To further satisfy the development of electric vehicles (EVs), Li-ion batteries need to be designed with higher volumetric energy density, longer cycling life, higher rate capability, lower cost and so forth. These improvements can be fully or partially achieved by applying new positive and/or negative electrode materials, suitable electrolytes and additives. For instance, Li[Ni_{0.52}Co_{0.20}Al_{0.08}]O_{2} (NCA), as a typical positive electrode material, exhibits high energy density and capacity, and has been used in many EVs1,2 and power tools.3

Ketones have one less oxygen atom than the corresponding ester and additives. For instance, Li[Ni_{0.85}Co_{0.10}Al_{0.05}]O_{2} (NCA), as a typical positive electrode material, exhibits high energy density and capacity, and has been used in many EVs1,2 and power tools.3

The most studied positive electrode materials in combination with lithium-ion cells were LiCoO_{2}5–8 and LiNixCo_{1-x}O_{2}, and the most promising candidate, MP, was characterized in NCA cells during high rate charging tests up to 2.4 C at room temperature. The reactions between the charged electrodes and MP-containing electrolytes at elevated temperatures were also characterized by accelerating rate calorimetry (ARC).

Experimental

Preparation and formation of pouch cells.—All the chemicals were used as received from BASF: LiPF_{6} (99.9% purity, water content 14 ppm), ethylene carbonate (EC): ethyl methyl carbonate (EMC): dimethyl carbonate (DMC) (25:5:70 by vol%); water content 19.7 ppm), vinylene carbonate (VC), methyl propionate (MP, 99.8% purity, water content 19.9 ppm), ethyl acetate (EA, 99.99% purity, water content 19.4 ppm) and methyl butyrate (MB, 99.8% purity, water content 18.1 ppm).

Dry and sealed 280 mAh (4.2V) Li[Ni_{1-x-y}Co_{x}Al_{y}]O_{2}/graphite (NCA) pouch cells that do not contain electrolyte were obtained. Before filling with the designed electrolyte, pouch cells were cut open and dried at 100°C under vacuum for 14 h to remove any residual moisture. Afterwards, pouch cells were filled with 0.85 mL electrolyte in an Ar-filled glove box and sealed with a pouch sealer machine (MSK-115A Vacuum Sealing Machine) under vacuum at a pressure of ~90 kPa (relative to atmospheric pressure). For the ester-containing cells, four different electrolyte blends were prepared: 95.5: 80, 20: 40 and 40: 60 for (EC:EMC:DMC) solutions by wt%.

In all cells, 2 wt% VC (of the overall electrolyte solvent) was added as an additive. Herein, cells containing the EC:EMC:DMC ternary electrolyte and 2% VC are designated as the control cells.
After filling, cells were charged at 1.5 V for 24 h to promote wetting. Pouch cells in a 40°C box were subsequently connected to a Maccor 4000 series charger and charged at a current corresponding to C/2 for 1 h. Afterwards, cells were aged in a 60°C box for 22 h. In order to remove the gas formed during the charging and aging process, the pouch cells were cut open and resealed under vacuum in the glove box. After degassing, cells were connected back to the Maccor charger. Cells were charged to 4.2 V at a current of C/2, held for 1 h and discharged back to 3.8 V at C/10. During this step, a negligible amount of gas was produced and the cell formation process was finished. Cells were subsequently removed from the Maccor charger for electrochemical impedance spectroscopy measurement.

**Electrochemical impedance spectroscopy (EIS).—**The electrochemical impedance spectra of the pouch cells were collected after formation, after 500 h storage at 60°C and after the high rate cycling tests at ambient temperature using a BioLogic VMP3 equipped with 2 EIS boards. The cells were charged or discharged to 3.8 V before EIS measurement and all the measurements were performed at 10.0 ± 0.2°C from 100 kHz to 10 mHz (10 mV input). Impedance spectra were measured at 10°C to amplify the differences between cells with different co-solvents.

**Gas volume measurement.**—The gas production in pouch cells during formation and cycling was measured using Archimedes’ principle. Each cell was suspended underneath a Shimadzu analytical balance (AUW200D) and weighed while submerged in nano-purified deionized (DI) water (18 MΩ cm). The produced gas (ΔV) in each cell is proportional to the change in apparent cell weight (Δm) that was caused by the buoyant force, as Equation (1):

\[ ΔV = \frac{−Δm}{ρ} \]

where ρ is the density of DI water.

**Long-term and high charging rate cycling.**—Long-term cycling was performed at 40.0°C with an upper cut off potential of 4.2 V on a Neware testing system (Shenzhen, China). The cells were charged and discharged with a current corresponding to C/3 between 3.0 and 4.2 V and the voltage was held at 4.2 V at the top of charge until the current dropped below C/20. After 100 cycles at 40.0°C, one cell containing MP was moved to a Neware testing system at ambient temperature (20 ± 1°C). Each cell was first charged and discharged at C/5 (C = 220 mA) for 5 cycles. Subsequently, cells were cycled with sequentially increasing charge rates of C/3, C/2, 1 C, 1.2 C, 1.4 C, 1.6 C, 1.8 C, 2 C, 2.2 C and 2.4 C, respectively. The discharging rate was constantly set at C/5. Eleven cycles at each charging rate were applied. Cycling ended as unwanted lithium plating occurred. After the high charging rate cycles of 1 C, 2 C, 2.2 C and 2.4 C, cells were charged and discharged at C/5 5 times to determine the capacity retention and the existence of unwanted lithium plating using the methods in Reference 20.

**Conductivity measurement.**—Electrolytic conductivity was measured using a Hach conductivity sensor (model 3455). Four identical conductivity sensors were used in this study. Each probe had an integrated PT1000 resistive temperature device (RTD) to monitor the temperature of the electrolyte. 14.5 mL of electrolyte was added to a custom-made stainless steel holder under a fume hood. The probe was then sealed to the holder by an O-ring. The seal was maintained using custom-made stainless steel clamps. Sealed conductivity probes were then placed in a temperature controlled bath (VWR Scientific model 1151) filled with ethylene glycol. The temperature of the bath was varied between 0°C and 40°C, in increments of 5°C. Conductivity and temperature measurements were recorded every 5 seconds using a Hach sc1000 controller so that these 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. In the case that multiple valid points were recorded after the temperature of the electrolyte was considered stable, the corresponding conductivities and measured temperatures of these points were averaged.

**Viscosity measurement.**—Viscosity measurements were carried out using an Ostwald viscometer (Siata Scientific Technology, Japan). Two different sized viscometers were used 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 viscosity of the electrolyte was measured using computer vision (CV) software developed by Beaulieu et al.21 A full description of the viscometer setup, including the data acquisition software is described in Reference 21. Viscosity measurements were taken for temperatures ranging from 5°C to 50°C. The raw data were interpolated to temperatures in 5 degree increments between 5°C and 50°C using a linear interpolation method in Matlab.

**Accelerating rate calorimetry (ARC) measurement.**—The ARC measurements were carried out on electrodes extracted from cells.
containing MP. The details of ARC sample preparation can be found in Reference 22. For NCA, 94 mg electrode material and 30 mg electrolyte were used for the ARC testing samples. The ARC starting temperature was set at 70°C. For graphite-SiO, the electrode-electrolyte mass ratios were 100 mg lithiated graphite-SiO with 100 mg electrolyte. The ARC starting temperature was set to 50°C. Data were collected under adiabatic conditions as the sample self-heating rate (SHR) exceeded 0.03°C/min. Experiments were stopped at 350°C or when the SHR exceeded 20°C/min. For the samples containing 20% and 40% MP, two identical ARC samples were prepared and measured to ensure reproducibility.

Results and Discussion

Figures 1a and 1b show the measured conductivity and viscosity of 1.2 M LiPF6 in EC:EMC:DMC:MP as a function of temperature. The conductivity was measured between 5°C and 40°C and viscosity was measured between 5°C and 50°C. Figures 1c and 1d show the conductivity and viscosity curves for EC:EMC:DMC:MB. Figure 1a shows that 20% and 40% MP helped enhance the conductivity of electrolyte blends at temperatures below 30°C. At above 30°C, electrolytes containing MP showed smaller conductivity than the control electrolyte. Figure 1b shows that the viscosity of EC:EMC:DMC:MP decreased significantly with the increasing proportion of MP over the whole temperature range. In Figures 1c and 1d, the electrolyte blends containing MB show lower conductivity and higher viscosity than electrolyte blends containing MP. The results in Figure 1c and 1d are surprising. Normally when a co-solvent is added that reduces viscosity, the conductivity of the electrolyte increases. This does not happen in the case of MB. This suggests a very high proportion of ionpairs in the 1.2 m LiPF6 solutions containing MB.

Figures 2a to 2c show the differential capacity versus potential of NCA pouch cells containing different amounts of MP, EA, MB from 0% to 60% during the first charge cycle (formation). In Figures 2a-2c, all cells exhibit a dQ/dV vs. V peak at 3.1 V, indicating the formation of solid electrolyte interphase (SEI). The formation of these cells was done at C/2 where overpotentials are negligible, so it is hard to estimate the potential of this peak versus Li/Li⁺ but our experience with the control electrolyte indicates that this peak corresponds to the reduction of VC. Figures 2a to 2c show that adding esters to the electrolyte does not significantly affect the dQ/dV vs. V curve so it is believed that VC reduction products still dominate the negative electrode SEI even when the ester content is as large as 60%.

Figures 2d to 2f show typical Nyquist curves for these pouch cells after formation. Cells were charged or discharged to 3.8 V for the measurement which was performed at 10°C. The diameter of the “semi-circle” predominantly represents the sum of the charge-transfer resistances, Rct, at both the positive and negative electrodes, the resistances associated with the passage of Li⁺ ions through the SEI layers and that associated with ion desolvation at the electrode electrolyte interfaces. For simplicity, we call the diameter of the semicircle “Rct” here. All cells exhibited a similar Rct of ∼25 Ωcm².

Figures 3a to 3c show the capacity versus cycle number data for all NCA cells that were measured at 40°C. Two cells were run for each blend of ester co-solvent but data for only one cell is shown for clarity. The data for the pair cells were virtually identical. Many cells were stopped at 150 cycles due to the need for charger channels for other experiments. Adding a small proportion of ester to the control electrolyte did not apparently compromise the capacity retention. However, if the percentage of added ester was more than 20%MP, 40%EA or 40%MB, respectively, then capacity retention was affected. When the ratio of ester:(EC:EMC:DMC) was 60:40, then all cells showed worse capacity retention. Figures 3d to 3f show the difference between average charge and discharge voltages (measured over the entire cycle), called ΔV here, as a sign of impedance growth, corresponding to the data in Figures 3a to 3c. Figures 3d to 3f show that ΔV increased much faster with cycle number for cells with 40 or 60% MP
or 60% EA, consistent with the poor capacity retention. In the case of cells with 60% MP, poor 4-wire connections to the pouch cell tabs affected the quality of the ΔV measurements. Therefore one should limit the percentage of these two esters below 40% or 60%, respectively, when blending with EC:EMC:DMC (25:5:70) (and with 2% VC) electrolyte to ensure unchanged long-term cycling compared to control electrolyte.

Figure 3. Long-term cycling curves (C/3 and 40 ± 0.1 °C) and corresponding voltage hysteresis of clamped NCA pouch cells with variable ester contents: (a-c): Long-term cycling of cells containing MP, EA and MB; (d-f): ΔV of cells containing MP, EA and MB. In the case of cells with 60% MP, poor 4-wire connections to the pouch cell tabs affected the quality of the ΔV measurements.

Figure 4 shows the open circuit voltage versus time for NCA cells during open circuit storage at 60 °C for 500 h. Cells were cycled twice between 3.0 and 4.2 V and subsequently held at 4.2 V or 2.5 V respectively for 24 h before the storage tests began. Figures 4a to 4c show voltage (initially at 4.2 V) vs. time for cells that contained MP, EA or MB, respectively. The sharp voltage drop at the beginning of testing is mainly related to the parasitic reactions at the positive

![Figure 4](image-url)
Beyond 5% EA, the higher the proportion of EA, the more likely it is that negative electrode SEI will form. If reactions between the electrolyte and the negative electrode (for NCA graphite cells) yield information about the stability of the SEI, then the lithium content in the graphite will be reduced, and the full cell potential will also decrease. What is initially surprising is that the negative electrode showed better storage performance with the increasing amount of ester content than cells with EA or MP.

Figures 4d to 4f show the 2.5 V open circuit voltage versus time for the same types of cells as in Figures 4a–4d. At a full cell potential of 2.5 V, the NCA electrode is in a region where its potential, \( V(Q) \), depends weakly on capacity, \( Q \), while the negative electrode is in a region where its \( V(Q) \) relation depends strongly on \( Q \). This is because the negative electrode is almost fully delithiated when the cell is at 2.5 V. Therefore, changes in OCV during storage experiments at 2.5 V (for NCA graphite cells) yield information about the stability of the negative electrode SEI. If reactions between the electrolyte and the intercalated Li can occur, then the lithium content in the graphite will decrease and the full cell potential will also decrease. What is initially surprising about the data in Figures 4d to 4f is that the cell potential initially increases for the first 50 hours or so, before it turns over and begins to decrease as expected. The voltage turnover is caused by the diffusion of Li ions from the negative electrode overhang (initially higher lithium content) to the portion of the negative electrode opposite the positive electrode. Once the overhang is depleted, then the cell potential starts to drop.

Figure 4d shows that cells with 5% or 20% MP show very close capacity versus cycle number during the high rate charge experiments. The reader should note that, based on work by Ma et al., adding more VC to electrolytes with EA or MB could improve the 2.5 V storage performance, but at the expense of an increased negative electrode SEI impedance which would limit cell rate capability.

VC has been reported to be highly reactive to the negative electrode. Figure 6b shows that after 2.5 V storage, all cells containing esters produced more gas than control cells. Figure 6c shows that after 4.2 V storage, all cells containing esters produced more gas than the control cells. Most striking is the clear increase in gas volume with EA content. In order to test the effect of esters as co-solvents on the high-rate charge capability of these NCA cells, cells containing MP were tested with charging rates ranging from C/3 to 2.4 C. The experiments are modelled after those developed by Liu et al. The cells were always discharged at C/5. The tests were performed at 20 °C. Before the charge rate capability tests, all cells were cycled at C/3 for 100 cycles at 40 °C and the capacity versus cycle number data for those cells is shown in Figure S1. Figure S1 shows that the capacity retention closely resembles those shown in Figures 3a and 3d. Figure 7 shows the cell capacity versus cycle number during the high rate charge experiments.

![Figure 5](image-url) - Impedance spectra of clamped NCA/Graphite-SiO pouch cells with different ester contents after 500 h storage tests at 60 °C: (a-c) cells containing MP, EA and MB were stored at 4.2 V; (d-f) cells containing MP, EA and MB were stored at 2.5 V.
The proportion of MP in EC:EMC:DMC:MP

Figure 6. Gas evolution of NCA pouch cells with differing MP, EA and MB contents after: (a) formation at 40 ± 0.1°C; (b) 500 h storage after charging to 4.2 V at 60 ± 0.1°C and (c) 500 h storage after charging to 2.5 V at 60 ± 0.1°C. The reader is cautioned that the y-axis scales in panels a), b) and c) are very different.

Figure 8. Gas production in NCA pouch cells containing MP after high rate cycling.

The charge-discharge cycling ceased when obvious capacity fade was observed. The cells containing 60% MP showed poor high-rate charge cycling and significant capacity fade was observed at C/3 and 1.4C respectively. Cells containing no MP, 5% and 20%MP could tolerate cycling at 1.8C and cells began to show rapid capacity fade at 2C. Adding 40% MP helped improve the high-rate cycling tolerance to 2C but cells showed rapid capacity loss at higher rates. The enhanced rate capability of MP-containing cells is mainly attributed to the improved ionic conductivity of electrolytes that contain MP as shown in Figure 1, considering similar solid state diffusion rates in all cells.29 Figure 7 also shows that the capacity of each cell measured sequentially at the low cycling rate (C/5) was retained well after high rate tests until the occurrence of unwanted lithium plating.

Figure 7 shows the amount of gas produced in the NCA cells after the high rate cycling shown in Figure 7. Only a small amount of gas was produced when MP accounted for 20% or less of the electrolyte. Careful viewing of Figure 7 shows cells with 40% and 60% MP showed significant capacity loss during cycles where unwanted lithium plating clearly occurred.20 Cells with 0%, 5% or 20% MP were
not “abused” to the point where substantial amounts of unwanted lithium plating occurred. Therefore, the large volume of gas in the cells with 40 and 60% MP is probably caused by reactions between unwanted plated lithium and the high-ester content electrolyte.

It is important to explore the potential impact of MP on the safety of Li-ion cells. Accelerating rate calorimetry (ARC) studies of charged electrode samples plus electrolyte were studied using ARC. Figure 9 shows the self-heating rate vs temperature curves for charged electrode samples mixed with baseline electrolyte or MP-containing electrolyte. Cells were charged to 4.2 V before the charged electrode samples were recovered for the ARC experiments. In general, no obvious changes in self-heating behavior were observed for both the positive (Figure 9a) and negative (Figure 9b) electrodes when MP was added to the electrolyte, suggesting that MP does not cause more dramatic electrode-electrolyte reactions than EC:EMC:DMC (25:5:70) at elevated temperatures. The onset temperatures of rapid SHR increase for both the charged NCA and the charged negative electrodes were about 150°C.

Conclusions

Esters as co-solvents were explored in NCA/Gr-SiO pouch cells. The baseline solvent system, EC:EMC:DMC (25:5:70 by vol%) was blended with three different ester compounds: MP, EA or MB and made into electrolytes by adding 1.2 M LiPF₆ and 2% VC as an additive. The studies performed showed that of the three esters, methyl propionate (MP) is the most preferred. Electrolytes with MP are compatible with both charged positive and negative electrode materials at least up to 20% MP. Long term cycling, high temperature storage, gas generation, impedance spectroscopy and accelerating rate calorimetry experiments showed no obvious drawbacks to incorporating 20% MP into these cells. Most importantly, the 60°C storage tests of pouch cells at 4.2 V and 2.5 V showed that MP behaved better as a co-solvent than EA or MB. Additionally, the ability of cells containing 40% MP to be charged more rapidly than cells with control electrolyte, without unwanted lithium plating, was demonstrated. When 40% of any of the esters was added to the cells at least one or more ‘showstoppers’ were encountered. It may be possible to increase the amount of esters that can be incorporated into the cells by changing the baseline solvent blend, incorporating different electrolyte additives or using sophisticated coatings on the electrode materials. Considering the significantly increased ionic conductivity and decreased freezing point of 80%(EC:EMC:DMC):20%MP, cells containing this quaternary electrolyte blend are also believed to perform better than EC:EMC:DMC ternary electrolyte blend at very low temperatures. Charged positive and negative electrodes in electrolytes with 0% to 40% MP in EC:EMC:DMC showed almost identical self-heating rates in ARC experiments up to 350°C, suggesting no additional safety issues associated with these ester components.

Acknowledgments

The authors thank Tesla Motors and the Natural Science and Engineering Research Council of Canada (NSERC) for financial support under the auspices of the Industrial Research Chairs program. The authors thank Dr. Jing Li of BASF for supplying most of the electrolyte solvents and additives used in this work.

References

1. H. Y. Tran, C. Taubert, and M. Wohlfahrt-Mehrens, Prog. Solid State Chem., 42, 118 (2014).
2. N. Nitta, F. Wu, J. T. Lee, and G. Yushin, Mater. Today, 18, 252 (2015).
3. http://www.molcel.com/bq/product/products12.html.
4. M. C. Smart, B. V. Ratnakumar, K. B. Chin, and L. D. Whitmanack, J. Electrochem. Soc., 157, A1361 (2010).
5. H. C. Shiao, D. Chua, Hsiu-ping Lin, S. Slane, and M. Salomon, J. Power Sources, 87, 167 (2000).
6. S. V. Sazhin, M. Y. Khimchenko, Y. N. Tritenichenko, and H. S. Lim, J. Power Sources, 87, 112 (2000).
7. S. Herreyre, O. Huchel, S. Barusseau, F. Pertot, J. M. Bodet, and Ph. Biensan, J. Power Sources, 97–98, 576 (2001).
8. A. Ohita, H. Koshina, H. Okuno, and H. Murai, J. Power Sources, 54, 6 (1995).
9. M. C. Smart, B. V. Ratnakumar, and S. Surampudi, J. Electrochem. Soc., 149, A361 (2002).
10. 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).
11. Shin-Ichi. Tobishima, K. Hayashi, Kei-Ichi. Saito, and Jun-Ichi Yamaki, Electrochim. Acta., 40, 537 (1995).
12. G. Yin, H. S. Lim, S. Herreyre, S. Biensan, P. Pertot, and S. Barusseau, US6399255 B2 (1998).
13. R. Petibon, J. Harlow, D. B. Le, and J. R. Dahn, Electrochim. Acta., 154, 227 (2015).
14. R. Petibon, C. P. Aiken, L. Ma, D. Xiong, and J. R. Dahn, Electrochim. Acta., 154, 287 (2015).
15. I. M. Smallwood, Handbook of organic solvent properties, John Wiley & Sons, New York (1996).
16. K. Xu, Chem. Rev., 104, 4303 (2004).
17. https://www.cdc.gov/niosh/ipcsnneng/neng0816.html.
18. http://www.chemspider.com/Chemical-Structure.8305456.html.
19. T. R. Jow, K. Xu, O. Borodin, and M. Ue, Electrolytes for Lithium and Lithium-ion batteries, Springer, New York (2014).
20. Q. Q. Liu, R. Petibon, C. Y. Du, and J. R. Dahn, J. Electrochem. Soc., 164, A1173 (2017).
21. L. Y. Beaulieu, E. R. Logan, K. L. Gering, and J. R. Dahn, An Automated System for Performing Continuous Viscosity versus Temperature Measurements of Fluids Using an Ostwald Viscometer, submitted to Rev. Sci. Instrum. June 2017.
22. L. Ma, M. Nie, J. Xia, and J. R. Dahn, J. Power Sources, 327, 145 (2016).
23. E. Fedel, J. Electrochem. Soc., 126, 2047 (1979).
24. J. C. Burns, R. Petibon, K. J. Nelson, N. N. Sinha, A. Kassam, B. M. Way, and J. R. Dahn, J. Electrochem. Soc., 160, A1668 (2013).
25. Jean-Marc Atebamba, J. Moskon, S. Pejovnik, and M. Gaberscek, J. Electrochem. Soc., 157, A1218 (2010).
26. N. N. Sinha, A. J. Smith, J. C. Burns, G. Jain, K. W. Eberman, E. Scott, J. P. Gardner, and J. R. Dahn, J. Electrochem. Soc., 158, A1194 (2011).
27. B. Ghenes, D. A. Stevens, V. L. Chevrier, and J. R. Dahn, J. Electrochem. Soc., 162, A278 (2015).
28. L. Ma, S. L. Glazier, R. Petibon, J. Xian, J. M. Peters, Q. Liu, J. Allen, R. N. C. Doig, and J. R. Dahn, J. Electrochem. Soc., 164, A5008 (2017).
29. Q. Liu, C. Du, B. Shen, P. Zuo, X. Cheng, Y. Ma, G. Yin, and Y. Gao, RSC Adv., 6, 88683 (2016).