Development of Electrolytes for Single Crystal NMC532/Artificial Graphite Cells with Long Lifetime

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NMC532/artificial graphite cells using single crystal NMC532 active material can have excellent long term lifetime at 4.4 V and elevated temperature if appropriate electrolytes are used. However, electrolytes developed earlier for these cells and reported in the literature cannot support even C/2 rates during charging without unwanted lithium plating at room temperature. This work thus focused on the development of new electrolytes for single crystal NMC532/artificial graphite cells that can yield long lifetime and support higher charging rates. Ex-situ and in-situ gas measurements, ultra-high precision coulometry, isothermal microcalorimetry, lithium plating tests and long term cycling tests were used for the screening of electrolytes. Electrolytes with 2% vinylene carbonate (VC) + 1% ethylene sulfite (DTD) additives or 2% fluoroethylene carbonate (FEC) + 1% DTD additives yield single-crystal NMC532/graphite cells with long lifetime that can support C-rate charging at 40 °C.

Materials.—Reagents used for the electrolytes included 3:7 w/w ethylene carbonate:ethyl methyl carbonate (EC:EMC, BASF, purity 99.99%, water content < 20 ppm) and lithium hexafluorophosphate (LiPF6, BASF, purity 99.9%, water content 14 ppm). Vinylene carbonate (VC, BASF, purity 99.97%, water content < 100 ppm), prop-1-ene-1,3-sultone (PES, Lianchuang Medicinal Chemistry Co., purity 98.20%), ethylene sulfite (DTD, Sigma Aldrich, purity 98%), tri (trimethylsilyl) phosphate (TTSPi, TCI America, purity < 95%), methylene methane disulfonate (MMDs) (Tinci Materials Technology, > 98.7%), and fluoroethylene carbonate (FEC, BASF, purity 99.94%), were used as electrolyte additives.

Pouch cells.—402035 size machine-made NMC532/artificial graphite (AG) pouch cells (240 mAh to 4.4 V) were obtained dry (no electrolyte) from LiFun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000). The negative electrodes in these cells each had a loading of 13.6 mg/cm² and were calendared to a density of 1.55 to 1.6 g/cm³. The negative electrodes had compositions of 95.2% active material, 2% carbon black with the remainder being carboxymethyl cellulose (CMC)/styrene butadiene (SBR) binder. The NMC532 used was called SC532 in an earlier publication by Li et al.22 The positive electrode loading was 21.3 mg/cm² and the electrodes were calendared to 3.5 g/cm³. The positive electrodes were 94% by weight active material with 4% conducting carbon additives and 2% by weight PVDF binder. Based on this design, the cells could be charged at low rate to 4.5 V without unwanted lithium plating. The dry cells were vacuum sealed before they were shipped to Canada. The cells were cut open below the heat seal and placed in a heated vacuum oven at 100 °C overnight (approximately 14 hours) to remove residual water. After drying, the cells were directly transferred to an argon-filled glove box without exposure to ambient air, where they were filled with 1.0 g electrolyte. The control electrolyte was 1.2 M LiPF6 in 3:7 w/w EC:EMC. Electrolyte additives used in this work were VC, FEC, PES, MMDS and DTD. The combinations of the above additives in control electrolyte studied were 2 wt% A (2A), 1 wt% A + 1 wt% MMDs (1A+1MMDs), 2 wt% A + 1 wt% MMDs (2A+1MMDs), 1 wt% A + 1 wt% DTD (1A+1DTD), 2 wt% VC + 1 wt% DTD (2A+1DTD).

Experimental

Capacity loss in lithium ion cells can be caused by the loss of lithium inventory to the solid electrolyte interphase (SEI).1-3 Active material loss due to structural degradation and due to electrical disconnection at the particle/electrode level can also lead to capacity loss. Internal impedance or polarization increase is another major contributor to capacity loss under high rate discharge conditions. Moreover, unwanted lithium plating, which can occur during high rate or low temperature charging, can also result in severe capacity fade. At high potentials, accelerated unwanted reactions in the electrolyte such as electrolyte oxidation occur and can hasten capacity loss by causing reconstruction of the positive electrode surface which can lead to impedance growth.1-5 In addition the oxidized by-products can migrate to the negative electrode surface and be reduced there.6,7 Such reactions can lead to the consumption of lithium ions from the electrolyte (to maintain charge neutrality in the electrolyte), a reduction in lithium inventory, as well as a thickening of the negative electrode SEI which together ultimately cause impedance growth and capacity loss.8,9 These processes are usually accelerated by higher charging potentials and higher temperatures. Novel electrolyte additives and modifications to positive electrode materials have been developed to improve the lifetime of Li-ion cells operated to high potential.10-21 Recently, J. Li et al. showed that single crystal Li[Ni0.5Mn0.3Co0.2]O2 (NMC532) materials in NMC532/artificial graphite cells can have excellent long term lifetime with an electrolyte consisting of 2 wt% prop-1-ene-1,3-sultone (PES) + 1 wt% ethylene sulfite (DTD) + 1 wt% tris (trimethylsilyl) phosphate (TTSPi) in 1 M LiPF6 in ethylene carbonate: ethyl methyl carbonate (3:7 by weight) (this electrolyte is called PES211 here).22 During testing to 4.4 V at 40 °C, more than 98% of the original capacity was maintained after testing for one year (~2000 cycles with C/2 rate, CCCV) and more than 82% was maintained after 18 months (3000 cycles with C/2 rate, CCCV). Figure S1 in the supplemental information shows the extended test results for the same cells shown in Figure 12 of Reference 22.

Liu et al. found that additives and electrolytes that increase the negative electrode area-specific resistance lead to a decreased onset current for unwanted lithium plating.23 Such additives are often those that also increase lifetime of cells under moderate rate conditions. PES211 electrolyte usually leads to large negative electrode charge transfer resistance and therefore is not suitable for applications requiring high rates during charging. Liu et al. showed that NMC111/graphite cells with PES211 electrolyte could not be charged at a C/2 rate at room temperature without unwanted lithium plating (detailed electrode information can be found in Reference 23).23 If single crystal NMC532 materials are commonly used, charging at C rate is desired. Hence, this work will focus on the development of alternative electrolyte additives for single crystal NMC532/graphite cells that can support long lifetime as well as C-rate charging at both room and elevated temperatures. Future work that focuses on the development of new solvent systems for higher charging rates will be reported later.

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where A was VC, FEC or PES. Once cells were filled with electrolyte, they were sealed with a compact vacuum sealer (MSK-115 V, MTI Corp.) to 94% of full vacuum (-95.2 kPa gauge pressure or 6.1 kPa absolute pressure) with a 4 second sealing time at 165 °C.

All cells were placed in a temperature-controlled box at 40 ± 0.1 °C and held at 1.5 V for 24 hours to ensure complete wetting. For the formation process, cells were clamped with rubber blocks in cell holding “boats” and charged at C/20 using a Maccor series 4000 automated test system (Maccor Inc.). The cells were charged to the upper cutoff voltage and discharged to 3.8 V at 40 °C. The cells were then transferred back to an argon-filled glove box and cut open under the previous seal to release any gas that was produced. The cells were then vacuum sealed again as previously described, clamped in boats and then ready for electrochemical impedance spectroscopy (EIS) measurements.

**Electrochemical impedance spectroscopy (EIS).**—All EIS spectra were measured at a temperature of 10 ± 0.1 °C using a Bio-logic VMP3 electrochemical test station. Data were collected with ten points per decade from 100 kHz to 10 mHz with a signal amplitude of 10 mV. 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. The area specific resistance reported here is extracted from a Nyquist plot as the total “diameter” of the “semicircle” which is the sum of charge (both ion and electron) transfer resistance (Rct) (both electrodes) from the full cell.

**Ultra-high precision coulometry (UHPC).**—The coulombic efficiency of cells was measured using the ultra-high precision chargers at Dalhousie University described in Reference 24. The cells after formation were tested at C/20 for 16 cycles between 3 and 4.3 V. The cells were placed at 40 ± 0.1 °C in temperature-controlled boxes during the tests.

**20 and 40 C long term cycling.**—The cells were tested for long term cycling with a C/3 rate between 3 and 4.2 or 4.3 V respectively. A cycle at a C/20 rate was included every 50 cycles. The cells were held at the top of charge until the current reached C/20 during each cycle. The tests were made at 20 or 40 ± 0.1 °C in temperature-controlled boxes. Neware (Shenzhen, China) chargers were used for these tests.

**20 C Plating tests.**—The NMC532/graphite cells were charged with a current (C-rates) of 210 mA (1C) for 30 cycles, 315 mA (1.5C) for 30 cycles and 420 mA (2C) for 30 cycles between 3 and 4.3 V using a Neware charger system at 20 ± 0.1 °C. The cells were discharged with a current of 105 mA (0.5C). In order to determine the active lithium loss during cycling, cells were cycled at C/5 three times before and after each high charge rate segment.

**Ex-situ gas measurement.**—The gas produced in cells due to electrolyte decomposition during cycling was measured using Archimedes’ principle.25 The pouch cells after cycling were first discharged to 3.8 V. Ex-situ gas measurements were carried out by suspending pouch cells from a fine wire “hook” attached under a Shimadzu balance (AUW200D) and then immersed in a beaker of de-ionized “nanopure” water (18 MΩ) that was at 20 ± 1 °C for measurement. The change in the weight of the cell suspended in fluid, before and after testing is directly related to the volume change by the change in the buoyant force. The change in weight of a cell, Δw, suspended in a fluid of density, ρ, is related to the change in cell volume, Δv, in mL by:

$$Δv = -Δw/(ρg)$$

where the weight is measured in milliNewtons, the density in g/mL and g is the acceleration due to gravity in m/sec². It is important to realize that w/g is what a balance reports as the mass in grams.

**In-situ gas measurement.**—The gas produced in cells due to electrolyte decomposition during testing was measured using Archimedes’ principle.25 A strain gauge load cell was used to measure changes in the buoyant force of cells submerged in mechanical pump oil kept at a steady temperature as the pouch cells were charged and discharged. A detailed account of this method was described by Aiken et al.25

One batch of cells filled with electrolyte underwent formation during simultaneous in-situ gas measurements between 3 and 4.7 V using currents corresponding to C/20. A new batch of cells after formation in the usual way were first tested using the in-situ gas equipment between 3–4.3 V for one cycle and then were charged and held at 4.4, 4.5 and subsequently 4.6 V for 100 h each. The current used during testing was ~C/20 calculated based on the capacity measured between 3–4.3 V. The tests were made at 40 °C. The changes in the volume of the cells during testing were tracked as a function of time.

**Isothermal microcalorimetry.**—Cells used for isothermal microcalorimetry measurements underwent formation, then were transferred into a TAM III Microcalorimeter (TA Instruments: stability ± 0.0001 °C, accuracy ± 1 μW, precision ± 1 nW) at 40 °C and connected to a Maccor 4000 series cycler. The baseline drift over the course of the experiments did not exceed ± 0.5 μW. All specifications and information regarding microcalorimetry calibration, cell connections and operation procedures can be found in previous literature.26

Cells were cycled four times at a C/20 rate between 2.8 V and 4.2 V to ensure a well formed, stable negative electrode SEI and were then cycled between 4.0 V and different upper cutoff limits: 4.2 V, 4.3 V (twice), 4.4 V (twice) and again to 4.2 V (twice) at 1 mA to investigate the performance and the parasitic heat flow in different voltage ranges. A description of the analysis techniques is provided in the Results and discussion section.

**Results and Discussion**

The electrolytes were designed to contain a primary additive of VC, FEC or PES, which are known to form stable passivation films on the graphite negative electrode and a secondary additive of MMDS or DTD which were used to improve electrolyte stability at high voltages based on the previous studies.27

Figures 1a and 1b show a summary of the area specific charge transfer resistance (Rct) of cells after formation and the volume of gas generated during formation, respectively, for cells with each electrolyte. The red, gray and green bars show the results for cells with PES, FEC and VC as the primary additive, respectively. Figure 1a shows that cells containing PES had significantly larger Rct than cells without PES, which was between 180–350 Ω cm². This result is consistent with previous reports that cells with PES usually have large Rct.12,28 For cells containing FEC, the addition of the secondary additive MMDS or DTD slightly increased Rct compared to cells with 2FEC only. Rct of cells containing FEC was around 90–100 Ω cm² in cells with VC as the primary additive. Rct increased with increasing VC content from 1% to 2% when the same secondary additive was used. In general, cells with MMDS showed slightly larger Rct than cells with DTD when the same primary additive was used.

Large amounts of gas produced during formation can lead to difficulties maintaining electrode stack integrity due to: a) deformation of the jelly roll due to gas bubbles and b) gas pushing electrolyte out of the electrode stack. So it is important to identify systems that simply produce too much gas and eliminate them from further consideration. Figures 1b shows that the replacement of 1% A, where A is a primary additive of PES, FEC or VC, with 1% DTD or 1% MMDS increased the amount of gas generated during formation compared to cells with 2% A. For instance, cells with 2PES and 2FEC showed 0.22(3) and 0.22(2) mL of gas, respectively, while cells with 1PES + 1DTD, 1FEC + 1DTD and 1VC + 1DTD showed 0.30(2), 0.54(1) and 0.77(2) mL of gas, respectively. Additionally, cells with 2A + 1DTD and 2A + 1MMDS produced less gas than cells with 1A + 1DTD and 1A + 1MMDS, respectively. For instance, cells with 2PES + 1DTD, 2FEC + 1DTD and 2VC + 1DTD...
produced 0.23(2), 0.38(3), and 0.60(2) mL of gas, respectively, while cells with 1PES+1DTD, 1FEC+1DTD and 1VC+1DTD produced 0.30(2), 0.54(1) and 0.77(2) mL of gas, respectively. When FEC and VC were used as primary additives, cells containing DTD produced more gas than cells with MMDS while the same primary additive was used. For instance, cells with 2FEC+1DTD produced 0.23(2), 0.38(3), and 0.60(2) mL of gas while cells with 2FEC+1MMDS and 2VC+1MMDS produced 0.26(2) and 0.23(1) mL of gas.

To generally evaluate the performance of the designed electrolytes, the cells with 2A, 1A+1DTD, 2A+1DTD, 1A+1MMDS and 2A+1MMDS, where A is a primary additive of FEC, VC or PES, were first tested with long term cycling at 40°C between 3.0 and 4.3 V. A current corresponding to C/3, assuming a capacity of 230 mAh, was used. Every 50 cycles, one C/20 cycle was performed. During every charge, the cells were held at the top of charge until the current reached C/20. Figures 2a1, 2b1 and 2c1 show the discharge capacity, normalized discharge capacity and ΔV (difference between the average charge and discharge voltage), respectively, as a function of cycle number for cells with FEC as the primary additive. Figures 2a2, 2b2 and 2c2 show the corresponding results for cells with VC as the primary additive, while Figures 2a3, 2b3 and 2c3 show the corresponding results for cells with PES as the primary additive. The blue squares, black triangles, red crosses, green diamonds and purple crosses show the results for cells with 2A, 1A+1DTD, 2A+1DTD, 1A+1MMDS and 2A+1MMDS, where A is the primary additive of FEC, VC or PES, respectively. When FEC was used as the primary additive, Figures 2b1 shows that cells with MMDS exhibited the worst capacity retention of only ~96% in 100 cycles. The cells with 2FEC + 1DTD exhibited better capacity retention, above ~95% after 850 cycles, than cells with 2FEC only. Figure 2c1 shows that cells with MMDS exhibited the highest ΔV growth of ~0.025(5) V after 100 cycles, while cells containing DTD showed the lowest ΔV growth of ~0.007(1) V after 850 cycles.

When VC was used as the primary additive, Figure 2b2 shows that cells with MMDS also exhibited the worst capacity retention of ~97% after 100 cycles. The cells with 2VC + 1DTD exhibited better capacity retention, above ~96% after 850 cycles, than cells with 2VC only. Figure 2c2 shows that cells with MMDS exhibited the largest ΔV growth of ~0.015(1) V after 100 cycles, while cells with DTD showed the lowest ΔV growth of ~0.008(1) V after 850 cycles.

When PES was used as the primary additive, Figure 2b3 shows that cells with PES all lost about ~2–3% capacity during the first 100 cycles. Additionally, Figure 2b3 shows that cells with 2PES + 1DTD exhibited the best capacity retention. Figures 2c3 shows that cells with PES all exhibited fast ΔV growth of ~0.005(1) V in 100 cycles, which is much worse than cells with FEC or VC with DTD. Overall, Figure 2 shows that combinations of FEC or VC with DTD can significantly improve the cell capacity retention and suppress the ΔV growth comparing to FEC or VC only. The following work, therefore, focuses on combinations of FEC or VC with DTD.

To test high rate charging capability of cells with the designed electrolytes, cells were charged with currents (C-rates) of 210 mA (1C) for 30 cycles, 315 mA (1.5 C) for 30 cycles and 420 mA (2 C) for 30 cycles between 2.8 and 4.3 V at 20 °C. The electrode loadings of the cells used in this work are listed in the Experimental section. The cells were discharged with a current of 105 mA (0.5 C). To determine the capacity loss due to unwanted lithium plating during high rate charging tests, cells were cycled at C/5 for three times before and after each high rate segment (30 cycles). Figures S2, S3 and S4 show the discharge capacity as a function of cycle number for cells with FEC, VC and PES as primary additive, respectively. Figure 3 shows a summary of the accumulated capacity losses after each high rate segment. The capacity loss was calculated by subtracting the discharge capacities of the third C/5 cycle after 1 C (cycle 37), 1.5 C (cycle 71) and 2 C (cycle 107) charging tests from the third C/5 cycle before any high rate tests (cycle 3), respectively. The gray, green and red bars show the capacity losses of cells after the 1 C, 1.5 C and 2 C charging tests, respectively. Figure 3 shows that cells with PES as the primary additive exhibited large capacity losses of ~50–90 mAh after testing with 1 C charging for 30 cycles, which is primarily due to unwanted lithium plating. Cells with FEC or VC or/and DTD showed negligible capacity loss during the 1 C charging test, indicating the absence of unwanted lithium plating. This result agrees well with Figure 1a which shows that cells with PES showed significantly higher Rct than cells with FEC or VC. Figure 3 also shows that cells containing VC had higher capacity losses than cells containing FEC after the 1.5 C charging test. The capacity losses for cells with 1FEC + 1DTD, 2FEC + 1DTD, 1VC + 1DTD and 2VC + 1DTD after the 1.5 C test were about 3.7(3), 2.5(3), 6(2) and 17(3) mAh, respectively. Cells with 2FEC + 1DTD could be charged at 1.5 C with little lithium plating, however, cells with 2VC + 1DTD experienced severe unwanted lithium plating. Further developments in the electrolyte system are required if 2VC + 1DTD is selected. This result agrees well with Figure 1a that cells with 2VC + DTD showed higher Rct than cells with 2FEC+1DTD. Additionally, Figure 3 shows that all cells exhibited significant capacity losses of more than 20 mAh after the 2 C charging test, indicating severe unwanted lithium plating at this rate regardless of the electrolyte additives selected. Nevertheless, Figure 3 shows that cells with 2FEC + 1 DTD or VC + 1DTD can be charged at 1 C without lithium plating at 20 °C, which is a significant improvement over the PES211 electrolyte which cannot support C/2 rate charging at room temperature without unwanted lithium plating.

To further investigate the gas generation during formation, cells after testing with electrolytes were charged to 4.7 V and then discharged to 3.8 V at 40°C with currents corresponding to C/20, while the volumes of gas produced in the cells due to electrolyte decomposition were measured in situ. Figure 4a shows the cell voltage as a function of time while Figure 4b shows the corresponding volume changes of...
Figure 2. The discharge capacity (a1), normalized discharge capacity (b1) and ΔV (difference between the average charge and discharge voltage) (c1), respectively, as a function of cycle number for cells with FEC as the primary additive. The discharge capacity (a2), normalized discharge capacity (b2) and ΔV (c2), respectively, as a function of cycle number for cells with VC as the primary additive. The discharge capacity (a3), normalized discharge capacity (b3) and ΔV (c3), respectively, as a function of cycle number for cells with PES as the primary additive. The blue squares, black triangles, red crosses, green diamonds and purple crosses show the results for cells with 2A, 1A+1DTD, 2A+1DTD, 1A+1MMDS and 2A+1MMDS, where A is the primary additive of FEC, VC or PES, respectively.

Figure 3. The summary of the accumulated capacity losses after each high rate segment. The capacity loss was calculated by subtracting the discharge capacities of the third C/5 cycle after 1 C (cycle 37), 1.5 C (cycle 71) and 2 C (cycle 107) charging tests from the third C/5 cycle before any high rate tests (cycle 3), respectively. The gray, green and red bars show the capacity losses of cells after the 1 C, 1.5 C and 2 C charging tests, respectively.

Figure 4. The cell voltage as a function of time (a) and the corresponding volumes of cells as a function of time (b) during in-situ gas measurement of cells at formation. Cells after filled with electrolytes were charged to 4.7 V and then discharged to 3.8 V with currents of C/20. The cell voltage as a function of time (c) and the corresponding volumes of cells as a function of time (d) during in-situ gas measurement of cells at high voltage holds. The cells after formation were charged and held at 4.4, 4.5 and 4.6 V for 100 h. The black, blue, red and green solid lines show the results for cells with 2VC, 2VC+1DTD, 2FEC and 2FEC+1DTD, respectively.
The UHPC results of cells with 1DTD, 2VC and 2VC+1DTD tested between 3 and 4.3 V using currents corresponding to C/20 at 40°C (a), and the UHPC results of cells with 1DTD, 2FEC and 2FEC+1DTD tested between 3 and 4.3 V using currents corresponding to C/20 at 40°C (b). Each panel includes a plot of coulombic efficiency (CE), charge end point slippage (Ch. End. Pt.), normalized discharge capacity (Qd), and ΔV (the difference between the average charge voltage and the average discharge voltage) as a function of cycle number, respectively.

The volumes of gas generated after the holds at 4.4, 4.5 and 4.6 V for 100 h were 0.03(1), 0.15(3) and 0.17(2) mL, respectively. Cells with 2VC generated slightly more gas at voltages higher than 4.4 V. The volumes of gas generated after the holds at 4.4, 4.5 and 4.6 V for 100 h were 0.03(1), 0.15(3) and 0.17(2) mL, respectively. Cells with 2VC+1DTD produced relatively more gas when the voltages were at and above 4.5 V, the corresponding volumes of gas generated were 0.11(1), 0.12(1) and 0.45(2) mL, respectively. This indicates that cells with 2VC+1DTD may have worse electrolyte stability than cells with 2FEC+1DTD at voltages above 4.4 V.

Figure 5 shows the results from UHPC measurements of cells tested between 3 and 4.3 V using currents corresponding to C/20 at 40°C. Each panel includes a plot of coulombic efficiency (CE), charge end point capacity slippage (Ch. End. Pt.), normalized discharge capacity (Qd), and ΔV (the difference between the average charge voltage and the average discharge voltage) as a function of cycle number. Figure 5a shows the UHPC results for cells with 1DTD (red crosses), 2VC (blue crosses) and 2VC + 1DTD (green diamonds). Figure 5a shows that the CEs of cells with 1DTD, 2VC and 2VC + 1DTD at the 16th cycles were ~0.99836(1), 0.99862(3) and 0.99876(6), respectively. The corresponding charge end point capacity slippage at the 16th cycle were 6.1(1), 4.7(1) and 4.2(2) mAh, respectively. Figure 5a shows that cells with 2VC+1DTD exhibited higher CE and smaller charge end point capacity slippage than cells with 2VC only and 1DTD only. This suggests that cells with 2VC+1DTD will have longer lifetime than cells with 2VC only and 1DTD only in low rate testing at 40°C. Figure 5b shows the UHPC results of cells with 1DTD (red crosses), 2VC (blue crosses) and 2VC+1DTD (green diamonds). Figure 5b shows that cells with 2VC+1DTD produced less gas at voltages below 3.5 V. Figure 4b shows that the peak gas volumes of cells with 2VC, 2VC + 1DTD, 2FEC and 2FEC + 1DTD in this region were about 0.36(2), 0.87(2), 0.34(2) and 0.73(2) mL, respectively. This shows that the addition of DTD leads to significant additional gas generation. Between 3.5 and 4.5 V (3–25.5 h), the cell volumes decreased due to gas consumption in the cells. Cells with DTD showed faster gas consumption rates than cells without DTD. The decrease in cell volumes of cells with 2VC, 2VC + DTD, 2FEC and 2FEC + DTD were 0.09(2), 0.26(2), 0.15(2) and 0.38(2) mL, respectively. Figure 4b shows the second region of gas generation above 4.5 V, which is primarily due to electrolyte oxidation. The volumes of gas generated in cells with 2VC, 2VC + DTD, 2FEC and 2FEC + DTD were 0.1(1), 0.04(1) and 0.11(2) mL after the holds at 4.4, 4.5 and 4.6 V for 100 h, respectively, while the corresponding volumes of gas generated in cells with 2FEC + 1DTD were 0.06(1), 0.06(1) and 0.12(2) mL, respectively. These are extremely small volumes of gas considering that the initial cell volume was about 2.5 mL. Cells with 2VC generated slightly more gas at voltages higher than 4.4 V. The volumes of gas generated after the holds at 4.4, 4.5 and 4.6 V for 100 h were 0.03(1), 0.15(3) and 0.17(2) mL, respectively. Cells with 2VC + 1DTD produced relatively more gas when the voltages were at and above 4.5 V, the corresponding volumes of gas generated were 0.11(1), 0.12(1) and 0.45(2) mL, respectively. This indicates that cells with 2VC + 1DTD may have worse electrolyte stability than cells with 2FEC + 1DTD at voltages above 4.4 V.

To further study the electrolyte stability at the positive electrode surface, the cells after formation were charged and held at 4.4, 4.5 and 4.6 V for 100 h while the volumes of gas produced in the cells due to electrolyte decomposition at high voltages were measured in-situ. The temperature of the experiment was 40.0°C. Figure 4c shows the cell voltage as a function of time while Figure 4d shows the corresponding volume changes of the cells as a function of time. The black, blue, red and green solid lines show the results for cells with 2VC, 2VC + 1DTD, 2FEC and 2FEC + 1DTD, respectively. Figure 4d shows that cells with 2FEC and 2FEC + 1DTD produced a minimal amount of gas during the high voltage holds. The volumes of gas generated in cells with 2FEC were 0.1(1), 0.04(1) and 0.11(2) mL after the holds at 4.4, 4.5 and 4.6 V for 100 h, respectively, while the corresponding volumes of gas generated in cells with 2FEC + 1DTD were 0.06(1), 0.06(1) and 0.12(2) mL, respectively. These are extremely small volumes of gas considering that the initial cell volume was about 2.5 mL. Cells with 2VC generated slightly more gas at voltages higher than 4.4 V. The volumes of gas generated after the holds at 4.4, 4.5 and 4.6 V for 100 h were 0.03(1), 0.15(3) and 0.17(2) mL, respectively. Cells with 2VC + 1DTD produced relatively more gas when the voltages were at and above 4.5 V, the corresponding volumes of gas generated were 0.11(1), 0.12(1) and 0.45(2) mL, respectively. This indicates that cells with 2VC + 1DTD may have worse electrolyte stability than cells with 2FEC + 1DTD at voltages above 4.4 V.
Figure 6. The coulombic inefficiency per hour (CIE/h) (a), the fractional slippage per hour (Fract. Slip./h) (b), and the fractional fade per hour (Fract. Fade/h) (c) as a function of electrolyte type. The black, gray, red, blue and green bars show the results for cells with 1DTD, 2FEC, 2FEC+1DTD, 2VC and 2VC+1DTD, respectively.

2FEC (black crosses) and 2FEC + 1DTD (red diamonds). Figure 5b shows that the CIEs of cells with 1DTD, 2FEC and 2FEC + 1DTD at the 16th cycle were \(-0.99836(1), 0.99844(1)\) and \(0.99864(1)\), respectively. The corresponding charge end point capacity slippage at the 16th cycle were \(6.1(1), 5.2(1)\) and \(4.61(4)\) mAh, respectively, while the corresponding normalized capacities at the 16th cycle were \(0.9895(1), 0.9829(7)\) and \(0.9885(8)\) correspondingly. Figure 5b shows that cells with 2FEC + 1DTD showed higher CE and smaller charge end point slippage capacity than cells with 2FEC only and 1DTD only. This suggests that cells with 2FEC + 1DTD will have longer lifetime than cells with 2FEC only and 1DTD only in low rate testing at 40°C.

Figures 6 shows summaries of the UHPC results, where Figures 6a, 6b and 6c show the coulombic inefficiency per hour (CIE/h), the fractional charge end point capacity slippage per hour (Fract. Slip./h), and the fractional capacity fade per hour (Fract. Fade/h) as a function of electrolyte type. The black, gray, red, blue and green bars show the results for cells with 1DTD, 2FEC, 2FEC + 1DTD, 2VC and 2VC + 1DTD, respectively. During each cycle,

\[
\text{CIE/h} = \frac{(1 - CE)}{t},
\]

where \(t\) is the time of each charge-discharge cycle and the results from the 16th cycle were plotted.

\[
\text{Fract. Slip./h} = \text{slope} \left\{ \text{Ch.End.Cap} / Q_d/t \right\},
\]

\[
\text{Fract. Fade/h} = \text{slope} \left\{ Q_d / Q_d/t \right\},
\]

\[
\text{CIE/h} = \text{Fract.Slip./h} + \text{Fract.Fade/h},
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as discussed by Harlow et al.30 and Smith et al.9

Figure 6a shows that cells with 2FEC + 1DTD or 2VC + 1DTD had lower CIE/h than cells with 2FEC, 2VC and 1DTD only. The CIE/h values for cells with 1DTD, 2FEC, 2FEC + 1DTD, 2VC and 2VC + 1DTD were \(-4.0(1), 3.88(2), 3.24(6), 3.42(5)\) and \(2.91(5)\), respectively, where cells with 2VC + 1DTD showed the lowest CIE/h. This suggests that cells with 2VC + 1DTD should have the longest lifetime in low rate testing at 40°C. Figure 6b shows that cells with 2FEC + 1DTD and 2VC + 1DTD had lower Fract. Slip./h than cells with 2FEC, 2VC and 1DTD only. The Fract. Slip./h values for cells with 1DTD, 2FEC, 2FEC + 1DTD, 2VC and 2VC + 1DTD were \(-2.79(2), 2.12(4), 2.04(3), 1.92(5)\) and \(1.76(6)\), respectively, where cells with 2VC + 1DTD showed the lowest Fract. Slip./h. This suggests that cells with 2VC + 1DTD should have the longest lifetime in low rate testing at 40°C. Figure 6b shows that cells with 2FEC + 1DTD and 2VC + 1DTD had lower Fract. Fade/h than cells with 2FEC, 2VC and 1DTD only. The Fract. Fade/h values for cells with 1DTD, 2FEC and 2FEC + 1DTD, 2VC and 2VC + 1DTD were \(-1.62(1), 2.19(9), 1.61(9), 1.98(8)\) and \(1.65(9)\), respectively. Cells with 2FEC + 1DTD and 2VC + 1DTD showed lower Fract. Fade/h than cells with 2VC + 1DTD.
Figure 8. The discharge capacity (a), normalized discharge capacity (b) and $\Delta V$ (c), respectively, as a function of cycle number for cells with an upper cutoff voltage of 4.2 V. The discharge capacity (A), normalized discharge capacity (B) and $\Delta V$ (C), respectively, as a function of cycle number for cells with an upper cutoff voltage of 4.3 V. The cells were tested at 40°C using currents corresponding to C/3. In every 50 cycles, one C/20 cycle was performed. During every charge, the cells were held at the top of charge until the current reached C/20.

2FEC and 2VC only, while cells with 1DTD only showed comparable Fract. Fade/h to cells with 2FEC + 1DTD and 2VC + 1DTD. This suggests that cells with 1DTD would have little fade in early cycles, however they would have shorter lifetime due to significant electrolyte oxidation as shown in Figure 6b (the worst Fract. Slip./h) during low rate testing at 40°C.

The cells with 2FEC + 1DTD and 2VC + 1DTD electrolytes were also studied with isothermal microcalorimetry to probe the magnitude of the parasitic reactions by separating the parasitic heat flow from the total measured heat flow from the cells. When current is applied to a cell, the measured heat flow comes from the voltage polarization, entropy changes in the electrode materials, and the parasitic reactions occurring in the cell. Since the entropic heat flow is reversible between charge and discharge, the average parasitic heat flow at each voltage point can be found by taking the average of charge and discharge heat flow and subtracting the average overpotential heat flow. The details of this method were introduced by S. Glazier et al. During the calorimetry experiments, cells were cycled between 4.0 V and different upper cutoff potentials: 4.2 V, 4.3 V (twice), 4.4 V (twice) and again to 4.2 V (twice) at 1 mA. The currents used corresponded to a C/100 rate for each type of cell. Figure 7a shows the resulting parasitic heat flow for cells between 4.0 V and 4.3 V. The red and green lines show the parasitic heat flow for cells with 2FEC + 1DTD and 2VC + 1DTD, respectively, as a function of voltage. Figure 7a shows that cells with 2VC+1DTD had much less parasitic heat flow than cells with 2FEC + 1DTD at the same voltage. Figure 7b shows a summary of the results by plotting the mean parasitic heat flow over each cycle (the average value in Figure 7a) to the various voltages, where the red and green circles show the mean parasitic heat flow for cells with 2FEC + 1DTD and 2VC + 1DTD pair cells, respectively. Figure 7b shows that cells with 2VC + 1DTD have a lower mean parasitic heat flow than cells with 2FEC + 1DTD in all voltage ranges, which suggests that cells with 2VC + 1DTD should have longer lifetime than cells with 2FEC + 1DTD during low rate cycling at 40°C. This result agrees well with the UHPC results (Figure 6).

Cells with 1DTD, 2FEC, 2FEC + 1DTD, 2VC, and 2VC + 1DTD were tested with long term cycling at 40°C using currents corresponding to C/3, assuming a capacity of 230 mAh, between 3 and 4.2 or 4.3 V. After every 50 cycles, one C/20 cycle was performed. During every charge, the cells were held at the top of charge until the current reached C/20. Figures 8a, 8b and 8c show the discharge capacity, normalized discharge capacity and $\Delta V$, respectively, as a function of cycle number for cells with an upper cutoff voltage of 4.2 V, whereas Figures 8A, 8B and 8C show corresponding results for cells with an upper cutoff voltage of 4.3 V. The purple triangles, black crosses, red diamonds, blue crosses and green diamonds show results for cells with...
Figure 9. The discharge capacity (a), normalized discharge capacity (b) and ΔV (c), respectively, as a function of cycle number for cells with an upper cutoff voltage of 4.2 V. The discharge capacity (A), normalized discharge capacity (B) and ΔV (C), respectively, as a function of cycle number for cells with an upper cutoff voltage of 4.3 V. The cells were tested at 20°C using currents corresponding to C/3. In every 50 cycles, one C/20 cycle was performed. During every charge, the cells were held at the top of charge until the current reached C/20.

1DTD, 2FEC, 2FEC + 1DTD, 2VC and 2VC + 1DTD, respectively. Figure 8b shows that cells with 2VC + 1DTD and 2FEC + 1DTD exhibited better capacity retention than cells with 1DTD only, 2VC only and 2FEC only. The normalized capacities of cells with 1DTD, 2FEC, 2VC, 2FEC + 1DTD and 2VC + 1DTD at cycle 400 were about 0.968, 0.964, 0.958, 0.976(1) and 0.973(1), respectively. Figure 8b shows the cells with 2FEC + 1DTD had ~93% capacity retention after 1500 cycles at 4.2 V. Figure 8B shows similar trends at 4.3 V. Cells with 2VC + 1DTD and 2FEC + 1DTD exhibited better capacity retention than cells with 1DTD only, 2VC only and 2FEC only. The normalized capacities of cells with 2FEC + 1DTD and 2VC + 1DTD were 0.917(3) and 0.931, respectively, after 1500 cycles when charged to 4.3 V. Cells with 2FEC only and 2VC showed the worst capacity retention with a normalized capacity of ~0.955 at cycle 550. Cells with 1DTD only showed a small capacity fade during early cycles as predicted from UHPC measurements. Figure 8C shows that cells with 1DTD only had faster ΔV growth rate than cells with 2FEC + 1DTD and 2VC + 1DTD. The ΔV growth rate for cells with 1DTD only was ~1.64(2) mV per 100 cycles while it was ~0.1.16(3) mV per 100 cycles for cells with 2FEC + 1DTD and 2VC + 1DTD in the first 800 cycles, however, the ΔV growth rate slowed down significantly to about 0.36(3) mV per 100 cycles for cells with 2FEC + 1DTD and 2VC + 1DTD after 800 cycles. This suggests that cells with 1DTD only would have shorter lifetime than cells with 2FEC + 1DTD and 2VC + 1DTD in the long term.

Figure 9 shows long term cycling results of cells tested at 20°C. The cycling protocol was the same as that for cells cycled at 40°C (Figures 8). Figures 9a, 9b and 9c show the discharge capacity, normalized discharge capacity and ΔV, respectively, as a function of cycle number for cells with an upper cutoff voltage of 4.2 V, while Figures 9A, 9B and 9C show the corresponding results for cells with an upper cutoff voltage of 4.3 V. The purple triangles, black crosses, red diamonds, blue crosses and green diamonds show the results for cells with 1DTD, 2FEC, 2FEC + 1DTD, 2VC and 2VC + 1DTD, respectively. Figure 9b shows that the capacity losses of all cells cycled at 4.2 V were small, less than 4% in 1400 cycles, however, the cells with 2FEC + 1DTD and 2VC + 1DTD showed better capacity retention than cells with 2FEC, 2VC and 1DTD. Additionally, Figure 9c shows that cells with 2FEC or 2VC had rapid ΔV growth rate while cells with 2FEC + 1DTD and 2VC + 1DTD showed the least ΔV growth in 1400 cycles. Similar trends were observed at 4.3 V. Figure 9B shows that cells with 2FEC + 1DTD and 2VC + 1DTD had less than 2% capacity fade in 1400 cycles, while cells with 2FEC showed ~10% capacity fade. Figure 9C shows that cells with 2FEC + 1DTD and 2VC + 1DTD showed the least ΔV growth in 1400 cycles while cells with 2FEC showed the largest ΔV increase.
temperature. More than 80% capacity was maintained after testing for 18 months (~3000 cycles with C/2 rate, CCCV) at 40 °C. However, the use of PES211 electrolyte usually leads to large negative electrode charge transfer resistance and therefore is not suitable for applications requiring high rates during charging. This work focused on the development of new electrolytes for single crystal NMC532/artificial graphite cells that can support long lifetime as well as 1C charging rates at room temperature.

Electrolytes with FEC, VC or PES as the primary additive and with MMDS or DTD as the secondary additive were first designed. Cells containing VC and FEC showed much smaller charge transfer resistance than cells containing PES. It was found that cells with DTD as the secondary additive had much better capacity retention than cells with MMDS during 40 °C cycling tests. High rate charging tests at 20 °C showed that cells with 2VC + 1DTD or 2FEC + 1DTD can support a 1C charging rate without unwanted lithium plating. UHPC results showed that cells with 2VC + 1DTD or 2FEC + 1DTD exhibited lower CIE/h and lower Fract. Slip./h than cells with 1DTD, 2VC or 2FEC only. Long term cycling results confirmed the predictions from UHPC testing and from microcalorimetry that cells with 2VC + 1DTD and 2FEC + 1DTD had better capacity retention than cells with 1DTD, 2VC or 2FEC only at 40 °C. Cells with 2VC + 1DTD or 2FEC + 1DTD exhibited more than 92% capacity retention after 1400 cycles to an upper cutoff of 4.3 V at 40 °C. The cells with 2FEC + 1DTD showed less than 2% capacity fade and had a stable ∆V for over 1400 cycles at room temperature. Cells with 2VC + 1DTD or 2FEC + 1DTD had comparable capacity retentions to the historical cells with PES211 electrolyte at 40 °C. Electrolytes containing 2VC + 1DTD or 2FEC + 1DTD as additives are excellent candidates for single-crystal NMC532/graphite cells which have long lifetime and can support C-rate charging at room temperature.

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Conclusions

Single crystal NMC532/artificial graphite cells can have excellent long term lifetime with PES211 electrolyte at 4.4 V and elevated
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