Methyl Acetate as a Co-Solvent in NMC532/Graphite Cells

Jing Li, Hongyang Li, Xiaowei Ma, Will Stone, Stephen Glazier, Eric Logan, Erin Marie Tonita, Kevin L. Gering, and J. R. Dahn

One goal of researchers focusing on lithium-ion batteries for electric vehicles is to decrease the time required for charging. This can be done by several methods, including increasing the electrolyte transport properties. Methyl acetate, used as a co-solvent in the electrolyte, has been shown by a number of researchers to increase cell rate capability dramatically but careful considerations of the impact of methyl acetate on cell lifetime have not been published to our knowledge. The impacts of methyl acetate as a co-solvent in NMC532/graphite cells were systematically studied in this work. Ex-situ gas evolution measurements, electrochemical impedance spectroscopy, high rate charging tests, ultra-high precision coulometry, isothermal microcalorimetry and long term cycling at both 20 and 40 °C were used to probe the impacts of including methyl acetate as a co-solvent. This work will be of great interest to Li-ion battery scientists developing cells that can support rapid charge and still maintain long lifetime.

© The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0861805jes]

Manuscript submitted January 17, 2018; revised manuscript received March 21, 2018. Published April 5, 2018.

Experimental

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), ethylene sulfate (DTD, Sigma Aldrich, purity 98%), and fluoroethylene carbonate (FEC, BASF, purity 99.94%), were used as electrolyte additives. Methyl Acetate was obtained for BASF (purity 99.99%) and was used as a co-solvent.

Pouch cells.—402035 size machine-made single crystal NMC532/artificial graphite (AG) pouch cells (240 mA/h 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. The positive electrode loading was 21.3 mg/cm2 and the electrodes were calendared to a density of 2.05 to 2.1 g/cm³. The positive electrodes had compositions of 80% active material, 18% carbon and 2% binder.

Lithium ion cells for electric vehicles should have long lifetime, high energy density and be able to support high rate charging. If cells are charged too rapidly for a given temperature, it is possible that unwanted lithium plating on the graphite negative electrode can occur and can accelerate cell capacity loss. There is a number of factors that influence the ability of cells to be charged rapidly. These include the thicknesses of the electrodes and the separator, the porosity and tortuosity of the electrodes and the separator and the electrolyte transport properties. In addition, Liu et al. recently highlighted the importance of the negative electrode solid electrolyte interphase (SEI) resistance on the ability of cells to be charged rapidly without unwanted lithium plating during charging.

For any given cell design, the easiest change to make in Li-ion cell manufacturing is a change in the electrolyte. All that entails, apart from possible materials compatibility issues, is filling cells with a different fluid. Electrolytes that promote high lithium-ion diffusion constants, low viscosity, high conductivity, a high lithium ion transference number and promote low resistance negative electrode SEI layers are preferred for cells designed for high rate charging. Esters are beneficial co-solvents that lower freezing points, increase ionic conductivity and lower viscosity. Esters have been applied to improve the low temperature rate capability of Li-ion cells and also improve rate capability at room temperature.3–10 Li-ion batteries with esters and positive electrodes of LiCoO2 were systematically studied in this work. Ex-situ gas evolution measurements, electrochemical impedance spectroscopy, high rate charging tests, ultra-high precision coulometry, isothermal microcalorimetry and long term cycling at both 20 and 40 °C were used to probe the impacts of including methyl acetate as a co-solvent. This work will be of great interest to Li-ion battery scientists developing cells that can support rapid charge and still maintain long lifetime.

© Electrochemical Society Member.
** Electrochemical Society Student Member.
*** Electrochemical Society Fellow.

E-mail: jeff.dahn@dal.ca

1 Physics and Atmosphere Science, Dalhousie University, Halifax, NS B3H 3J5, Canada
2 Department of Biological & Chemical Processing, Idaho National Laboratory, Idaho Falls, Idaho 83415-3732, USA
directly transferred to an argon-filled glove box without exposure to ambient air, where they were filled with 1.0 g electrolyte. 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.

To study the impact of MA as a co-solvent, the base electrolytes were 1.2 M LiPF6 in [(1-x)(3:7)] (EC: EMC): xMA by weight, where x = 0, 0.2 and 0.4. The base electrolytes will be referred to as 0 MA, 20 MA and 40 MA, respectively. For instance, the base electrolyte with x = 0.2 is 20 MA. Electrolyte additives used in this work were VC, FEC and DTD. The combinations of the additives used in the base electrolytes studied were 2 wt% FEC (2FEC), 2 wt% FEC + 1 wt% DTD (2FEC + 1DTD), 2 wt% VC (2VC), 2 wt% VC + 1 wt% DTD (2VC + 1DTD). The electrolyte will then be designated based on the additives and the base electrolyte. For example, 2FEC + 1DTD in 20 MA will be referred as 2FEC + 1DTD 20MA, where the first part indicates the additives and latter indicates the base electrolyte.

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. Then cells were clamped with rubber blocks in cell holding “boats” while they were charged at C/20 using a Maccor series 4000 automated test system (Maccor Inc.), where C/20 is the current required to complete a full charge or discharge in 20 hours. 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 were 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 Biologic VMP3 electrochemical test station. Ten data points per decade were collected from 100 kHz to 10 mHz with a signal amplitude of 10 mV. Reproducible solution resistance measurements were not possible due to variations in cable and connector resistances. Therefore, all impedance spectra were manually shifted to zero on the real axis at the highest frequency measured. Nyquist plots were used to extract the charge (both ion and electron) transfer resistance (Rct) (both electrodes) from the full cell as the total “diameter” of the impedance “semicircle”.

**Measurement of conductivity and viscosity.**—Viscosity measurements were carried out using an Ostwald viscometer (Sibata Scientific Technology, Japan). Two different sized viscometers were used in these experiments, with capillary diameters of 0.5 mm and 0.75 mm, respectively. The temperature of the electrolyte in the viscometer was controlled by a circulating bath (Thermo Scientific) filled with ethylene glycol. The temperature of the bath was varied between 0°C and 50°C in increments of 10°C. Conductivity and temperature measurements were recorded every 5 seconds using a Hach SC1000 controller so that these parameters could be monitored continuously. At each temperature step, a constant temperature was maintained for at least 40 minutes to allow for the electrolyte temperature to equilibrate with the bath. Data was only considered valid after the temperature of the electrolyte was stable.

**Ultra-high precision coulometry (UHPC).—**The coulombic efficiency of cells was measured using the ultra-high precision chargers at Dalhousie University described in Reference 16. 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°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 C/20 rate every 50 cycles was included. The cells were held at the top of charge until the current reached C/20 during each cycle. The tests were made at 20 ± 1 or 40 ± 0.1°C in temperature-controlled boxes. Newark (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 2.8 and 4.3 V using a Newark charger system at 20 ± 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 rate charging segment.

**Ex-situ gas measurement.**—The gas produced in cells due to electrolyte decomposition during cycling was measured using Archimedes’s principle.17 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.

**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 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.18 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 and 4.3 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**

Figure 1 shows the measured and calculated ionic conductivity and viscosity as a function of LiPF6 concentration in EC:EMC:MA 30:(70-x):x, by weight, as co-solvents where x = 0, 10 and 20. The closed circles show the measured results and the solid lines show the calculated results from the Advanced Electrolyte Model (AEM version 2.17.4).19 The blue, black and green points show the results for
x = 0, 10 and 20, respectively. Figures 1a and 1b show the conductivity results at 10 and 20 °C, respectively. The calculated results agree very well with the measured data. Figures 1a and 1b show that the ionic conductivity increases markedly with increasing MA content when the salt concentration and temperature remained constant. The measured conductivities for 1 m LiPF$_6$ in EC:EMC:MA 30:(70-x):x wt % with x = 0, 10 and 20 were about 7.91, 9.57 and 11.09 mS/cm, respectively, at 20 °C. Figures 1c and 1d show the viscosity versus molarity results at 10 and 20 °C, respectively. The results calculated using AEM v2.17.4 agree well with the measured viscosities at all salt concentrations. Figures 1c and 1d show that the viscosity of the solutions decreased with increasing MA content when the salt concentration and temperature remained constant. The measured viscosities for 1 mLFP$_6$ in EC:EMC:MA 30:(70-x):x with x = 0, 10 and 20 were about 3.39, 2.91, and 2.29 cP, respectively, at 20 °C. In the data of Figure 1, the EC content remained unchanged, which is slightly different than the solvent system used in the following pouch cell tests where the EC and EMC ratio was maintained constant when blending with MA. The base electrolytes in the following studies were 1.2 M LiPF$_6$ in [(1-x) (3:7):x (EC:EMC):MA by weight, where x = 0, 0.2 and 0.4. Nevertheless, Figure 1 shows that the use of MA as a co-solvent with EC:EMC can significantly increase the ionic conductivity and decrease viscosity of the electrolytes.

Figures 2a and 2b show the volume of gas generated during formation and the summary of the area specific charge transfer resistance (Rct) of cells after formation, respectively. The red, blue and green bars show the results for cells with 0, 20 and 40 MA, respectively. Figure 2a shows that in cells with 2FEC or 2VC only, the volume of gas produced during formation increased with increasing MA content. For instance, the gas produced in cells with 2FEC containing 0, 20 and 40 MA were 0.19(1), 0.27(3) and 0.40(4) mL, respectively. For cells with 2FEC + 1DTD or 2VC + 1DTD, the volume of gas produced during formation remained large and did not increase significantly with increasing MA content. Cells with 2VC + 1DTD produced the largest amount of gas during formation when the same base electrolyte was used (fixed MA content). The gas volumes of cells with 2VC + 1DTD in 0, 20 and 40 MA were 0.60(2), 0.57(4) and 0.65(3) mL, respectively. Figure 2b shows that the area specific charge transfer resistance (Rct) decreased with increasing MA content when the same additives were used. Rct values of cells with 2FEC + 1DTD in 0, 20 and 40 MA were 94.2(4), 77(6) and 66(4) Ω cm$^2$, respectively. Cells with 2VC + 1DTD exhibited the highest Rct when the same solvent was used (fixed MA content). Rct values of cells with 2VC + 1DTD in 0, 20 and 40 MA were 102(1), 88(11) and 81(7) Ω cm$^2$, respectively.

To test the impact of MA on high rate charging capability of cells with the designed electrolytes, 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 (2 C) for 30 cycles between 2.8 and 4.3 V at 20 ± 0.1 °C. 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 S1 and S2 in the supporting information show the discharge capacity as a function of cycle number for cells containing FEC and VC as additives, respectively. Figure 3 shows a summary of the accumulated capacity loss 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 all the cells had negligible capacity loss during the 1 C charging test regardless of the MA content, indicating the absence of unwanted lithium plating. Figure 3 also shows that cells containing FEC had small capacity losses after the 1.5 C charging test and the capacity loss decreased with increasing MA content. The capacity losses for cells containing 2FEC + 1DTD in 0, 20 and 40 MA after the 1.5 C charging test were 2.5(5), 1.15(5), and 1.1(1) mAh, respectively. Additionally, cells with 2VC + 1DTD in 0 MA showed a significant capacity loss of 17(3) mAh after the
Figure 3. Summary of the accumulated capacity losses after each high rate charge segment. The capacity loss was calculated by subtracting the discharge capacities of the third C/5 cycle after 1C (cycle 37), 1.5C (cycle 71) and 2C (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 1C, 1.5C and 2C charging tests, respectively.

1.5 C charging test, which is a sign of unwanted lithium plating. With increasing MA content, the capacity loss after the 1.5 C charging test decreased significantly. The capacity losses for cells with 2VC + 1DTD in 20 and 40 MA were 1.3(5) and 0.9(5) mAh, respectively. After the 2C charging test, cells without MA all showed large capacity loss. For instance, cells with 2FEC + 1DTD in 0 MA showed capacity losses of 22(2) and 66(2) mAh, respectively, due to unwanted lithium plating. With increasing MA content, the capacity losses decreased significantly to 3.5(9) and 1.2(5) mAh for cells with 2FEC + 1DTD in 20 and 40 MA, respectively, and 1.6(4) mAh for cells with 2VC + 1DTD in 20 and 40 MA, respectively. These cells with 2FEC + 1DTD and 2VC + 1DTD in 40 MA appear to be able to be charged at a 2C rate with little or no unwanted lithium plating. Overall, Figure 3 shows that the onset current of unwanted lithium plating for cells with 2FEC + 1DTD and 2VC + 1DTD increased with increasing MA content. Cells with 2FEC + 1DTD and 2VC + 1DTD in 20 MA can support 1.5 C charging rate at room temperature with little or no unwanted lithium plating while cells with 2FEC + 1DTD and 2VC + 1DTD in 40 MA can support 2C charging rate.

Figure 4 show 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, respectively. Figure 4a shows the UHPC results of cells with 2FEC in 0 MA, 2FEC + 1DTD in 0 MA, 2FEC in 20 MA, 2FEC + 1DTD in 20 MA, 2FEC in 40 MA, and 2FEC + 1DTD in 40 MA, which are shown as red crosses, red diamonds, blue crosses, blue diamonds, green crosses and green diamonds, respectively. Figure 4a shows that the CEs of cells with 2FEC in 0, 20 and 40 MA and cells with 2FEC + 1DTD in 0, 20 and 40 MA at the 16th cycles were 0.99844(1), 0.99806(2), 0.9979(1), 0.99864(1), 0.99836(8) and 0.9981(1), respectively. The CE of cells with the same additives decreased (bad) with increasing MA content. The cells with 2FEC + 1DTD showed much higher CE (good) than cells with 2FEC only in the same base electrolyte. Figure 4a also shows that the charge end point capacity slippages for the corresponding cells at the 16th cycle were 5.21(8), 5.94(8), 6.3(2), 4.61(4), 5.6(5) and 5.6(3) mAh, respectively, while the corresponding normalized capacities at the 16th cycle were 0.9829(7), 0.9789(3), 0.9801(9), 0.9885(8), 0.988(2) and 0.983(1), respectively. Figure 4a shows that the charge end point slippage capacity of cells with the same additives increased (bad) with the increasing MA content. The cells with 2FEC + 1DTD showed a
lower charge end point slippage capacity (good) than cells with 2FEC only in the same base electrolyte. This suggests that blending with MA as a co-solvent decreased the electrolyte stability at high voltages due to electrolyte oxidation. Additionally, the capacity fade of cells with the same additives also increased slightly with increasing MA content, however, the increase was less severe than that of the charge end point slippage capacity.

Figure 4b shows the UHPC results of cells with 2VC in 0 MA, 2VC + 1DTD in 0 MA, 2VC in 20 MA, 2VC + 1DTD in 20 MA, 2VC in 40 MA and 2VC + 1DTD in 40 MA, which are shown as red crosses, red diamonds, blue crosses, blue diamonds, green crosses and green diamonds, respectively. Figure 4b shows similar trends in Figure 4a, that the CE of cells with the same additives decreased with increasing MA content. Cells with 2VC + 1DTD showed much higher CE (good) than cells with 2VC only in the same base electrolyte. The CEs of cells with 2VC in 0, 20 and 40 MA and cells with 2VC + 1DTD in 0, 20 and 40 MA at the 16th cycle were ~0.99862(3), 0.99838(6), 0.99833(1), 0.99876(6), 0.99859(4), and 0.99854(4), respectively. Figure 4b also shows that the charge end point slippage capacity of cells with the same additives increased with increasing MA content. The cells with 2VC + 1DTD showed lower charge end point capacity slippage (good) than cells with 2VC only in the same base electrolyte. The charge end point capacity slippages of the corresponding cells at the 16th cycle were 4.7(2), 5.4(3), 5.79(1), 4.2(2), 5.2(2) and 5.3(2) mAh, respectively. This indicates that the addition of MA as a co-solvent decreased the electrolyte stability at high voltages due to electrolyte oxidation. Additionally, the capacity fade of cells with the same additives also increased slightly (bad) with the increasing MA content. The corresponding normalized capacities at the 16th cycle were 0.984(1), 0.9816(3), 0.9811(9), 0.9873(9), 0.9855(7) and 0.9851(5), respectively.

Figure 5 shows a summary of the UHPC results, where Figures 5a, 5b and 5c show the coulombic inefficiency per hour (CIE/h), the fractional charge end point slippage per hour (Fract. Slip/h), and the fractional fade per hour (Fract. Fade/h) as a function of MA content. The red circles connected by a dashed line, red diamonds with a solid line, green circles with a dashed line and green diamonds with a solid line show the results for cells with 2FEC, 2FEC + 1DTD, 2VC and 2VC + 1DTD additives, respectively. In each cycle, 

$$CIE/h = (1 - CE)/t,$$  

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

$$Fract. Slip./h = \text{slope(Ch. End. Cap./Q_{d1})},$$

$$Fract. Fade./h = \text{slope(Q_{d1}/Q_{d1})},$$

where $Q_{d1}$ is the first discharge capacity. The slope was calculated from the data in Figure 4 using the 12th to the 16th cycles. We expect the CIE, fractional slippage and fractional fade to be related by:

$$CIE/h = Fract. \text{ Slip.} /h + Fract. \text{ Fade.} /h,$$  

as discussed by Harlow et al.\textsuperscript{20} and Smith et al.\textsuperscript{21}

Figure 5a shows that the CIE/h increased (bad) with the increasing MA content for cells with the same additives. Additionally, cells with 2FEC + 1DTD and 2VC + 1DTD showed better CIE/h (good) than cells with 2FEC only and 2VC only, respectively, when the same base electrolyte was used. Moreover, cells with 2VC + 1DTD showed the lowest CIE/h (good) for each MA content. The CIE/h for cells with 2VC + 1/DTD in 20 MA and 2FEC + 1/DTD in 20 MA were 3.6(1) and 3.9(4) (10^{-3} h^{-1}), respectively. Figure 5b shows the Fract. Slip/h increased with increasing MA content (bad) for cells with the same additives. Additionally, cells with 2FEC + 1/DTD and 2VC + 1/DTD showed lower Fract. Slip/h (good) than cells with 2FEC only and 2VC only, respectively, when the same base electrolyte was used. Cells with 2VC + 1/DTD showed the lowest Fract. Slip/h (good) for each MA content. Figure 5c shows that the Fract. Fade/h increased slightly with increasing MA content for cells with the same additives. However, notice that the increase in Fract. Fade/h was much smaller than the increase in Fract. Slip/h with increasing MA content, for cells with the same additives. Hence, the increase in CIE/h with the increasing MA content was mostly caused by the increase in Fract. Slip/h, which indicates that one of the major impacts of MA is to decrease the electrolyte stability at the positive side especially at high voltages. Additionally, cells with 2FEC + 1/DTD and 2VC + 1/DTD showed lower Fract. Fade/h (good) than cells with 2FEC only and 2VC only, respectively, when the same base electrolyte was used. The UHPC results presented in Figure 5 indicate that cells with 2FEC + 1/DTD and 2VC + 1/DTD showed longer lifetimes than cells with 2FEC only and 2VC only, respectively, when the same base electrolyte is used. Additionally, cells with higher MA content will have shorter lifetimes when the same additives were used.

Figure 5. 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 MA content. The red circles connected by a dashed line, red diamonds connected with a solid line, green circles connected with a dashed line and green diamonds connected with a solid line show the results for cells with 2FEC, 2FEC + 1/DTD, 2VC and 2VC + 1/DTD additives, respectively.
Figure 6. 3D bar chart of CIE/h as a function of cell upper cutoff voltage and MA content for cells with 2FEC (a), 2FEC + 1DTD (b) and 2VC + 1DTD (c) electrolyte, respectively. 3D bar chart of Fract. Slip./h as a function of cell upper cut-off voltage and MA content for cells with 2FEC (A), 2FEC + 1DTD (B) and 2VC + 1DTD (C) electrolyte, respectively. For cells with the same MA content, cells with 2VC + 1DTD had lower CIE/h and Fract. Slip./h than cells with 2FEC + 1DTD in the same voltage range. This indicates that cells with 2VC + 1DTD_20 MA should have longer lifetime than cells with 2FEC + 1DTD_20 MA when cycled to the same upper cutoff voltages. Additionally, cells with 2VC + 1DTD_20 MA showed very similar CIE/h and Fract. Slip./h to cells with 2FEC + 1DTD.

Cells with and without MA 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...
Figure 7. The parasitic heat flow of cells as a function of voltage between 4.0 and 4.3 V during the first (a) and second cycle (b), respectively. The solid and dashed lines show the parasitic heat flow for cells with 2FEC only and 2FEC + 1DTD as additives, respectively, as a function of voltage. The black, blue and red lines show the results for cells with 0, 20 and 40 MA, respectively. The mean parasitic heat flow over each cycle to the various voltages (c), where the electrolytes corresponding to the various symbols are indicated in the legend.

subtracting the average overpotential heat flow. The details of this method were introduced by S. Glazier et al.23 During the calorimetry experiments, cells were cycled between 4.0 V and different upper cutoff potentials: 4.2 V and 4.3 V (twice) at 1 mA. These currents corresponded to a C/100 rate for each type of cells. Figures 7a and 7b show the resulting parasitic heat flow of cells between 4.0 V and 4.3 V measured during the first and second cycles to 4.3 V, respectively. The solid and dashed lines show the parasitic heat flow for cells with 2FEC only and for cells with 2FEC + 1DTD, respectively, as a function of voltage. The black, blue and red lines show the results for cells with 0, 20 and 40 MA, respectively. Figures 7a and 7b show that the parasitic heat flow increased with increasing MA content for cells with the same electrolyte additives. Figures 7a and 7b also show that cells with 2FEC + 1DTD had much lower parasitic heat flow than cells with 2FEC only when the same MA content was used. The cells with 2FEC + 1DTD in 20 MA showed similar parasitic heat flow as the cells with 2FEC only in 0 MA. Figure 7c shows a summary of the results by plotting the mean parasitic heat flow during each cycle (the average value in Figures 7a and 7b) to the various voltages, where the blue, black and red circles show the mean parasitic heat flow for cells with 0, 20 and 40 MA, respectively. The closed circles (solid lines) and open circles (dashed lines) show the results for cells with 2FEC only and 2FEC + 1DTD, respectively. Figure 7c shows that cells with 2FEC + 1DTD have a lower mean parasitic heat flow than cells with 2FEC only when the MA content was the same, which suggests that cells with 2FEC + 1DTD will have a longer lifetime than cells with 2FEC only. The cells with 2FEC + 1DTD in 20 and 40 MA showed comparable parasitic heat flows to the cells with 2FEC only in 0 and 20 MA, respectively. Additionally, Figure 7c shows that the mean parasitic heat flow of cells with the same additives increased with the increasing MA content. These results agree well with the UHPC results (Figure 5). Figures 5, 6 and 7 suggest that cells with higher MA content will have shorter lifetime.

Cells with 0 MA, 20 MA and 40 MA 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. Every 50 cycles,
Figure 8. 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 40°C using currents corresponding to C/3. 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.

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 ΔV, respectively, as a function of cycle number for cells with an upper cutoff voltage of 4.2 V. The crosses and triangles show the results for cells with 2FEC only and 2FEC + 1DTD, respectively. The red, blue and black colors show the results for cells with 0 MA, 20 MA and 40 MA, respectively.

Figure 8B shows that cells with 2FEC + 1DTD exhibited better capacity retention than cells with 2FEC only when the MA content was the same. Figure 8b also shows that the cells with higher MA content showed worse capacity fade when the same electrolyte additives were used. Cells with 2FEC + 1DTD in 0 and 20 MA showed 92.7(2)% and 90.7(1)% capacity retention, respectively, after 1500 cycles which represents about 13 months of continuous testing at 40°C.

Figure 8B shows similar trends for cells tested to 4.3 V at 40°C. Capacity fade increased with the increasing MA content when the same electrolyte additives were used. For instance, the normalized capacities of cells with 2FEC + 1DTD in 0, 20 and 40 MA were 0.977(3), 0.969(1) and 0.956(1) at the 400th cycle, respectively. Figure 8B also shows that the cells with 2FEC + 1DTD showed much better capacity retention than the cells with 2FEC only when the MA content was the same. The cells with 2FEC + 1DTD in 20 MA showed similar capacity retention to cells with 2FEC only in 0 MA. These results agree well with the UHPC and isothermal calorimetry predictions. The cells with 2FEC + 1DTD in 0 and 20 MA showed capacity retentions of 92.2(3)% and 89.2%, respectively, after 1600 cycles which represents about 13 months of continuous testing at 40°C.

Figure 8C shows that the cells with higher MA content exhibited faster ΔV growth rate when the same additives were used. The ΔV growth rates for cells with 2FEC + 1DTD in 0, 20 and 40 MA were 0.92(7), 1.16(3) and 2.04(1) mV per 100 cycles. Figure 8C also shows that cells with 2FEC only had much faster ΔV growth than cells with 2FEC + 1DTD in the same base electrolyte. The cells with 2FEC only in 20 and 40 MA showed accelerated ΔV growth after 250 cycles with a ΔV growth rate of 24.4(5) and 5.8(3) mV per 100 cycles, respectively. This indicates that the addition of DTD can significantly increase the stability of MA-containing electrolytes at high voltages, which agrees well with the UHPC and isothermal microcalorimetry results.

Figure 9 shows the 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. The crosses and triangles show the results for cells with 0 MA, 20 MA and 40 MA, respectively.

Figure 9b shows that the cells tested at 4.2 V were stable at 20°C, which makes it difficult to distinguish the differences between cells with 0, 20 and 40 MA
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 20°C using currents corresponding to C/3. 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.

Figure 9. 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 20°C using currents corresponding to C/3. 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.

when DTD was present. However, capacity fade increased with the increasing MA content when only FEC was used. Figure 9b shows that cells containing 2FEC with 40 MA started to fail after about 900 cycles, while cells containing 2FEC + 1DTD with 40 MA still have ~97% capacity retention. Figure 9c shows that cells with 2FEC + 1DTD had minimal $\Delta V$ growth over 1500 cycles regardless of the MA content. However, cells with only 2FEC showed obvious $\Delta V$ growth and the $\Delta V$ growth rate increased with the increasing MA content. Cells with 2FEC in 0, 20 and 40 MA showed $\Delta V$ growth rates of 2.4(1), 4.8(1) and 4.9(1) mV per 100 cycles, respectively. This suggests that cells with only 2FEC having higher MA content would fail first due to higher $\Delta V$ growth.

Figure 9B shows that the cells with 2FEC + 1DTD in 0 and 20 MA exhibited ~99% and 93% capacity retention after about 1500 cycles when tested to 4.3 V. The cells with 2FEC + 1DTD in 40 MA had ~92(2)% capacity retention at the 1050th cycle and started to show signs of failure. Figure 9B shows that cells with only 2FEC had much worse capacity retention than cells with 2FEC + 1DTD in the same base electrolyte. Cells with only 2FEC in 0, 20 and 40 MA showed capacity retention of ~97% at the 800th cycle, 86(6)% at the 800th cycle and ~85% at the 700th cycle, respectively. The cells with only 2FEC in 20 and 40 MA showed signs of failure beginning after about 500 cycles. Figure 9C shows that the cells with only 2FEC in 0, 20 and 40 MA showed significant $\Delta V$ increases when tested to 4.3 V. The cells with only 2FEC in 0, 20 and 40 MA showed $\Delta V$ growth rates of 12.9(2), 33(2) and 27(2) mV per 100 cycles after cycle 400. This shows that the addition of DTD as a co-additive can significantly improve the stability of electrolytes containing MA.

Figure 10 shows a comparison of the long term cycling results of cells with 2FEC + 1DTD and 2VC + 1DTD in 0 and 20 MA tested to 4.3 V at both 20 and 40°C. Figures 10a, 10b and 10c show the discharge capacity, normalized discharge capacity and $\Delta V$, respectively, as a function of cycle number for cells tested at 20°C, whereas Figures 10A, 10B and 10C show the corresponding results for cells cycled at 40°C. The cells were tested using the same protocol as discussed in Figures 8 and 9. The blue and red triangles show the results for cells with 2FEC + 1DTD and 2VC + 1DTD without MA, respectively, while the blue and red crosses show the results for cells with 2FEC + 1DTD and 2VC + 1DTD in 20 MA, respectively. Figure 10b shows that cells with 2FEC + 1DTD, 2VC + 1DTD and 2VC + 1DTD_20 MA exhibited less than 2% capacity fade after ~1400 cycles at 20°C, while cells with 2FEC + 1DTD_20 MA showed the worst capacity retention which is ~94.5% after ~1400 cycles. Figure 10B shows that cells with 2VC + 1DTD had better capacity retention than cells with 2FEC + 1DTD at 40°C when the MA content is the same, which agrees well with the UHPC data. Cells with 2VC + 1DTD and 2FEC + 1DTD in 20 MA showed ~92.8% and 92.2% capacity retention, respectively, after 1300 cycles, while cells with 2FEC + 1DTD_20 MA showed almost the same capacity retention as cells with 2FEC + 1DTD, which agrees well with the UHPC results shown in Figure S4 in the supporting information that showed that their CIE/h was similar.
Conclusions

It was found that 2FEC + 1DTD and 2VC + 1DTD electrolyte can provide comparable capacity retention for single crystal NMC532/graphite cells to PES211 electrolyte at 40°C. These electrolytes give small negative electrode charge transfer resistance and can support 1C charging rates at room temperature without lithium plating. To further improve the high rate charging capability, methyl acetate was selected as a co-solvent with EC and EMC for single crystal NMC532/artificial graphite cells. Blends of methyl acetate with EC and EMC as solvent were shown to increase the conductivity and decrease the viscosity of the electrolyte. The impacts of methyl acetate as a co-solvent in single crystal NMC532/artificial graphite cells were systematically studied. High rate charging test results show that the onset current of unwanted lithium plating for cells with 2FEC + 1DTD and 2VC + 1DTD increased with the increasing MA content. Cells with 2FEC + 1DTD and 2VC + 1DTD in 20 MA can support 1.5C charging rates at room temperature without lithium plating. UHPC results showed that the CIE/h, Fract. Slip./h and Fract. Fade/h increased with increasing MA content for cells with the same additives. Cells with 2FEC + 1DTD and 2VC + 1DTD showed better CIE/h than cells with only 2FEC and only 2VC, respectively, when the same MA content was used. The increase in CIE/h with increasing MA content was mostly caused by an increase in Fract. Slip./h. This suggests the major impact of MA is to decrease electrolyte stability at the positive side especially at high voltages. Isothermal microcalorimetry results showed that the mean parasitic heat flow of cells with the same electrolyte additives increased with increasing MA content. Cells with 2FEC + 1DTD had a lower mean parasitic heat flow than cells with only 2FEC in all voltage ranges when the MA content was the same. UHPC and isothermal microcalorimetry results both suggested that cells with higher MA content would have shorter lifetime during low rate cycling when the same additives were used. However, the use of DTD as a co-additive with FEC and VC can significantly improve the stability of MA containing electrolytes.

Long term cycling results confirmed that cells with higher MA content showed worse capacity retention and faster ΔV growth at both 20 and 40°C when the same electrolyte additives were used. Cells with 2FEC + 1DTD showed much better capacity retention than cells with only 2FEC when the MA content was the same. Through the selection of appropriate electrolyte additives, 2FEC + 1DTD and 2VC + 1DTD, and modification of the solvent system with methyl acetate, single crystal NMC532/graphite cells that can support both high charging rate and long lifetime were developed. Cells with 2VC + 1DTD and 2FEC + 1DTD in electrolytes with 20% MA showed capacity retentions of ∼92.8% and 91.2%, respectively, after 1300 cycles, when tested to 4.3 V at 40°C. This work will be of great interest to Li-ion battery scientists around the world who are trying to make cells that can support both fast charging and long lifetime.

Unwanted lithium plating significantly shortens the lifetime of cells requiring high rate charging at 20°C. Adding MA significantly reduces the likelihood of unwanted lithium plating at high-rate charging at 20°C. Therefore the impact of MA on battery life depends on the application. It is worth noting that substituting DMC for EMC also improves ability for fast charging and that adding MA to EC:DMC electrolytes further increases the charging rates before unwanted lithium plating occurs. The impact of MA additions on lifetime in EC:DMC electrolytes with FEC + DTD and VC + DTD additives is very
similar to what is reported here for EC:EMC electrolytes. The details will be reported soon in an upcoming publication.

Acknowledgments

The authors thank NSERC and Tesla Motors for the funding of this work under the auspices of the Industrial Research Chairs program. The authors thank Dr. Jing Li of BASF for providing most of the solvents and electrolyte additives used in this work. S.L.G thanks NSERC and the Walter C. Sumner Foundation for support. E.M.T thanks NSERC for support under the USRA program and H.L thanks the Nova Scotia Graduate Scholarship program for support.

ORCID

Jing Li  https://orcid.org/0000-0003-3698-7102
J. R. Dahn  https://orcid.org/0000-0002-6997-2436

References

1. J. C. Burns, D. A. Stevens, and J. R. Dahn, J. Electrochem. Soc., 162, A959 (2015).
2. Q. Q. Liu, R. Petibon, C. Y. Du, and J. R. Dahn, J. Electrochem. Soc., 164, A1173 (2017).
3. M. C. Smart, B. V. Ratnakumar, K. B. Chin, and L. D. Whitcanack, J. Electrochem. Soc., 157, A1361 (2010).
4. H. C. Shiao, D. Chua, H. P. Lin, S. Slane, and M. Salomon, J. Power Sources, 87, 167 (2000).
5. S. V. Sazhin, M. Y. Khimchenko, Y. N. Tritchenenko, and H. S. Lim, J. Power Sources, 87, 112 (2000).
6. S. Herreyre, O. Huchet, S. Barusseau, F. Pertot, J. M. Bodet, and P. Biensan, J. Power Sources, 97–98, 576 (2001).
7. A. Ohta, H. Koshiba, H. Okuno, and H. Murai, J. Power Sources, 54, 6 (1995).
8. M. C. Smart, B. V. Ratnakumar, and S. Surampudi, J. Electrochem. Soc., 149, A361 (2002).
9. M. C. Smart, B. V. Ratnakumar, S. Surampudi, Y. Wang, X. Zhang, S. G. Greenbaum, A. Hightower, C. C. Ahn, and B. Fultz, J. Electrochem. Soc., 146, 3963 (1999).
10. S. I. Tobishima, K. Hayashi, K. I. Saito, and J. I. Yamaki, Electrochim. Acta, 40, 537 (1995).
11. R. Petibon, J. Harlow, D. B. Le, and J. R. Dahn, Electrochim. Acta, 154, 227 (2015).
12. J. Li, A. R. Cameron, H. Li, S. Glazier, D. Xiong, M. Chatzidakis, J. Allen, G. A. Botton, and J. R. Dahn, J. Electrochem. Soc., 164, 1534 (2017).
13. J. Li, H. Li, W. Stone, S. Glazier, and J. R. Dahn, J. Electrochem. Soc., 165(3), A626 (2018).
14. M. C. Smart, B. V. Ratnakumar, L. D. Whitcanack, K. B. Chin, S. Surampudi, H. Croft, D. Tile, and R. Staniewicz, J. Power Sources, 119–121, 349 (2003).
15. L. Y. Beaulieu, E. R. Logan, K. L. Gering, and J. R. Dahn, Rev. Sci. Instrum., 88, 095101 (2017).
16. T. M. Bond, J. C. Burns, D. a. Stevens, H. M. Dahn, and J. R. Dahn, J. Electrochem. Soc., 160, A521 (2013).
17. C. P. Aiken, J. Xia, D. Y. Wang, D. a. Stevens, S. Trussler, and J. R. Dahn, J. Electrochem. Soc., 161, A1548 (2014).
18. L. J. Krause, L. D. Jensen, and J. R. Dahn, J. Electrochem. Soc., 159, A937 (2012).
19. K. L. Gering, Electrochim. Acta, 51, 3125 (2006).
20. J. E. Harlow, D. A. Stevens, J. C. Burns, J. N. Reimers, and J. R. Dahn, J. Electrochem. Soc., 160(11), A2306 (2013).
21. A. J. Smith, J. C. Burns, D. Xiong, and J. R. Dahn, J. Electrochem. Soc., 158, A1136 (2011).
22. L. E. Downie and J. R. Dahn, J. Electrochem. Soc., 161, A1782 (2014).
23. S. L. Glazier, R. Petibon, J. Xia, and J. R. Dahn, J. Electrochem. Soc., 164, A567 (2017).