Improving Linear Alkyl Carbonate Electrolytes with Electrolyte Additives

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The effectiveness of some selected electrolyte additives were studied in ethylene carbonate-free linear alkyl carbonate electrolyte mixtures containing 1 M LiPF6/ethylene carbonate (98:2 w:w). The electrolytes were used in Li(Ni0.4Mn0.4Co0.2)O2/graphite pouch type Li-ion cells tested to 4.5 V at elevated temperature. The results showed that cells with linear alkyl carbonate electrolytes outperformed cells with EC-based electrolytes having state-of-the-art additive blends and cells with fluorinated electrolytes during short-term and long-term cycling at elevated temperatures. The addition of triallyl phosphate or pyridine phosphorus pentfluoride as electrolyte additives to the EC-free electrolyte provided cells with better capacity retention during long-term cycling than cells containing vinylene carbonate alone. These results suggest that small quantities of electrolyte additives can be used to create EC-free, linear alkyl carbonate electrolytes that perform well at high voltages.

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Energy-dense, long-lasting lithium-ion cells are in high demand for electric vehicles, portable electronics and many other important technologies. The easiest way to increase the energy density of a conventional lithium-ion cell is to increase its upper charge cutoff potential when certain layered oxide positive electrode materials are used. However, increasing the upper cutoff potential normally decreases cell lifetime because of the rate of unwanted parasitic reactions like electrolyte oxidation increase with potential. Parasitic reactions involving ethylene carbonate (EC)—a ubiquitous co-solvent in lithium-ion electrolytes—at high potential has proven to be one of the most important factors to overcome.1

Until recently, EC has been regarded as an essential component of lithium-ion electrolytes and it has been used in nearly all commercial Li-ion cells produced today. EC was first considered as an electrolyte co-solvent by Elliot in 19642 and was used as an electrolyte component in cells with lithiated graphite electrodes by Fong et al. in 1990.3 EC was found to preferentially react with Li+ and electrons at the surface of the graphite electrode prior to lithium intercalation, forming a solid electrolyte interface (SEI) on the surface of the graphite electrode that then allowed the reversible intercalation and de-intercalation of lithium ions into the graphite electrode at very low potentials (<0.20 V).3–5 It was generally believed that the graphite electrode could not be electrochemically lithiated in most common solvents, including ethers, esters, butyrolactones and propylene carbonate, without the sacrificial reaction of EC to form the SEI.5

While the passivation of graphite is virtually complete during the first few cycles, the remaining EC in the electrolyte can be oxidized at high voltages, causing the performance of cells containing EC to diminish as the upper charge voltage increases above 4.4 V.7,8 Electrolyte oxidation at the positive electrode at high potentials can lead to salt consumption and gas evolution.10 Precipitation of electrolyte oxidation by-products onto the surface of the positive and negative electrodes causes polarization and impedance growth,11,12 which can limit cycle life.

Petibon et al.13 showed that EC-free electrolytes, containing 1 M LiPF6 dissolved in 98 wt% ethyl methyl carbonate (EMC) and 2% wt vinylene carbonate (VC), can cycle over 1000 cycles (less than 4% capacity loss) in Li[Ni0.5Mn0.4Co0.1]O2 (NMC422)/graphite pouch cells charged to 4.4 V at room temperature. The cells were tested using a current corresponding to C/2. The addition of 2% VC in these cells sufficiently passivated the graphite negative electrode, without the need for EC. The cycling performance of this EC-free, linear alkyl carbonate electrolyte can be further improved by substituting VC by fluoroethylene carbonate (FEC) or difluoro ethylene carbonate (DiFEC).15 EC-free, linear alkyl carbonate-electrolytes with SEI-enabling additives have been shown to have acceptable conductivity, acceptable ability to dissolve LiPF6, good wetting of the separator, good tolerance to high voltage and their use leads to Li-ion cells with long cycle and calendar lifetime, when compared to EC-containing electrolytes with state-of-the-art electrolyte additive packages.14

In an effort to further improve EC-free 1 M LiPF6 in EMC:VC 98:2 electrolyte, various additives to this electrolyte were carefully studied in NMC442/graphite Li-ion pouch cells. The additives selected for this study are well-known in the literature and have been shown to improve the quality of the negative electrode SEI or to reduce parasitic reactions at high voltage in NMC442/graphite cells. The additives used in this study were prop-1-ene, 1,3-sultone (PES),15,16 methylene methanedisulfonate (MMDS),17 propanediol cyclic sulfate (trimethylene sulfate - TMS),18 1,3,2-dioxathiolan-2,2-oxide (ethylene sulfate - DTD),19 tri(trimethylsilyl) phosphate (TTSP),20 Tris(trimethylsilyl) phosphate (TTSP),20 pyridine boron trifluoride (PBF),20 pyridine phosphorus pentfluoride (PFP),21 maleic anhydride (MA),22 succinic anhydride (SA),23 4-(trifluoromethyl) benzonitrile (4-TB),24 hexamethylene diisocyanate (HDI)25 and triallyl phosphate (TAP).26 The chemical structures of these additives are shown in Figure 1. The reasons for choosing these additives and their combinations are explained in References 15–26.

The performance of EC-free electrolytes in these work were compared to the state-of-the-art ternary electrolyte additive blend, 2% PES + 1% DTD + 1% TTSP (PES211), added to 1 M LiPF6 in EC:EMC (3:7 by wt).27–29 The EC-free, linear alkyl carbonate electrolytes in this work were also compared to fluorinated electrolyte systems: 1 M LiPF6 in FEC:TEFC (1:1 by wt) using 2% PES + 0.5% MMDS as electrolyte additives.30 These two electrolyte systems have shown the best demonstrated cycling and storage performance in NMC(442)/graphite cells tested to 4.4 or 4.5 V. Experiments were made using Ultra High Precision Coulometry (UHPC),31 a precision storage system,32 an ex-situ gas evolution apparatus33 as well as electrochemical impedance spectroscopy (EIS).34 Long-term cycling results were also conducted to compare the EMC:VC electrolyte system containing additives to the EC-based and fluorinated electrolyte systems.

Experimental

Electrolyte preparation.—1 M LiPF6 in ethylene carbonate (EC): ethyl methyl carbonate (EMC) (3:7 wt% ratio) a conventional electrolyte blend, henceforth referred to as “control” electrolyte was used to compare the performance of the novel EC-free electrolytes. 2% PES + 1% DTD + 1% TTSP (wt%) was added
A control electrolyte to make the electrolyte henceforth referred to as PES211. The EC-free electrolytes were composed of 1 M LiPF6 in EMC:VC (98:2 wt% ratio), with electrolyte additives added at 1% by weight. These additives included PES, MMDS, TMS, DTD, TTSPi, TTSP, PBF, PPF, MA, SA, 4-TB, HDI and TAP (See Figure 1 for the structural information about these additives). EC-free, linear alkyl carbonate electrolyte blends were also compared to fluorinated electrolytes, composed of 1 M LiPF6 in FEC:TFEC (1:1 by wt) with 2% PES and 0.5% MMDS added. The purities and the suppliers of all solvents and additives used in this paper are listed in Table S1 (supporting information). Electrolytes were prepared in an argon-filled glove box, without exposure to air or moisture.

**Pouch cell, formation and degassing.—** Figure S1 shows a typical Li[Ni0.4Mn0.4Co0.2]O2 (NMC442)/graphite pouch cell and SEM images of the particles that make up the electrodes. The 402035-size pouch cells were manufactured by Li-Fun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000). The cells were balanced for 4.7 V operation and had a capacity of 180 mAh at 4.5 V, the maximum voltage used in this study. The negative electrodes of these cells were 96% artificial graphite particles (BTR New Materials Technology, China) (15–30 μm), 2% carbon black conductive diluent and 2% binder (Na carboxymethylcellulose (CMC)/styrene butadiene rubber (SBR)). The positive electrodes were 96% Li[Ni0.4Mn0.4Co0.2]O2 (NMC442) (Umicore, Korea) particles (5–15 μm), 2% carbon black conductive diluent and 2% polyvinylidene fluoride (PVDF) binder. The pouch cells were sealed under vacuum without electrolyte in China 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 hours to remove residual water. Then the cells were transferred, without exposure to air, to an argon-filled glove box where they were filled with 0.75 mL (0.86 g for 1 M LiPF6 in EMC, 0.90 g for 1 M LiPF6 in EC:EMC 3:7) of electrolyte. After filling, the cells were vacuum-sealed with a compact vacuum sealer (MSK-115A, MTI Corp.) at a gauge pressure of ~90 kPa. After filling, the cells were placed in a temperature box at 40 °C, where they were held at 1.5 V for 24 hours, to allow for the completion of wetting. Then the cells were charged at 9 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. The NMC442/graphite cells destined for 4.5 V operation were charged to 4.5 V at C/20 and degassed a second time at 4.5 V. These degassing voltages were selected based on the in-situ gas evolution experiments, which showed that most of the gas evolves in the formation cycle at voltages below 3.5 V and above 4.3 V. After the two degassing processes, cells were then discharged to 3.8 V where impedance spectra were measured.

**UHPC barn-charge protocols.—** The “barn-charge” cycling procedure (see Figure S2 in the supporting information),10 was designed so that the cells were exposed to higher potentials for significant fractions of their testing time, thereby highlighting the effects of electrolyte oxidation at high voltage. Barn charge testing to rank cells based on the coulombic efficiency and charge end point capacity slip-page was carried out using the Ultra-High Precision Charger (UHPC) at Dalhousie University. The “barn-charge” protocol consisted of a C/15 charge to 4.200 V, followed by a slower, C/40 charge to 4.500 V. The cells were then discharged, using a slow, C/40 current to 4.200 V, followed by a C/15 discharge to 2.800 V. This process was repeated on the UHPC for 15 cycles. The tests were made at 40 ± 0.1 °C.

**Storage protocols.—** After formation step 2 (charge to 4.5 V), cells were moved to a Maccor charger for precycling at 40 ± 0.1°C. First,
cells were discharged to 2.8 V and charged to 4.5 V twice with a standard cycler using currents corresponding to C/20. Then the cells were held at 4.5 V for 24 h. After the pre-cycling processes, cells were carefully moved to the storage system which monitored their open circuit voltage every 6 hours for a total storage time of 500 h. The first storage experiments were conducted at 40 ± 0.1 °C. After the first storage experiments, the cells were charged to 4.5 V again and stored at 60 ± 0.1 °C for a second time.

Ex-situ gas volume measurements.—Changes in cell volume, due to gas evolution, were determined using Archimedes' principle: the change in buoyant force on a cell submerged in fluid before, during and after testing is directly related to the volume change by Equation 1. The change in weight of a cell, ∆m, suspended in a fluid of density, ρ, is related to the change in cell volume, ∆V, by

\[ ∆V = -\frac{∆m}{ρ} \]  

[1]

The weight of the submerged cell was acquired by suspending pouch cells from a fine wire “hook” attached under a Shimadzu balance (AUW200D). The pouch cells were immersed in a beaker of de-ionized “nanopure” water (18 MΩ) at room temperature. Before weighing, all cells were charged or discharged to 3.80 V.

Electrochemical impedance spectroscopy.—Electrochemical impedance spectroscopy (EIS) measurements were conducted on the cells after formation and after cycling tests involving the UHPC. 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, using a Biologic VMP-3 potentiostat. 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.

Long-term cycling.—The long-term cycling cells were the same cells used for the UHPC cycling experiments and the long-term cycling began immediately after the UHPC cycling completed. For long-term cycling, cells were housed at 40 °C ± 1 °C in a temperature controlled box connected to Neware (Shenzhen, China) cyclers. Cells were cycled between 2.8 and 4.4 V or 4.5 V using a constant current (CC) of 80 mA, corresponding to ~C/2.2. A constant voltage (CV) step was added at the top of charge and applied until the current dropped below C/20.

Results and Discussion

Figure 2 shows the differential capacity (dQ/dV) vs. V curves for cells with different electrolyte additives measured during the formation cycle (very first charge) at C/20 and 40 °C. From the onset of the peaks in dQ/dV vs. V plots, the approximate reduction potential of the electrolyte components can be deduced. Figure 2 shows that cells without any EC or electrolyte additives (cells containing only 1 M LiPF6 in EMC) have a pronounced peak around 3.2 V (0.45 V vs. Li/Li+). This peak is associated with reduction of EMC on the surface of the graphite electrode. The large area under this peak indicates that a large amount of EMC reacted, and that the reduction products of EMC do not form a good passivating film on the negative electrode. The inability of EMC to form an adequate negative electrode SEI was discussed by Nie et al. When 2% VC was added to EMC electrolyte, the 3.2 V peak is replaced by a much smaller peak at 2.85 V, which is associated to the reduction of VC. This indicates that VC effectively passivates the negative electrode and prevents the reduction of EMC at any potential. Figure 2 shows when additives were added to EMC:VC 98:2 electrolyte, the peak position and peak intensity change with the additives added. These peaks are associated with the reduction of the additives on the graphite electrode during the formation of the negative electrode SEI. Table S2 (Supporting Information) compares the initial reduction potential vs. Li/Li+ of these additives in EMC and EC:EMC electrolytes. Table S2 shows that the reduction potential of VC is slightly lower than that of EMC. The results indicate that the reduction potential of EC additives depends on dielectric constant of the electrolyte (EC has a large dielectric constant) or the presence of neighboring EC molecules. Only two additives, HDI and TAP, show a change in reduction potential of greater than or equal to 0.3 V. The selectivity of CV (CIE = 1 – CE) values used for comparative purposes in the summary figures that follow were calculated from the CE taken as an average of the final three data points (cycles 13–15) collected on the UHPC. Smaller values of CIE mean the cells had higher CE and should have longer cycle and calendar life in similar cycling conditions (i.e. low rate cycling). For instance, Figure 3a shows that cells containing 2% VC+1%TAP in EMC electrolyte had much higher CE than cells containing PES211 in EC:EMC electrolyte. Cells containing 2% VC+1%TAP in EMC are thus expected to have longer life time than cells containing PES211 in EC:EMC electrolyte in tests to 4.5 V.

Figure 3 contains a representative expanded data set comparing the best-performing EC-containing electrolyte, (PES211, in black) to the best-performing EC-free electrolyte (1% TAP (red)). Figures 4, 5, and 7 are bar charts which contain information extracted from expanded data sets such as the one shown in Figure 3. Figure 3a shows the coulombic efficiency (CE) vs. cycle number for the two electrolyte systems during the barn-charge protocol on the UHPC chargers (see the protocol in Figure S2 where the testing was done at 40 °C and the upper cutoff was 4.5 V). The coulombic inefficiency (CIE = 1 – CE) values used for comparative purposes in the summary figures that follow were calculated from the CE taken as an average of the final three data points (cycles 13–15) collected on the UHPC. Smaller values of CIE mean the cells had higher CE and should have longer cycle and calendar life in similar cycling conditions (i.e. low rate cycling). For instance, Figure 3a shows that cells containing 2% VC+1%TAP in EMC electrolyte had much higher CE than cells containing PES211 in EC:EMC electrolyte. Cells containing 2% VC+1%TAP in EMC are thus expected to have longer life time than cells containing PES211 in EC:EMC electrolyte tests to 4.5 V.

Figure 3b shows the charge-end point capacity vs. cycle number for EC-containing PES211 and 2% VC+1%TAP in EMC during testing on the UHPC with the barn-charge protocol. The charge end point capacity slippage rate values displayed in the summary bar charts that follow were calculated from the slope of a best fit line to the final five points (cycles 11–15) of the charge end point capacity versus cycle number curves. Charge end point capacity slippage is caused by undesired reactions at the positive electrode, such as electrolyte oxidation, oxidation of other species created in the cell or transition metal dissolution at the positive electrode. High rates of electrolyte oxidation ultimately lead to depletion of the electrolyte, impedance growth and cell failure. Cells with lower rates of electrolyte oxidation generally have longer life-times, as shown by Burns et al. Figure 3b shows that cells containing 2% VC+1%TAP in EMC electrolyte had lower rates of electrolyte oxidation than PES211.
smaller charge end point capacity slippage (less electrolyte oxidation) than cells containing PES211 in EC:EMC electrolyte. Once again, cells with the 2% VC + 1% TAP in EMC electrolyte are expected to have a longer life-time in tests to 4.5 V than the cells with PES 211 in EC:EMC electrolyte.

Figure 3c shows typical open circuit voltage (OCV) versus time during 500 h storage at 40. ± 0.1 °C for cells with the two electrolyte systems. The voltage drop (\(V_{\text{drop}}\)) during storage is caused by self-discharge due to electrolyte oxidation at the positive electrode and has been shown to correlate well with charge end point capacity slippage.\(^{18}\) That is, cells with large charge end point capacity slippage during cycling normally have large \(V_{\text{drop}}\) during storage. Figure 3c shows cells containing 2% VC +1% TAP in EMC electrolyte had smaller \(V_{\text{drop}}\) (less electrolyte oxidation) than cells containing PES 211 in EC:EMC electrolyte, which agrees well with Figure 3b.

Figure 3d shows the capacity versus cycle number for the NMC442/graphite pouch cells containing the two electrolytes during long-term cycling. Figure 3d shows cells containing 2% VC+1% TAP in EMC electrolyte had much better capacity retention than cells containing PES 211 in EC:EMC electrolyte. The results of long-term cycling are in good agreement with the accelerated cycling tests done with UHPC, shown in Figures 3a and 3b.

Figure 3e shows the impedance spectra for cells containing the two kinds of electrolytes measured after UHPC cycling. The diameter of the semicircle represents the sum of the charge-transfer resistances, at both the positive and negative electrodes along with the desolvation energy of Li\(^+\), charge transfer resistance from the current collector to the active material.\(^{30-42}\) In this work, the sum of these contributions is referred as \(R_{\text{ct}}\). \(R_{\text{ct}}\) was calculated from the width of the semicircle in the Nyquist representation of the electrochemical impedance spectra. Smaller values of \(R_{\text{ct}}\) as well as low rates of \(R_{\text{ct}}\) growth are desirable. Figure 3e shows cells containing 1% TAP in EMC:VC 98.2 electrolyte had larger \(R_{\text{ct}}\) than cells containing PES 211 in EC:EMC electrolyte. However, the impedance of the cells containing 1% TAP in EMC:VC 98.2 electrolyte increases more slowly than the impedance of cells containing PES 211 in EC:EMC electrolyte (see Figures 4c, 9b and 10b).

Figure 3f shows the gas evolution for the cells containing the two different electrolytes after storage at 4.5 V and after UHPC cycling. Smaller values of gas evolution are desired for cells cycled during the same period of time. The initial volume of the pouch cells is 2.2 mL. A volume change during cycling less than 10% (0.22 mL) is desired in order to prevent pressure buildup in hard-can cell designs and loss of stack pressure in cell designs with soft enclosures. Figure 3f shows that cells containing 2% VC+1% TAP in EMC electrolyte and cells containing PES211 in EC:EMC electrolyte produce very small amounts gas (less than 1% volume change) during UHPC cycling at 40. °C. In fact, cells containing PES211 in EC:EMC electrolyte have a tiny negative volume change during UHPC cycling. This is a normal phenomenon of gas consumption in the PES-containing cells which has been shown in in-situ gas measurements detailed in a previous publication.\(^{16}\) Figure 3f shows cells containing 1% TAP in EMC:VC 98:2 produced smaller amounts of gas than cells containing PES211 in EC:EMC electrolyte during storage at 4.5 V and 60. °C.

Figure 4 summarizes the cycling data collected on the UHPC, including CIE, charge end point capacity slippage and the increase in \(\Delta V\)/cycle for cells with different electrolytes at 40. ± 0.1 °C, using barn-charge protocols (see Figure S2) to 4.5 V. The detailed data for CE, discharge capacity, charge end point capacity and \(\Delta V\), all plotted vs cycle number data are given in Figures S3, S4, S5 and S6 in the supporting information. The charge end point capacity slippage and the increase in \(\Delta V\)/cycle were calculated from the slope of a best fit line to the final five points (cycles 11–15) of the cycling curves given in Figures S3, S4, S5 and S6. Each data point in Figure 4 represents the average of two cells, and the error bars are the range of the results. The color of the bars marked in cyan,
red and green in Figure 4 represent cells containing EC:EMC, EMC and FEC:TFEC electrolytes, respectively. Figure 4 shows adding VC to control (EC:EMC) electrolyte increased CIE, while adding PES or PES211 decreased CIE during the barn-charge protocol at 4.5 V. This is consistent with the data presented by Xia et al.43 which showed that the addition of VC to NMC442/graphite cells cycled to 4.5 V does not lead to any improvement, while the addition of PES or PES211 improves capacity retention and decreases impedance growth and gas evolution during high voltage cycling.12,29,43 Figure 4 shows that cells containing fluorinated electrolyte had lower CIE and lower charge end point capacity slippage than cells containing PES or PES211 in EC:EMC electrolyte at high voltages. Again this is consistent previous work which shows fluorinated electrolytes have superior performance to cells containing PES211 in EC:EMC electrolyte30 in terms of CIE and charge slippage when operated to 4.5 V. Figures 4a and 4b show that cells containing EMC:VC 98:2 electrolyte without other additives had lower CIE and lower charge end point capacity slippage than cells containing PES211 in EC:EMC or 2% PES + 0.5% MMDS in FEC:TFEC electrolyte. Figures 4a and 4b show that the addition of additives to EMC:VC 98:2 electrolyte generally decreased the CIE and charge end point capacity slippage during UHPC cycling. Figure 4c shows cells containing EMC:VC 98:2 electrolytes with additives had lower ΔV (less impedance growth) during UHPC cycling than cells containing PES211 in EC:EMC or 2% PES + 0.5% MMDS in FEC:TFEC electrolyte. Figure 4c shows that cells containing 1% PES, 1% TTSP and 1% TAP in EMC:VC 98:2 electrolyte have the lowest increase in ΔV (the least impedance growth) during UHPC cycling experiments.

Figures 5a and 5b summarize the voltage drop during 500 h storage at 4.5 V at 40.0°C and 60.0°C, respectively. Detailed storage data are given in Figures S7 (40°C) and S8 (60°C). Smaller voltage drop during storage means cells have less self-discharge due to electrolyte degradation at the positive electrode.36 Figure 5a shows cells containing 2% VC, 2% PES or PES211 in EC:EMC all had smaller Vdrop than cells containing control electrolyte at 40°C. Figure 5a shows cells containing FEC:TFEC electrolyte have lower Vdrop than cells containing PES or PES211 in EC:EMC electrolyte, which agrees with previous results.30 Figure 5a shows cells containing EMC:VC 98:2 electrolyte without additives had smaller Vdrop than all cells with EC-containing electrolyte or FEC:TFEC electrolyte. Figure 5a shows that adding most additives to the EMC:VC 98:2 electrolyte did not dramatically impact Vdrop. Figure 5a shows that cells containing 1% TAP in EMC:VC 98:2 electrolyte had the smallest Vdrop among all the additives tested.

Figure 5b summarizes the voltage drop during the second 500 h storage at 4.5 V and at 60°C for the same cells shown in Figure 5a. The second storage began immediately after the first storage completed. Figure 5b shows that Vdrop at 60°C is much bigger than that measured at 40°C, indicating a temperature dependence of parasitic reactions occurring in the cells. Figure 5b shows that cells containing 2% VC in EC:EMC electrolyte had much larger Vdrop than cells containing control electrolyte, while cells containing 2% PES or PES211...
Figure 5. Summary of the 4.5 V open-circuit voltage storage experiments at a) 40°C and b) 60°C for NMC442/graphite pouch cells containing different electrolytes as indicated. Results for EC-containing electrolytes are shown in cyan; EC-free electrolytes are shown in red; fluorinated electrolytes are shown in green.

Figure 6. Charge end point capacity slippage during UHPC cycling plotted vs $V_{\text{drop}}$ after a) the first storage period at 40°C and b) the second storage period at 60°C. $R_{\text{ct}}$ after UHPC cycling plotted vs. $R_{\text{ct}}$ after c) the first storage period at 40°C and d) after the second storage at 60°C.
Figure 7. Summary of the volume changes measured during a) formation b) 500 h storage at 4.5 V and 40°C, c) 500 h storage at 4.5 V and 60°C and d) UHPC cycling at 40°C.

in EC:EMC electrolyte had much lower Vdrop than control cells. Figure 5b shows that cells containing EMC:VC 98:2 electrolyte without additives had lower Vdrop than cells containing PES211 in EC:EMC electrolyte. Figure 5b shows that the addition of MMDS, DTD, HDI and TAP to EMC:VC 98:2 electrolyte further decreased Vdrop at 60°C. This suggests that the addition of co-additives can further lower the oxidation rate of the electrolyte at the positive electrode in cells containing EMC:VC electrolyte.

Figures 6a and 6b show the charge end point capacity slippage measured for the last 5 cycles during UHPC cycling (to 4.5 V) plotted vs Vdrop during the first storage period at 40°C and 4.5 V and during the second storage at 60°C, respectively. Figures 6a and 6b show that the charge end point capacity slippage increases as Vdrop increases. Figure 6a shows a better correlation between charge end point capacity slippage and Vdrop at 40°C than Figure 6b shows for storage at 60°C. This may be due to the temperature difference between UHPC cycling (40°C) and the second storage test at 60°C. The best additives in Figures 6a and 6b should be in the bottom left corner since they give the least amount of electrolyte oxidation (smallest charge end point capacity slippage and smallest Vdrop). Therefore, additives such as PBF, PPF, TTSP, TTSPi, SA, MA, and TAP should be studied further at 40°C while additives such as TAP, MMDS, DTD and HDI need further study at 60°C in EMC:VC electrolyte.

Figure 7a shows the volume of gas produced during formation step 1 (charge to 3.5 V) and formation step 2 (charge from 3.5 V to 4.5 V). The gas during formation step 1 was generally caused by the reaction of electrolyte components at the negative electrode while the gas during formation step 2 was caused by reactions at the NMC electrode when the electrode was first charged to 4.5 V. Figure 7a shows that adding VC, PES or PES211 to EC:EMC electrolyte greatly decreased the volume of gas produced during formation step 1 due to the protective SEI formed by these additives on the graphite electrode. Figure 7a shows that cells containing the fluorinated electrolyte produced almost no gas during both formation step 1 and formation step 2. Figure 7a shows that cells containing EMC:VC 98:2 electrolyte with or without electrolyte additives did not produce large amounts of gas during both formation step 1 and step 2, compared to cells containing control electrolyte.

Figures 7b–7d show the volume of gas produced during 500 h storage at 4.5 V and 40°C, 500 h storage at 4.5 V and 60°C and UHPC cycling at 40°C.
600 h UHPC cycling at 40 °C, respectively. Figures 7b and 7d show cells containing FEC:TFEC electrolyte produced large amounts of gas during storage and cycling at 40 °C, which agrees well with previous results. Figures 7b–7d show all the cells containing EMC:VC or EC:EMC electrolyte had no significant gassing during storage or UHPC cycling at 40 °C. Figures 7 shows that cells stored at 4.5 V and 60 °C produced more gas than the cells stored at 4.5 V and 40 °C. Figure 7c shows that adding additives MMDS, MA, SA, HDI or TAP to EMC:VC 98:2 electrolyte decreased the gas evolution during storage at 60 °C. Figure 7c shows that cells containing 4-TB produced large amount gas during storage at 60 °C.

Figures 8a–8d show a summary of the EIS data after formation, after 500 h storage at 4.5 V and 40 °C, 500 h storage at 4.5 V and at 60 °C and after 600 h UHPC cycling, respectively. Detailed EIS spectra for all of the cells tested are given in Figures S9–S12. All the EIS measurements were made at 3.80 V and 10. ± 0.1 °C. Figure 8 shows the impedance of the cells containing 2% VC in EC:EMC electrolyte increased a lot after UHPC cycling or 60 °C storage, indicating failure of VC-containing cells in EC:EMC electrolyte at high voltages mainly comes from the impedance growth, not gas evolution (Figure 7). Figure 8 shows that cells containing 2% PES or PES211 in EC:EMC electrolyte had lower impedance than cells containing control electrolyte after storage or cycling tests. This again is one of the advantages of the addition of such additive blends to EC-based electrolytes in NMC(442)/graphite cells cycled to high voltage.

Figure 8 shows that cells containing FEC:TFEC electrolyte had high impedance after storage or cycling, which may limit its high rate cycling performance. Figure 8 shows that cells containing EMC:VC 98:2 electrolyte had low impedance after formation, storage or cycling tests. Figure 8 shows that cells containing EMC:VC 98:2 electrolyte with additives had low impedance, with the exceptions being cells containing SA, HDI and TAP which had high impedance after storage or cycling.

Figures 6c and 6d show Rct after UHPC cycling plotted vs Rct after the second storage period at 60 °C, respectively. Figures 6c and 6d show a good correlation between Rct after UHPC cycling and Rct after storage at both 40 °C and 60 °C. Figures 9 and 10 show the long-term cycling data (capacity retention and AV vs cycle number) for cells with all the electrolyte blends cycled to 4.4 V and 4.5 V, respectively. The long-term cycling cells were the same cells used for the UHPC cycling experiments and the long-term cycling began immediately after the UHPC cycling completed. All cells in Figures 9 and 10 were cycled at 40. ± 0.5 °C using currents corresponding to about C/2.2 (80 mA).

**Figure 8.** Summary of charge transfer resistances, Rct, measured after a) formation b) 500 h storage at 4.5 V and 40 °C, c) 500 h storage at 4.5 V and 60 °C and d) UHPC cycling at 40 °C.

| Additives                          | Rct (Ω·cm²) | Rct (Ω·cm²) | Rct (Ω·cm²) | Rct (Ω·cm²) |
|-----------------------------------|------------|------------|------------|------------|
| Control                           | 2% VC      | 2% PES     | 2% VC      | 2% VC      |
| 2% VC                             | 2% PES     | 2% VC      | 2% VC      | 2% VC      |
| PES 211                           | 2% VC      | 2% PES     | 2% VC      | 2% VC      |
| 2% VC+1%PES                       | 2% VC      | 2% PES     | 2% VC      | 2% VC      |
| 2% VC+1%MMDS                      | 2% VC      | 2% PES     | 2% VC      | 2% VC      |
| 2% VC+1%MA                        | 2% VC      | 2% PES     | 2% VC      | 2% VC      |
| 2% VC+1%SA                        | 2% VC      | 2% PES     | 2% VC      | 2% VC      |
| 2% VC+1%TMS                       | 2% VC      | 2% PES     | 2% VC      | 2% VC      |
| 2% VC+1%BPB                       | 2% VC      | 2% PES     | 2% VC      | 2% VC      |
| 2% VC+1%PBF                       | 2% VC      | 2% PES     | 2% VC      | 2% VC      |
| 2% VC+1%TSSP                      | 2% VC      | 2% PES     | 2% VC      | 2% VC      |
| 2% VC+1%TTPS                      | 2% VC      | 2% PES     | 2% VC      | 2% VC      |
| 2% VC+1%TAP                       | 2% VC      | 2% PES     | 2% VC      | 2% VC      |

**Additives**
- 1M LiPF6 in EC:EMC 3:7
- 1M LiPF6 in EMC
- 1M LiPF6 in FEC:TFEC 1:1

**Figure 7c** shows that cells containing 4-TB produced large amount gas during storage at 60 °C.
Figure 9. a, c, e) Discharge capacity vs. cycle number and b, d, f) ΔV vs. cycle number for cells containing different additive blends, undergoing long-term CCCV cycling between 2.8 V and 4.4 V. All cells were cycled at 40 ± 0.5 °C using currents corresponding to about C/2.2 (80 mA).

Figure 10. a, c, e) Discharge capacity vs. cycle number and b, d, f) ΔV vs. cycle number for cells containing different additive blends, undergoing long-term CCCV cycling between 2.8 V and 4.5 V. All cells were cycled at 40 ± 0.5 °C using currents corresponding to about C/2.2 (80 mA).
Figure 11. % capacity loss at cycle 350 for NMC442/graphite pouch cells containing the different electrolyte formulations cycled to a) 4.4 V and b) 4.5 V. When the cycle number at end of life was less than 350, the cycle number recorded in brackets represents end of life.

previous results. Previous cycling results showed that cells containing EMC:VC 98:2 without additives had similar capacity retention to PES211 at 4.4 V, but better capacity retention at 4.5 V compared to cells containing PES211 in EC:EMC electrolyte. Figures 9 and 10 show that adding TAP or PPF to EMC:VC 98:2 electrolyte increased the capacity retention and decreased the impedance growth at both 4.4 and 4.5 V during long-term cycling.

Figures 11a and 11b show the % capacity loss at cycle 350 for NMC442/graphite pouch cells containing the different electrolyte formulations cycled to 4.4 V (cycling data in Figure 9) and 4.5 V (cycling data in Figure 10), respectively. When the cycle number is less than 350, the cycle number recorded in the Figures is the end of cycle life. Figures 11a and 11b show that cells containing 2% VC in EMC have similar performance to cells containing PES211 in EC:EMC electrolyte at 4.4 V but much better cycle performance at 4.5 V. This is thought to be due to the continuous oxidization of EC, especially at higher voltages. Figure 11a shows that adding PPF, 4-TB, HDI or TAP can provide similar or better performance to cells containing 2% VC in EMC electrolyte at 4.5 V. In any case, cells containing 2% VC+1% TAP show the best capacity retention.

Figures 12a and 12b show the % capacity loss during long-term cycling at 4.4 V (Figure 9) and 4.5 V (Figure 10) plotted vs. CIE during UHPC cycling (Figure 4), respectively. Figure 12 shows that only a weak correlation between % capacity loss during long-term cycling and CIE exists at 4.4 V and 4.5 V. There are two reasons for this. First, the UHPC cycling was done using the low rate “barn” protocol while the continuous cycling used high rate constant current conditions. Thus, the fraction of time that the cells were exposed to high potentials differed between the UHPC and long-term cycling conditions. Second, Figures 9 and 10 show that the charge-discharge polarization vs. cycle number is a “mirror” image of the capacity vs. cycle number plots. This suggests that impedance growth, not the rate of all parasitic reactions, is the main factor determining the failure in the high-rate, high voltage cycled cells, and this is not captured by the CIE measurement. There is one feature of Figure 12 that is very interesting. In spite of all the electrolyte solvents and additives used, there is a “wall” in CIE near 0.0035 under the conditions used for
the UHPC test. There are many cells that end up with a CIE near this value but none that have less.

Figures 13a and 13b show a summary of the volume change and EIS data collected after the long-term cycling experiments of the same cells shown in Figures 9 and 10. Figure 13 shows cells containing EC:EMC electrolyte had dramatic impedance growth during long-term cycling, which is consistent with the results in Figures 9 and 10 that showed these cells had rapid polarization increase. Figure 13a shows that all cells containing EMC:VC 98:2 electrolyte plus additives cycled to 4.5 V had more gas generation and higher impedance than cells cycled to 4.4 V, although the gas volumes generated were very small. Figure 13b shows cells containing EMC:VC 98:2 electrolyte plus additives had much smaller impedance than cells containing EC:EMC or FEC:TFEC electrolyte after long-term cycling. Further work, most likely involving electrode material coatings, EC-free electrolytes and additives, is required to continue to improve the long term high voltage cycling performance of NMC/graphite cells.

Conclusions
The performances of EC-free linear alkyl carbonate-based electrolytes with electrolyte additives were carefully studied in
NMC442/graphite pouch cells. These were compared to NMC424/graphite cells with other two electrolyte systems: the ‘PE5211’ electrolyte additive blend in EC/EMC and FEC/TFEC electrolyte with electrolyte additives. The results of coulombic efficiency (CE), charge end point capacity slippage, and changes in ΔV during UHPC “barn protocol” testing to 4.5 V and at 40°C were reported. Storage experiments at 40°C and at 60°C were made to measure the potential drop during storage and the volume of evolved gas. Electrochemical impedance spectroscopy as well as long-term cycling results were considered and compared.

The results showed that cells containing EC-free linear carbonate electrolytes provided higher CE (good), lower charge end point capacity slippage (good) and lower impedance growth (good) than PES 211 in EC/EMC or 2% PES + 0.5% MMDS in FEC/TFEC during low rate UHPC cycling. The cycling and storage performance of the EC-free linear carbonate electrolytes could be further improved by adding electrolyte additives. For example, adding, MA, SA, PBF, PPF, TTSP, TTSPi and TAP increased the coulombic efficiency during UHPC cycling to 4.5 V at 40°C. Adding MMDS, DTD, HDI and TAP reduced the voltage drop, Vdrop, and gas evolution during storage at 60°C. Of all the additives used in EC-free electrolytes, PPF and TAP provided better capacity retention during long-term cycling at both 4.4 V and 4.5 V without showing high initial impedance. The benefit of these additives is mainly on the positive electrode. By reducing the rate of electrolyte oxidation, cells containing these additives in EMC-based electrolyte have smaller voltage drop during storage (Figure 5) as well as a smaller charge end point capacity slippage rates during UHPC cycling (Figure 4b).

Despite the excellent short-term UHPC cycling performance attained by cells containing EC-free electrolytes with MMDS, MA, TTSP and TTSPi, the long-term cycling performance of the same cells at high rate does not correlate well with the UHPC cycling results. This disagreement is mainly due to the high impedance growth under the same conditions, especially when cycled to 4.5 V during high rate long-term cycling to 4.4 and 4.5 V which is not considered and compared.

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