrolyte additives. Through symmetric cell studies, Petibon et al. [17] showed that the majority of the impedance growth occurs at the positive electrode. This suggests that electrolyte/positive electrode reaction - electrolyte oxidation – is the major problem that must be overcome.

Song et al. [18] showed that a 3% by weight coating of $LaPO_4$ on $Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O_2$ (NMC532) was very effective at improving charge–discharge capacity retention, compared to uncoated materials, in Li/NMC532 coin cells with 1 M $LiPF_6$ ethylene carbonate/dimethyl carbonate (EC/DMC) (50:50 vol.%) electrolyte. The effects of electrolyte additives were not investigated by Song et al. Tsunozaki et al. [19] explored the use of many coating materials on NMC532 and showed benefit but did not consider the effects of electrolyte additives. Paulsen et al. [20] show the benefit of many different coatings on many different electrode materials but do not consider the impact of electrolyte additives at all. Yuan et al. [21] investigated different coating materials on different positive electrode materials but did not consider the effect of any electrolyte additives. Yun et al. [22] studied coatings of porous metal films, porous metal oxide films or porous carbon film on different positive electrode materials. They showed the coated materials had improved rate capability and capacity retention but did not consider the effect of any electrolyte additives.

In this paper, the effect of several electrolyte additive blends on the performance of both $LaPO_4$-coated NMC442/graphite and uncoated NMC442/graphite pouch cells were compared head to head. Experiments were made using ultra high precision coulometry (UHPC) [23], a precision storage system [24] and electrochemical impedance spectroscopy (EIS) [25]. Coulombic efficiency (CE), charge end point capacity slippage, voltage drop during storage experiments as well as long-term cycling stability were compared to make an overall evaluation of the effect of electrolyte additives in both coated and uncoated NMC442/graphite Li-ion cells. These results should be of great interest to battery manufacturers and researchers who want to develop high voltage Li-ion cells with longer life time.

2. Experimental

1 M $LiPF_6$ EC/EMC (3:7 wt.% ratio, BASF, 99.99%) was used as "control" electrolyte in the studies reported here. To this electrolyte, additives were added either singly or in combination with other additives. Additive components were added at 1 or 2 wt.% in the electrolyte. The reasons for choosing some of these additives and their combinations are explained in Ref 7 and depicted in detail in Supporting Information. Tri allyl phosphate (TAP) was not included in the studies of Ref. 7, but was chosen because Xia et al. [26] showed that TAP is a useful additive in high voltage NMC cells. The purities and the suppliers of the additives used are listed in Table 1 and the structure information of these additives is given in Fig. S1.

The 402035-size pouch cells used in this study were uncoated $Li[Ni_{0.42}Mn_{0.42}Co_{0.16}]O_2$ (NMC442)/graphite cells with a capacity of 240 mAh and $LaPO_4$-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. The coated positive electrode material was coated with 3 wt% of $LaPO_4$ which appears as nanoparticles on the NMC particle surfaces. The $LaPO_4$ coating was performed at 3M 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 with the capacity ratio of negative electrode to positive electrolyte (N/P ratio) of about 1.2. That means that Li-plating will not occur at any voltage below 4.7 V. The bottom panels in Figs. S2 and S3 show SEM images and EDS spectra taken from the fresh positive and negative electrodes from both type of pouch cells to show the morphology of the particles that make up the electrodes. The pouch cells were manufactured by Li-Fun Technology (Zhuzhou, China). The uncoated positive electrodes contained 96:2:2 by weight of active material, binder and carbon black, respectively, while the coated electrodes contained 93:3:2:2 by weight of active material, $LaPO_4$, binder and carbon black. 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 any residual water. The cells were then transferred immediately to an argon-filled glove box for filling and vacuum sealing. The NMC442/graphite pouch cells were filled with 0.75 mL (0.90 g) of electrolyte. After filling, cells were vacuum-sealed with a compact vacuum sealer (MSK-115A, MTI Corp.). Then cells were placed in a temperature box at 40.°C where they were held at 1.5 V for 24 h, to allow for the completion of wetting. Cells were then charged at 12 mA (C/20) to 3.5 V. This step is called formation step 1. After formation step 1, cells were transferred into the glove box, cut open to release any gas generated and vacuum sealed again. These cells were then charged again from 3.5 V at 12 mA (C/20) to 4.5 V. This

Table 1
List of abbreviations, additives used and additive purity, as well as their suppliers.

Additive	Purities	Supplier
PES - prop-1-ene-1,3-sultone	98.20%	Lianchuang Medicinal Chemistry Co., Ltd., China
DTD - 1,3,2-Dioxathiolane-2,2-dioxide– also called ethylene sulfate	98%	Sigma–Aldrich
MMDS - 1,5,2,4-dioxadithiane-2,2,4,4-tetraoxide – also called methylene methane disulfonate	>98.7%	Tinci Materials Technology
TTSPi - tris(trimethylsilyl) phosphite	≥95.0% (GC)	Sigma–Aldrich
TAP - triallyl phosphate	>99%	TCI America
SN - succinonitrile	>99%	Acros Organics
ADN - adiponitrile	99%	Sigma–Aldrich

step is called formation step 2. After formation step 2, the cells were transferred into the glove box, cut open to release any gas generated and then vacuum sealed again. These degassing voltages were selected based on the in-situ gas evolution experiments [27] that show most of the gas evolves in the formation step at voltages below 3.5 V and then more gas is evolved above 4.3 V. After the two degassing processes, cells were then discharged to 3.8 V where impedance spectra were measured at 10.°C.

The cycling/storage procedure was carried out using the Ultra High Precision Charger (UHPC) at Dalhousie University [23]. Testing was between 2.8 and 4.4 V at 40. ±0.1 °C. Cells were first charged to 4.400 V using currents corresponding to C/10, then stored open circuit for 20.00 h and then discharged to 2.800 V using currents corresponding to C/10. This process was repeated on the UHPC for 15 cycles. The cycling/storage procedure was designed so that the cells were exposed to higher potentials for significant fractions of their testing time. All pouch cells were cycled without clamps so there was no applied stack pressure apart from that generated by vacuum sealing. For long-term storage experiments, cells were first discharged to 2.8 V and charged to 4.5 V twice at 40. ±0.1 °C. Then the cells were held at 4.5 V until the measured current decreased to 0.0025 C. A Maccor series 4000 cycler was used for the preparation of the cells prior to storage. After the pre-cycling process, cells were carefully moved to the storage system which monitored their open circuit voltage, recording the voltage every 6 h during 500 h of storage [24]. Storage experiments were made at 60. ±0.1 °C.

Ex-*situ* (static) gas measurements were used to measure gas evolution during formation and during cycling [28]. The measurements were made using Archimedes' principle with cells suspended from a balance while submerged in liquid. The changes in the weight of the cell suspended in fluid, before and after testing are directly related to the volume changes by the change in the buoyant force. The change in mass of a cell, Δm, suspended in a fluid of density, ρ, is related to the change in cell volume, Δv, by

$$\Delta v = -\Delta m/\rho \tag{1}$$

Ex-situ measurements were made by suspending pouch cells from a fine wire "hook" attached under a Shimadzu balance (AUW200D). The pouch cells were immersed in a beaker of deionized "nanopure" water (18.2 MΩ) that was at 20. ±1 °C for measurement.

Electrochemical impedance spectroscopy (EIS) measurements were conducted on NMC111/graphite pouch cells after formation and after cycling on the UHPC [25]. Cells were charged or discharged to 3.80 V before they were moved to a 10. ±0.1 °C temperature box. Alternating current (AC) impedance spectra were collected with ten points per decade from 100 kHz to 10 mHz with a signal amplitude of 10 mV at 10. ±0.1 °C. A Biologic VMP-3 was used to collect these data. The experimental setup did not allow for reproducible solution resistance measurements due to cable and connector impedance. Therefore, all impedance spectra were shifted to 0 on the real axis at the highest frequency measured.

3. Results and discussion

Fig. 1 shows the differential capacity (dQ/dV) vs. V curves for both coated and uncoated NMC442/graphite pouch cells with

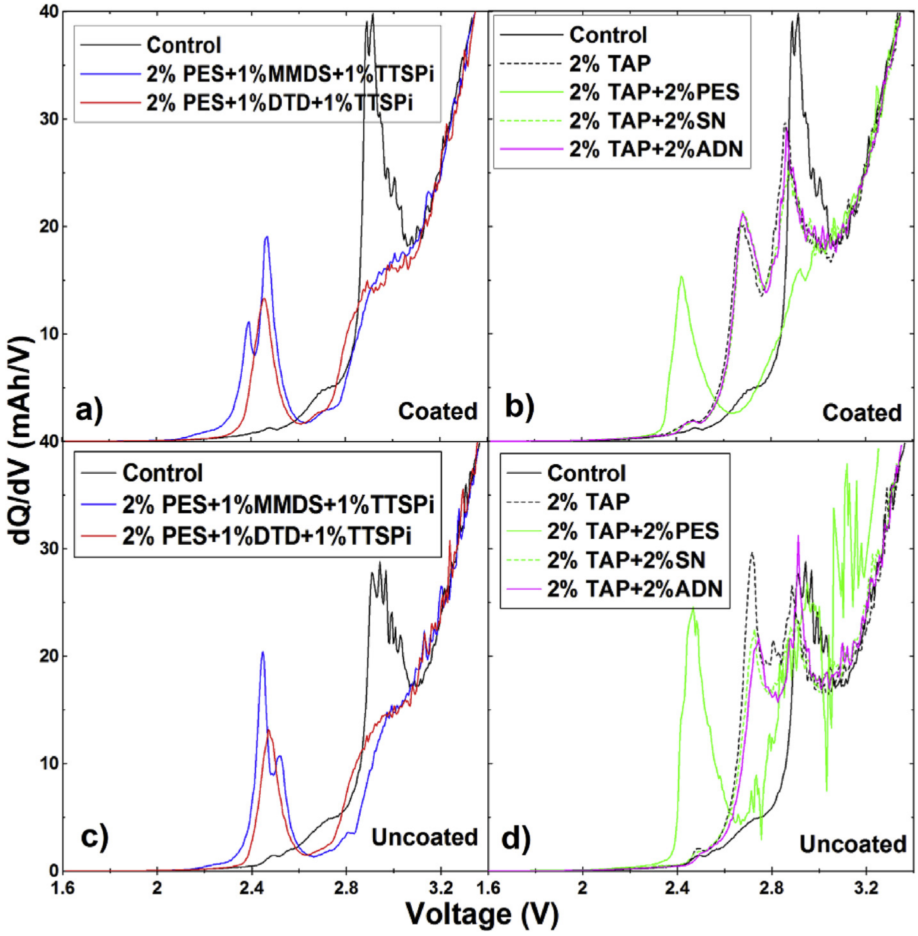

Fig. 1. Differential capacity (dQ/dV) versus voltage (V) during the formation step 1 for the both coated and uncoated NMC/graphite pouch cells with different electrolyte additives as indicated.

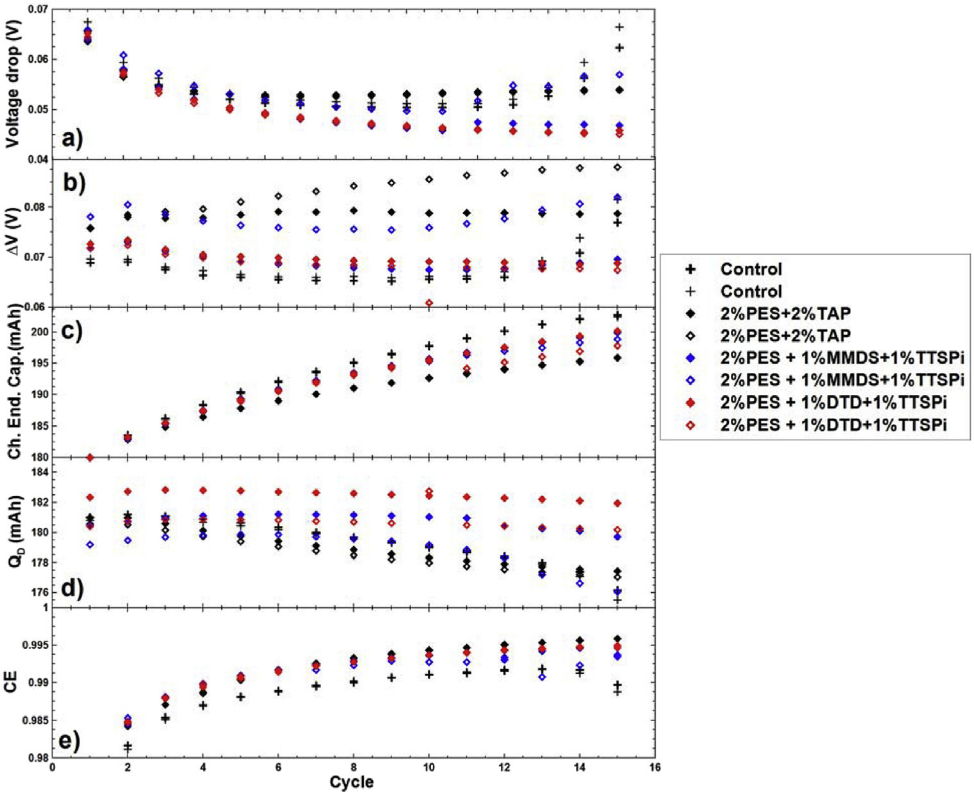

Fig. 2. Typical data collected on the UHPC including: V_{drop}, ΔV, the charge endpoint capacity, the discharge capacity, and CE. All are plotted versus cycle number for $LaPO_4$-coated NMC442/graphite cells with different electrolyte additives as indicated. These cells were cycled using the protocol shown in Fig. S4a.

different additive combinations during formation step 1. From the dQ/dV vs. V curves, one can infer at which potential the additives initially react with $Li^+ + e^-$ at the graphite electrode. Fig. 1 shows that no matter which additives were used, the peak positions in the dQ/dV vs. V curves were the same for the same additives in both types of pouch cells, confirming, as expected, that the $LaPO_4$ coating on the cathode does not have an obvious impact on the reaction of the additives with $Li^+ + e^-$ at the graphite surface.

In real devices, Li-ion cells are often left at open circuit for extended periods after charging. Therefore, it is important and practical to study the effect of extended periods at high voltage on impedance growth and cycling performance. The cycling/storage protocol used in the UHPC studies was designed for this purpose. The details of cycling/storage protocol are shown in Fig. S4 as well as in Ref. [29]. One issue with the method selected is that cells that have more electrolyte oxidation have larger voltage drops and thus are exposed to a lower average potential during the open circuit period than cells that are more resistant to electrolyte oxidation. Fig. S4 shows that the cells with the cycle/store protocol have much worse CE than cells with continuous cycling. Obviously, the cycle/store procedure is much more aggressive than continuous cycling since cells are exposed to high potentials for larger fractions of time.

Fig. 2 shows the typical cycling/storage data collected using the UHPC during some of these experiments on $LaPO_4$-coated NMC442/graphite pouch cells. Four electrolyte additive blends including control, 2% PES+ 2% TAP, 2% PES +1% DTD +1% TTSPi and 2% PES +1% MMDS +1% TTSPi were selected for comparison. From top to bottom, the 5 panels in Fig. 2 show: the voltage drop during the 20 h storage period at the beginning of each cycle, V_{drop} (see Fig. S4a); the difference between the average cell voltage during charge and the average cell voltage during discharge, ΔV; the charge endpoint capacity; the discharge capacity; and the coulombic efficiency (CE), all plotted versus cycle number. The differences in V_{drop} from cell to cell are caused by differences in the rate of the electrolyte oxidation on the positive side [30] and also by differences in DC cell resistance which affects the rapid voltage change when the cells switch from charge to open circuit. Differences in ΔV are caused by differences in cell polarization during cycling and smaller values of ΔV generally indicate lower DC resistance [31]. Therefore some degree of correlation is expected between V_{drop} and ΔV in Fig. 2a and b.

Fig. 2e shows cells with these additive combinations had higher CE than that of control cells. Fig. 2d shows cells containing 2% PES +1% DTD +1% TTSPi had better capacity retention than cells with other combinations. Fig. 2c shows cells with 2% PES+ 2% TAP had lower charge endpoint capacity slippage than other cells, suggesting cells with 2% PES+ 2% TAP had less electrolyte oxidation on the positive electrode. Fig. 2a and b shows that V_{drop} and ΔV for control cells rises rapidly during the last five cycles due to impedance growth. By contrast, cells with other additives combinations do not show this rapid increase during the last 5 cycles tested.

Fig. 3a summarizes the coulombic inefficiency (CIE = 1 − CE) for the selected electrolyte additive blends which were tested in both coated and uncoated NMC442/graphite cells at 40. ±0.1 °C on UHPC. The detailed CE vs cycle number data are given in Figs. S5a, S6a, S7a and S8a in the Supporting Information. Each data point in Fig. 3 represents the average of two cells and the error bars are the standard deviation of the results. The CIE is calculated from the CE taken as an average of the final three data points (cycles 13–15) collected on the UHPC (see Fig. 2e). Smaller values of CIE mean the cells had higher CE and therefore one expects longer cycle and calendar life. Fig. 3a shows that additive combinations which have lower CIE (better CE) in coated NMC442/graphite cells also have lower CIE in uncoated NMC442/graphite cells. Electrolyte additive

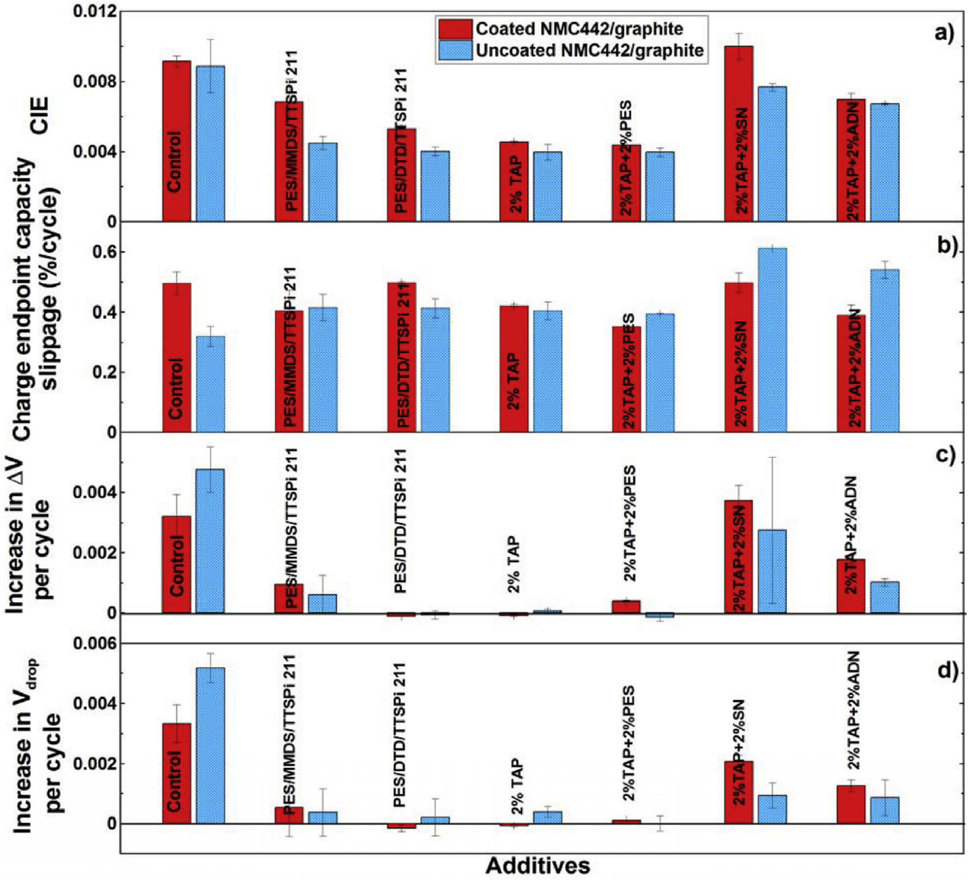

Fig. 3. Summary of the high precision data using the cycle/store protocol in UHPC (C/10, 40 °C, 20 h store at top of charge which was 4.4 V) including: (a) coulombic inefficiency (CIE); (b) percentage charge endpoint capacity slippage (the percentage of cell capacity by which the charge endpoint slips each cycle); (c) slope of ΔV versus cycle number and (d) slope of V_{drop} during the 20 h storage period versus cycle number for both $LaPO_4$-coated and uncoated NMC442/graphite cells with different electrolyte additives as indicated. These cells were cycled using the protocol shown in Fig. S4a.

sets such as 2% PES +1% MMDS +1% TTSPi, 2% PES +1% DTD +1% TTSPi, 2% TAP and 2% TAP +2% PES showed low CIE in both coated and uncoated NMC442/graphite pouch cells. All uncoated NMC442/graphite cells have lower CIE than coated NMC442/graphite cells.

Fig. 3b summarizes the charge endpoint capacity slippage for the selected electrolyte additive blends tested in both coated and uncoated NMC442/graphite cells at 40. ±0.1 °C using the protocol in Fig. S4. Detailed charge endpoint capacity vs cycle number data are given in Figs. S5c, S6c, S7c and S8c in the Supporting Information. The charge endpoint capacity slippage was calculated from the slope of a best fit line to the final five points (cycles 11–15) of the charge endpoint capacity versus cycle number curves (see Fig. 2c). Charge endpoint capacity slippage is caused by undesired reactions such as electrolyte oxidation or transition metal dissolution at the positive electrode [32]. Fig. 3b shows that the charge endpoint capacity slippage is similar for coated and for uncoated cells which incorporate additives that give low CIE (i.e. 2% PES +1% DTD +1% TTSPi, 2% TAP and 2% TAP +2% PES). Control cells, cells with 2% TAP +2% SN and cells with 2% TAP +2% ADN show larger charge endpoint capacity slippage and also greater differences between coated and uncoated cells.

Fig. 3c and d shows that control cells, cells with 2%TAP +2%SN and cells with 2% TAP +2%ADN exhibit marked impedance growth as both the charge–discharge polarization and the voltage drop during storage increase markedly per cycle, suggesting these additive mixtures and also control electrolyte are not competitive. Fig. 3c and d shows that all cells (i.e. both coated or uncoated) with 2% PES +1% DTD +1% TTSPi, 2% TAP and 2% TAP +2% PES additive blends have very small impedance growth during the UHPC cycling. For interested readers, detailed ΔV and V_{drop} vs cycle number data are given in Figs. S5d, S6d, S7d, S8d and S9 in the Supporting Information. Fig. 3c and d shows that the impedance growth rate is lower for coated cells than uncoated cells when control electrolyte is used. This may be one reason why coatings are given such attention in the literature where electrolytes without additives are generally used in comparative studies of positive electrode materials with and without coatings. However, when additives are used, the distinction between cells with coated and uncoated NMC442 becomes less clear and, if anything, uncoated cells perform better in the UHPC cycling protocol used here.

Fig. 4a shows typical open circuit voltage (OCV) versus time during 500 h storage at 60. ±0.1 °C for $LaPO_4$-coated NMC442/graphite cells. V_{drop} during storage indicates the occurrence of electrolyte oxidation at the positive electrode and has been shown to correlate well with charge endpoint capacity slippage [31]. That is, cells with large charge endpoint capacity slippage during cycling normally have large voltage drops during storage. Fig. 5 explores this relationship by plotting the charge endpoint capacity slippage measured during UHPC cycling (40 °C, 4.4 V, protocol in Fig. S4a) versus the voltage drop during the 500h storage (60.°C, 4.5V). Fig. 5b shows an excellent correlation for cells with uncoated NMC442 electrodes, apart from the cell with control electrolyte (data point highlighted). Control cells have artificially small charge endpoint capacity slippage due to impedance growth during UHPC

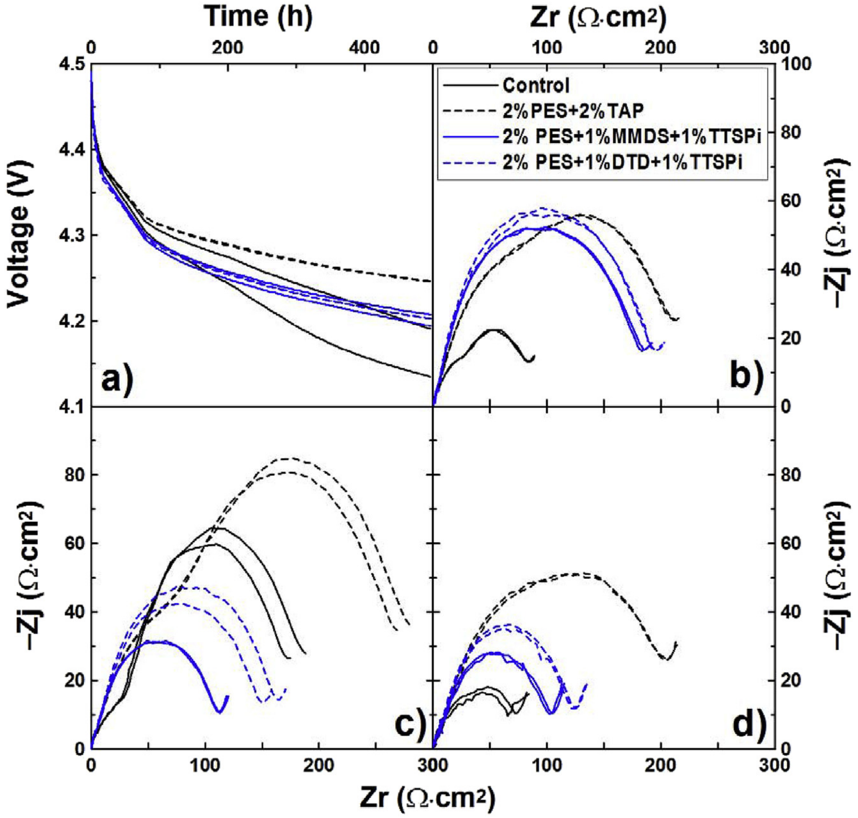

Fig. 4. Typical data for a) open circuit voltage versus time during storage at 4.5 V and 60 °C and b) impedance spectra after formation, c) after UHPC cycling (Fig. 2 and 3) and d) after storage at 60. ±0.1 °C. All the data in Fig. 4 is for $LaPO_4$-coated NMC442/graphite cells.

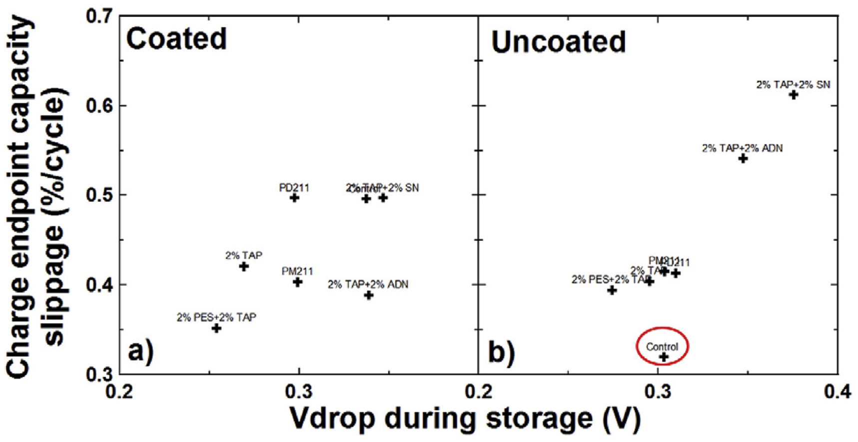

Fig. 5. Percentage charge endpoint capacity slippage per cycle (40 °C, C/10 with 20 h hold at TOC at 4.4 V, 15 cycles) plotted versus V_{drop} during storage (60.°C, 4.5 V, 500 h) for a) $LaPO_4$ coated and b) uncoated NMC442/graphite cells.

testing, leading to cells reaching the upper cutoff potential early. Fig. 5a shows that the correlation between the storage and UHPC results is less clear for the cells with $LaPO_4$-coated NMC442. This may be because the coating causes different responses at 40.°C and at 60.°C.

Fig. 4b, c and d show impedance spectra taken from $LaPO_4$-coated NMC442/graphite cells after formation, after UHPC cycling and after 500 h of 60.°C storage, respectively. The EIS measurements were made at 10.°C with a cell voltage of 3.80 V. The diameter of the semicircle represents the sum of the charge-transfer resistances, R_{ct}, at both the positive and negative electrodes. A comparison of Fig. 4b and c shows that cells with control electrolyte show a significant increase in R_{ct} during UHPC cycling at 40 °C while cells with 2% PES +2% MMDS +2% TTSPi or 2% PES +1% DTD +1% TTSPi show a decrease in R_{ct}.

Fig. 6a summarizes the voltage drop during 500 h storage (60.°C, 4.5 V) for both coated and uncoated NMC442/graphite cells. Fig. 6a shows V_{drop} for all cells with additives are similar to control in the uncoated NMC442/graphite cells, except for cells with nitrile additives, which are significantly worse. For $LaPO_4$-coated cells, the additives 2% TAP and 2%TAP +2%PES give the best storage behavior, while again, cells with nitriles are significantly worse.

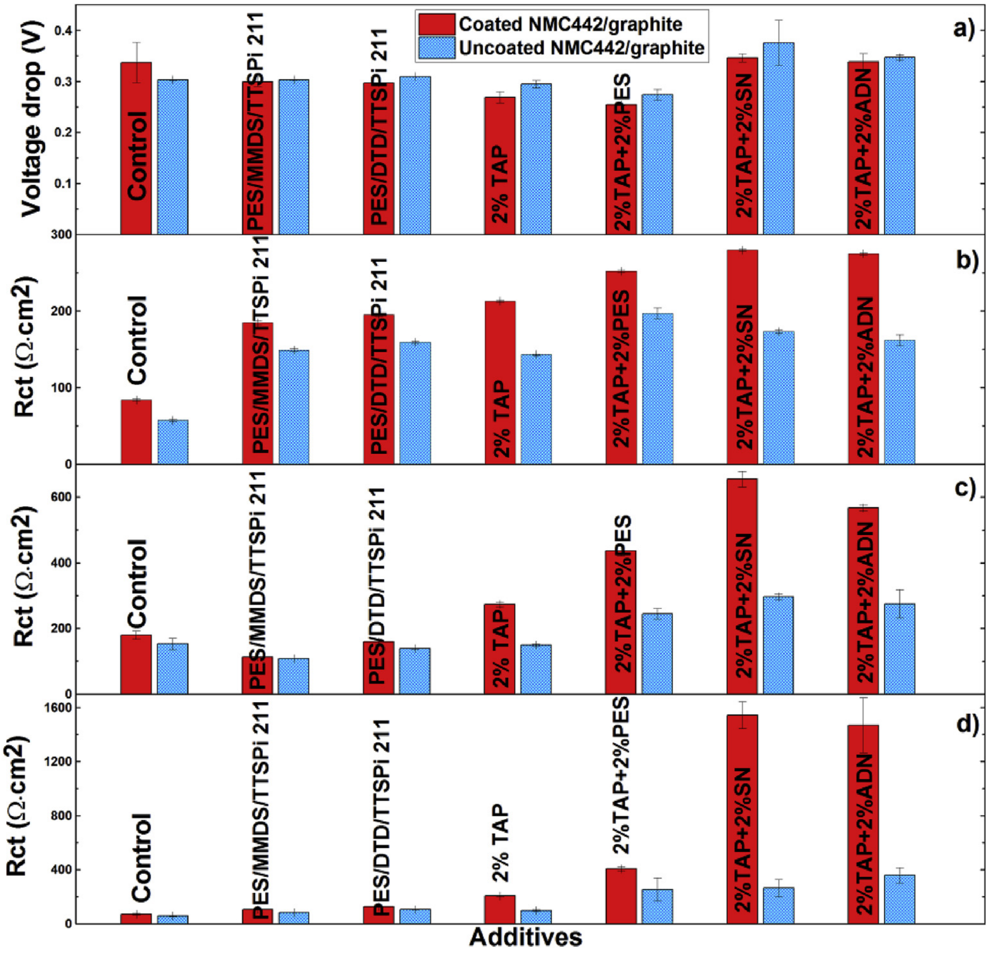

Fig. 6. Summary of (a) V_{drop} during 500 h storage at 4.5 V and 60 °C; (b) R_{ct} after formation; (c) R_{ct} after UHPC cycling (40 °C, C/10 with 20 h hold at TOC at 4.4 V, 15 cycles) and (d) R_{ct} after storage at 4.5 V and 60. ±0.1 °C.

Fig. 6b, c and d show a summary of EIS data after formation, after UHPC cycling (40 °C, protocol shown in Fig. S4a) and after the 500 h storage test (60.°C, 4.5 V), respectively. Fig. 6b shows that all the coated NMC442/graphite cells have larger impedance after formation than the uncoated NMC442/graphite cells, indicating $LaPO_4$ coating on the positive electrode surface increases the impedance. Fig. 6c (note the change of vertical scale compared to Fig. 6b) shows that the impedance of cells containing control, 2% TAP + 2% PES, 2% TAP + 2% SN or 2% TAP + 2% ADN increased substantially after UHPC cycling while the impedance of cells containing 2% PES + 1% MMDS + 1% TTSPi and 2% PES + 1% DTD + 1% TTSPi decreased after UHPC cycling. The impedance of cells containing 2% TAP was nearly the same as before cycling. Fig. 6d (note the change of scale in Fig. 6d) shows that the impedance after storage has the same basic trends as the EIS data after UHPC cycling. Minimizing impedance growth during cycling or storage is very important to ensure long-lived cells with acceptable rate capability. PES-containing cells as well as cells with 2% TAP (but no nitriles), which have small impedance growth, and the highest CE, should impart longer cycle life and calendar life.

Fig. 7a, b, c and d show the volume of gas produced in both $LaPO_4$-coated and uncoated NMC442/graphite pouch cells with some selected electrolyte additive blends during formation step 1, formation step 2, UHPC cycle-storage at 40. ±0.1 °C and during 500 h of storage at 60. ±0.1 °C and 4.5 V Fig. 7a and b shows that PES-based electrolyte blends produced much less gas than control or TAP-based electrolyte additive blends during formation steps 1 and step 2, which is expected based on the properties of PES [34,35]. Fig. 7c (notice the significant change of scale between the panels of Fig. 7) shows the TAP-based electrolyte additive blends produced less gas than control or PES-based electrolyte blends during the UHPC cycle-store testing at 40 °C (protocol shown in Fig. S4a). Fig. 7c also shows the coated NMC442/graphite cells produced more gas than the uncoated NMC442/graphite cells during the UHPC cycle-store process. However, all of these cells produced less than 0.1 mL gas during UHPC cycling. Fig. 7d shows the gas evolution during 500 h storage at 4.5 V and 60. ±0.1 °C. The volume change at 60. ±0.1 °C was much larger than that at 40. ±0.1 °C, indicating the side-reactions in the cells are temperature-dependent [36]. Readers are reminded that storage tests at 4.5 V and 60. ±0.1 °C are very challenging for any Li-ion cells. Based on the storage experiments at 60. ±0.1 °C, cells containing 2% TAP +2% PES are most interesting because they had the lowest voltage drop during storage (see Fig. 6a) and produced the least amount of gas during storage (Fig. 7d). Additionally, impedance growth for cells with 2% PES +2% TAP is small as shown in Fig. 7b, c and d.

Fig. 8a and b shows the capacity versus cycle number results for both $LaPO_4$-coated and uncoated NMC442/graphite pouch cells with some selected electrolyte additive blends. All cells were continuously cycled between 2.8 V and 4.5 V at 40. ±0.5 °C using currents corresponding to C/2.4 (80 mA for the $LaPO_4$-coated and 100 mA for the uncoated). The long-term cycling cells were the

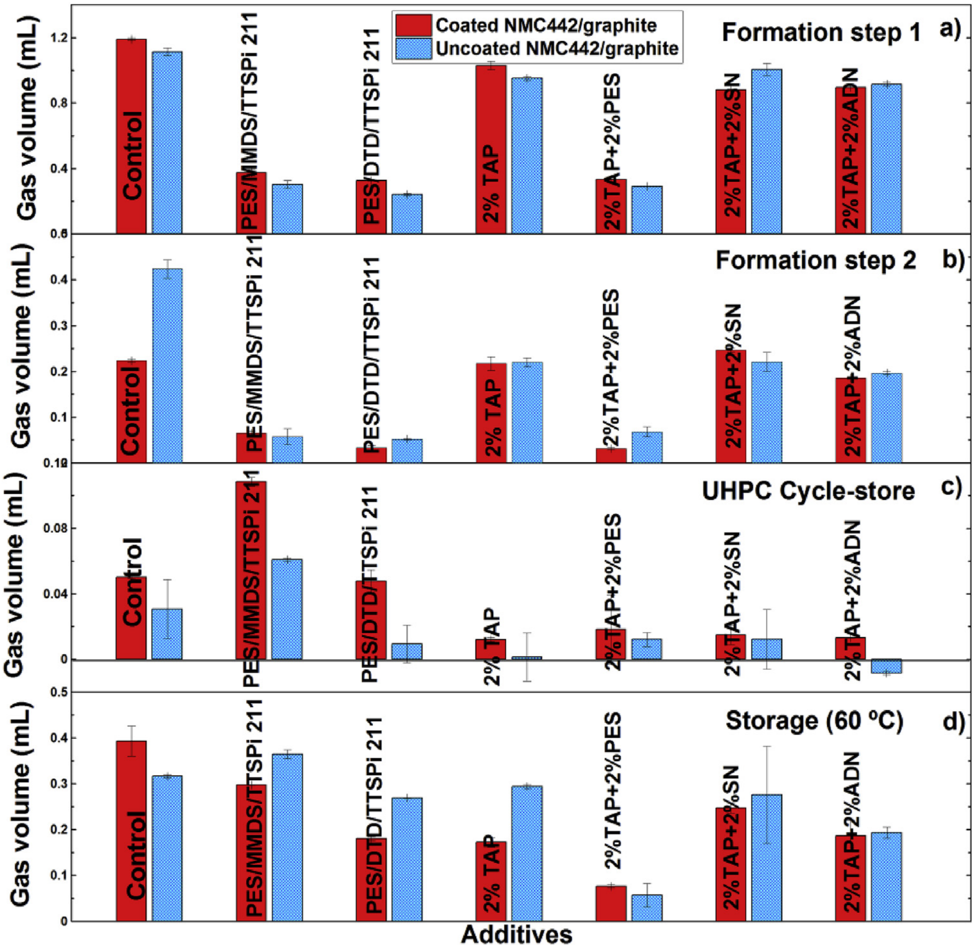

Fig. 7. Volume of gas evolved during (a) formation step 1, (b) formation step 2, (c) the 600 h UHPC cycle/store testing at 40.0 ± 0.1 °C and (d) the 500 h storage period at 60.0 ± 0.1 °C for $LaPO_4$ coated and uncoated NMC442/graphite cells.

same cells used for the UHPC cycling experiments and the long-term cycling began immediately after the UHPC cycling completed. Fig. 8c and d shows the difference between average charge and discharge voltage (ΔV) vs cycle number for the same cells shown in Fig. 8a and b, respectively. Fig. 8a and b shows the control cells have much less capacity fade when the NMC442 is coated with $LaPO_4$, indicating the $LaPO_4$ coating gives a benefit when cells are charged to higher voltage and when electrolyte additives are not used. Both $LaPO_4$-coated and uncoated cells with the electrolyte additive sets 2% PES +1% MMDS +1% TTSPi, 2% PES +1% DTD +1% TTSPi and 2% TAP +2% PES show the best capacity retention. These results agree well with the CE results in Fig. 3a which show these electrolyte blends have lower CIE than other electrolyte blends. The coated NMC442/graphite pouch cells with these additive sets could cycle more than 500 times to an upper cutoff of 4.5 V at 40 °C with less than 20% capacity loss, which is very promising for application in real devices.

The $LaPO_4$ coating certainly provides a benefit in capacity retention when control electrolyte is used. When additives are employed, the impact of the coating was less apparent but still beneficial even when state-of-the-art additives like 2% PES +1% MMDS +1% TTSPi, 2% PES +1% DTD +1% TTSPi or 2% PES +2% TAP are used. However, the benefit of the additives is larger than the benefit of the coating.

Figs. S10a and S10b show a summary of EIS and volume change data collected after long-term cycling for the same cells shown in Fig. 8. The detailed EIS spectra are shown in Figs. S11 and S12. For cells containing control, 2% TAP +2% SN or 2% TAP +2%ADN, the impedance was measured when the cells had zero capacity (cells had died). These results are less meaningful to compare the R_{ct} after cycling with these additives since the scanned frequency (100 kHz–10 mHz) did not cover the whole semi-circle (see Fig. S11). The results in Fig. S10a show the same trends as the EIS data after UHPC cycling as shown in Fig. 6c. That is, the coated cells show higher impedance after long-term cycling than the uncoated cells. Moreover, cells containing 2% PES +1% MMDS +1% TTSPi and 2% PES +1% DTD +1% TTSPi still have reasonable impedance and manageable gas after ~500 cycles.

Figs. S2 and S3 show scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) spectra of positive and negative electrodes taken from fresh cells and cells containing 2% TAP electrolyte additive after 300 cycles (as shown in Fig. 8). The cycled cells were fully discharged before they were opened. Electrodes were not rinsed, only left to dry before SEM and EDS were taken. The SEM images in Figs. S2 and S3 show the positive electrode did not change much after cycling. However, some reaction products appeared on the surface of the negative electrode, which agrees with previous results [33]. The EDS spectra show that comparable amounts of Mn were found in the negative electrodes of both coated and uncoated NMC442/graphite cells. In the coated cells, lanthanum was observed only on the positive electrode, even after cycling. This suggests that the $LaPO_4$ coating is well adhered to the active material.

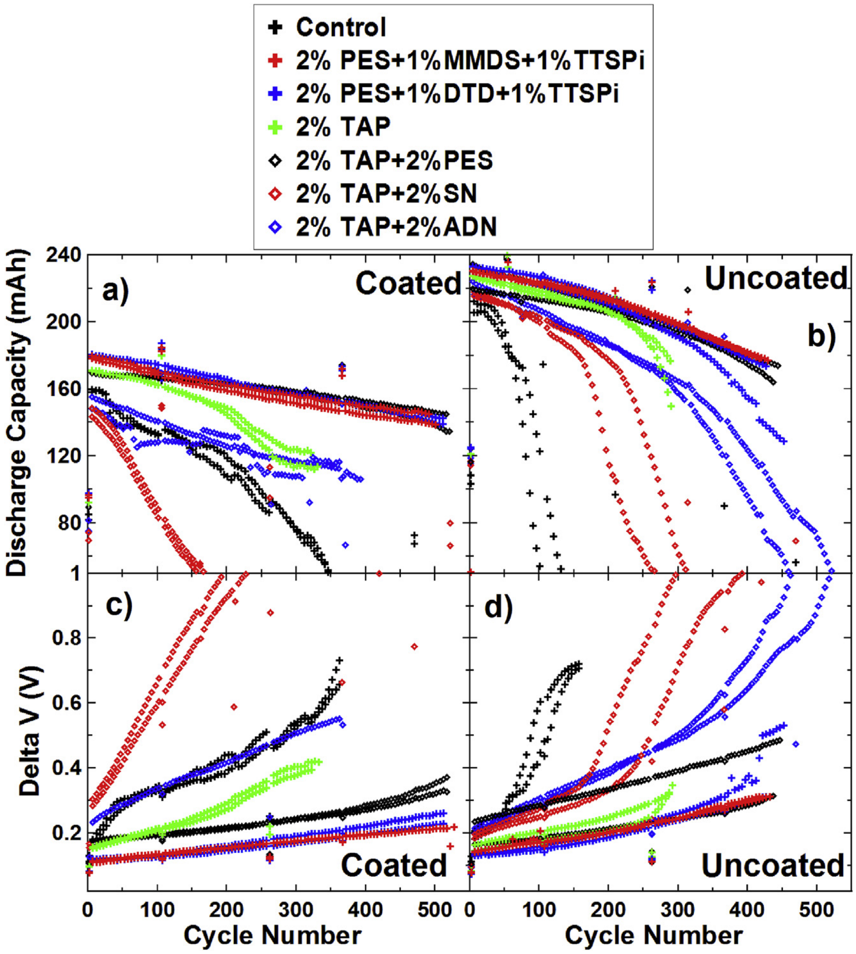

Fig. 8. (a, b) Discharge capacity and (c, d) ΔV, both plotted vs cycle number, for $LaPO_4$-coated NMC442/graphite (a, c) and uncoated NMC442/graphite pouch cells (b, d). The cycling was between 2.8 and 4.5 V at C/2.4 and 40. ± 0.1 °C with different additive sets as indicated.

4. Summary and conclusions

Several electrolyte additive blends were carefully studied in both $LaPO_4$-coated and uncoated NMC442/graphite pouch cells. The results of CE, charge endpoint capacity slippage, changes in ΔV and V_{drop} during UHPC cycle/store testing to 4.4 V and at 40 °C, V_{drop} during 500 h storage at 60 °C and 4.5 V, gas evolution, EIS as well as long-term cycling results were considered. The summary will be split to consider the 4.4 V results and the 4.5 V results separately. This is because work by Nelson et al. [16] and Downie [37] suggests that significantly different degradation processes begin above 4.4 V:

4.1. Summary of 4.4 V results

1. UHPC, EIS and gas evolution results show no beneficial impact of $LaPO_4$ coating for cells tested to 4.4 V. For cells with state-of-the-art additives like 2% PES +1% MMDS +1% TTSPi, 2% PES +1% DTD +1% TTSPi or 2% PES +2% TAP, the CIE, charge endpoint capacity slippage and increase in cell polarization with cycling are equal or better for uncoated cells (See Fig. 3)
2. For cells with state-of-the-art additives like 2% PES +1% MMDS +1% TTSPi, 2% PES +1% DTD +1% TTSPi or 2% PES +2% TAP, the impedance is smaller after formation and after cycling for uncoated cells (See Fig. 6b and c)
3. For cells with state-of-the-art additives like 2% PES +1% MMDS +1% TTSPi, 2% PES +1% DTD +1% TTSPi or 2% PES +2% TAP, the volume of gas generated after UHPC cycling is smaller for uncoated cells (See Fig. 7c).

4.2. Summary of 4.5 V results

1. Voltage drop during 4.5 V, 60 °C, 500 h storage is less for $LaPO_4$-coated cells with electrolyte additives than for uncoated cells (see Fig. 6a) and R_{ct} after storage is similar for cells with state-of-the-art additives like 2% PES + 1% MMDS +1% TTSPi, 2% PES + 1% DTD + 1% TTSPi or 2% PES + 2% TAP. However, all cells show significant voltage drop during storage which is only slightly less than control cells.
2. The volume of gas generated during 4.5 V, 60 °C, 500 h storage is less for $LaPO_4$-coated cells with electrolyte additives than for uncoated cells, except for 2% PES +2% TAP where the volumes are very small and similar (See Fig. 7d).
3. The long term cycling tests (2.8 V - 4.5 V, 40 °C, C/2.4) indicate that $LaPO_4$-coated cells with state of the art additives like 2% PES + 1% MMDS +1% TTSPi, 2% PES + 1% DTD + 1% TTSPi or 2% PES + 2% TAP have better capacity retention than uncoated cells (See Fig. 8a and b).
4. State of the art additives like like 2% PES +1% MMDS +1% TTSPi, 2% PES +1% DTD +1% TTSPi or 2% PES +2% TAP, dramatically

improve the capacity retention of both $LaPO_4$-coated and uncoated cells, primarily through control of impedance growth, not by preventing electrolyte oxidation (See Fig. 8c and d (impedance control) and Fig. 6a (electrolyte oxidation))

5. Gas evolution during long term cycling to 4.5 V was dramatically improved using state-of-the-art additives like 2% PES +1% MMDS +1% TTSPi, 2% PES +1% DTD +1% TTSPi or 2% PES +2% TAP.

It is clear from the studies presented here that a $LaPO_4$-coating on NMC442 has limited value for cells to be operated to 4.4 V but may have value for cells operated to 4.5 V. However, the impact of state-of-the-art electrolyte additives like 2% PES +1% MMDS +1% TTSPi, 2% PES +1% DTD +1% TTSPi or 2% PES +2% TAP is far greater than the impact of the coating. It may be the case that other coating materials provide better benefits than $LaPO_4$ but it is only through massive studies like this, that also include the consideration of electrolyte additives, will it be possible to truly determine the value of coatings. It is our opinion that literature papers which only consider the impact of coatings in the presence of control electrolyte, without additives, have extremely limited value.

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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.2015.11.115.

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