Measuring the Parasitic Heat Flow of Lithium Ion Pouch Cells Containing EC-Free Electrolytes

S. L. Glazier,* R. Petibon, b J. Xia, a,* and J. R. Dahn a,b,*,**

a Department of Physics and Atmospheric Science, Dalhousie University, Halifax NS, B3H 4R2, Canada
b Department of Chemistry, Dalhousie University, Halifax NS, B3H 4R2, Canada

A recent study has shown that removing ethylene carbonate (EC) from electrolytes in Li[Ni0.4Mn0.4Co0.2]O2/graphite lithium ion pouch cells significantly increases the cycle life and lifetime at high voltage operation. This work investigates the performance of EC-free electrolytes by adding small amounts of electrolyte additives to 1 M LiPF6 ethyl-methyl carbonate in Li[Ni0.4Mn0.4Co0.2]O2/graphite pouch cells and measuring the parasitic heat flow during high voltage operation. EC-free electrolytes yielded higher parasitic heat flow at lower voltages but performed better than EC-containing electrolyte above 4.3 V. Additionally, EC-free electrolytes were able to recover to a lower parasitic heat flow after high voltage exposure than those containing EC. Most EC-free electrolytes had lower impedance and acceptable gas evolution compared to electrolytes containing EC throughout the experiment. EC-free electrolytes shed light on a new area of high voltage electrolyte development, using a simple and cost effective chemistry.

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Future and present day applications for lithium ion batteries such as electric vehicles and grid energy demand increase significantly longer lifetimes, lower costs and higher energy density. One promising way to achieve these goals is to develop an electrolyte capable of performing well at high voltages for long periods of time. A significant amount of work has been focused on electrolyte additives, which can improve the voltage tolerance of traditional carbonate solvents.1–4 Other works have used alternative solvent systems, such as fluorinated carbonates, which are more stable at high voltages, but produce large quantities of gas during operation.5–7

Recently it has been discovered that ethylene carbonate (EC), which has been thought to be necessary for good lithium ion battery performance, is not required at all for high voltage operation and is in fact detrimental to performance.8 By creating a simple electrolyte containing ethyl methyl carbonate (EMC) and a small amount of vinylene carbonate (VC) as a passivating agent, cell cycle life and coulombic efficiency (CE) during 4.4 V cycling was greatly improved over electrolytes containing EC. Co-additives were found to further improve aspects of cycle performance and safety.

The relative performance of EC-free electrolytes with different additive combinations is studied here by measuring the parasitic heat flow of cells during high voltage operation using isothermal microcalorimetry. Petibon and Xia et al.8 found that 2% (wt) VC9–11 in EMC yielded improved performance at 4.4 V compared to EC-containing electrolytes. This work investigated the effects of adding 1% (wt) of tris(trimethylsilyl)phosphate (TTSP),12 pyridine phosphorus pentfluoride (PPF),13 or triallyl phosphate (TAP)14 to EMC:VC (98:2 wt). These results are compared to those of a control electrolyte, EC:EMC (3:7 wt) with 2% prop-1-ene-1,3-sultone (PES)15–17 1% 1,3,2-Dioxathiolane-2,2-dioxide (DTD),18 and 1% tris(trimethylsilyl)phosphate (TTSPi).12,19 The ternary additive blend of PES, DTD (or methylene methane disulfonate) and TTSPi is known to greatly improve the performance of EC:EMC-based electrolytes in NMC111/graphite and NMC442/graphite Li-ion cells.7,20,21 The chemical structures of solvents and additives used in this study are shown in Figure 1.

Downie et al.22 found that at very low rates of C/200, the parasitic heat flow of a cell can be very well approximated by the averaged heat flow during charge and discharge. Using this approach, the parasitic heat flow of these EC-free electrolytes is reported for voltage ranges up to 4.6 V.

The greatly improved performance of EC-free electrolytes means simple, cost effective electrolytes for high voltage lithium ion applications are possible and should be studied in great detail to optimize the performance, with a specific focus on reducing gas while maintaining low impedance and good safety.

Experimental

The EC-containing solvent blend was ethylene carbonate (EC):ethylmethyl carbonate (EMC) (3:7 wt) (BASF, <20 ppm water). EC-free electrolytes contained only EMC (BASF, 99.92%, <6 ppm water) as the solvent. Additives used in this work were prop-1-ene-1,3-sultone (PES) (Lianchuang Medicinal Chemistry Co., 98.20%), 1,3,2-Dioxathiolane-2,2-dioxide (DTD) (Sigma Aldrich, 98%), tris(trimethylsilyl)phosphate (TTSP) (TCI America, >95%), vinylene carbonate (VC) (BASF, >99.8%), tris(trimethylsilyl)phosphate (TTSP) (TCI America, >98%), triallyl phosphate (TAP) (TCI America, >94.0%), and pyridine phosphorus pentfluoride (PPF) (3 M Company, >99%). Each electrolyte contained 1 M LiPF6 (BASF 99.99%). Electrolyte compositions are shown in Table I.

* Electrochemical Society Student Member.
** Electrochemical Society Fellow.
* E-mail: jeff.dahn@dal.ca

Figure 1. Chemical structures of solvents: ethylene carbonate (EC) and ethyl methyl carbonate (EMC) and additives: vinylene carbonate (VC), prop-1-ene-1,3-sultone (PES), 1,3,2-Dioxathiolane-2,2-dioxide (DTD), tris(trimethylsilyl)phosphate (TTSP), tris(trimethylsilyl)phosphate (TTSP), pyridine phosphorous pentfluoride (PPF), tri-allyl phosphate (TAP) used in this work.
Sealed LiNi0.4Mn0.4Co0.2O2 (NMC442)/graphite machine-made pouch cells (capacity 220 mAh, balanced to 4.7 V) with no electrolyte were obtained from Lifun Technology (Ximna Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000). Cells were cut open and dried in a vacuum oven at 80 °C for > 14 hours, then transferred into an argon-filled glove box without exposure to air. Cells were filled with 0.75 mL of electrolyte and sealed for 6 seconds at 165 °C with a vacuum sealer (MSK-115 V, MTI Corp.). Cells were then connected to a Maccor series 4000 charger (Maccor Inc.) and held at 1.5 V for 24 hours to ensure proper wetting before being subjected to the following formation protocol. Cells were charged to 3.5 V at a C/20 rate and held at 3.5 V for one hour. Degassing of cells was performed in an argon glove box by cutting open the pouch cells and resealing with the vacuum sealer. Cells were charged to 4.2 V and discharged to 3.8 V at a C/20 rate, then held at 3.8 V for one hour. Cell volumes were recorded before and after each formation using an ex-situ Archimedes’ principle apparatus outlined by Aiken et al.23

Two cells of each electrolyte were connected to a Maccor charger and inserted into a TAM III Microcalorimeter (TA Instruments, stability ± 0.0001 °C, accuracy ± 1 μW, precision ± 1 nW) at 40.0 °C. 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.24,25 Cells were cycled four times at a C/20 rate between 2.8 V and 4.2 V to ensure a well formed, stable SEI and were then charged between 3.9 V and different upper cut off limits at 1 mA to investigate the performance and the parasitic heat flow in different voltage ranges. Each pair of cells yielded near identical performance, so only one set of heat flow data is presented for each electrolyte. The 1 mA cycling protocol was:

1. Charge to 4.2 V, discharge to 3.9 V
2. Charge to 4.3 V, discharge to 3.9 V
3. Charge to 4.4 V, discharge to 3.9 V (repeat)
4. Charge to 4.5 V, discharge to 3.9 V (repeat)
5. Charge to 4.6 V, discharge to 3.9 V
6. Charge to 4.2 V, discharge to 3.9 V (repeat)

Some voltage ranges were repeated in order to investigate the electrolyte recovery from parasitic reactions after long term exposure to high potential.

Cells were then discharged to 3.8 V and removed from the microcalorimeter. The cell volume was measured and recorded using Archimedes principle and electrochemical impedance spectroscopy was then performed in a 10. ± 0.1 °C temperature-controlled box. AC impedance spectra were collected from 10 kHz to 10 mHz with a signal amplitude of 10. mV. Finally, cells were completely discharged and disassembled in a fume hood, where the separators were photographed for qualitative comparison.

An additional two cells of each electrolyte were tested on the ultra-high precision charger (UHPC) at Dalhousie University.26 These cells underwent an identical cell filling and formation protocol. The cells were cycled in a 40. ± 0.1 °C temperature-controlled box between 2.8 V and 4.5 V using a “barn-cycling” method, in which from 2.8 V to 4.3 V a current of 15 mA was used, and from 4.3 V to 4.5 V a 4 mA current was used in order to increase time spent at high voltage to enhance degradation effects.

## Table I. Electrolyte compositions (1 M LiPF6).

| Name            | Solvent       | Additives (wt%) |
|-----------------|---------------|-----------------|
| Control         | EC:EMC (3:7)  | 2% PES 1% DTD 1% TTSPi |
| EMC:VC          | EMC           | 2% VC           |
| EMC:VC + TTSP   | EMC           | 2% VC 1% TTSP   |
| EMC:VC + PPF    | EMC           | 2% VC 1% PPF    |
| EMC:VC + TAP    | EMC           | 2% VC 1% TAP    |

Figure 2 demonstrates the benefit of EC-free electrolytes during UHPC high voltage cycling, using the “barn-cycling” procedure, outlined by Xia et al.27 and shown in the inset of Figure 2b. Coulombic efficiency (CE) is the ratio of discharge capacity to previous charge capacity and is shown in Figure 2a. Figure 2b shows the charge end point slippage, which demonstrates the capacity at the top of charge shifting mainly due to parasitic reactions at the positive electrode.26 The discharge capacity during each cycle is shown in Figure 2c. Electrolytes containing no EC performed better than the control cells, which consisted of the EC:EMC (3:7) solvent with an additive blend (PES 2%, DTD 1%, TTSPi 1%) known to perform well compared to many other additive blends typically used in research and commercial applications.21 Understanding the reasons behind the observed increases in CE and decreases in charge end point slippage are...
important in order to further the development of electrolytes and gain insight into mechanisms responsible for high voltage performance. Isothermal microcalorimetry (IMC) is a powerful tool for investigating the complex reactions occurring in lithium-ion cells.

IMC has been used to measure the time and voltage dependence of parasitic reactions, and to help characterize internal reactions in lithium ion cells based on theoretical calculations. When current is applied to a lithium-ion pouch cell, the sources of heat flow are due to cell polarization (exothermic), entropy changes in the positive and negative electrode material ( reversible between charge and discharge), as well all other parasitic reactions occurring in the cell and is given by:

$$\dot{q} = |I| \eta + \frac{T}{e} \left[ \left( \frac{ds_+}{dx} \right) - \left( \frac{ds_-}{dx} \right) \right] + \dot{q}_p$$

where $I$ is the applied current, $\eta$ is the cell overpotential, $T$ is the temperature, $s_+$ and $s_-$ are the positive and negative electrode entropies respectively, and $\dot{q}_p$ is the parasitic heat flow.

In Downie’s work, the contributions to heat flow including overpotential were calculated using polynomial fitting as well as a combination of polynomial fitting and extrapolating the overpotential contribution from electrochemical measurements. This work utilizes the reversible nature of the entropy term in Equation 1, and the parasitic heat flow (red line in Figure 3) is found from the average heat flow between charge (solid black line in Figure 3) and discharge (dashed black line in Figure 3) in small voltage ranges at low current, minus the average contribution to heat flow from the cell overpotential, $|\eta|$ (blue and green lines in Figure 3) which was calculated as the difference from the average voltage at each state of charge per cycle using the Maccor cycler data. This is demonstrated in Figure 3, in which a cell was charged and discharged between 3.9 V and 4.2 V at a very low rate of 1 mA or C/200. The quick decrease in heat flow during charge at 3.9 V was due to the cell switching from a C/20 (10 mA) charge up to 3.9 V. The heat flow from 3.90 V to $\sim$3.92 V was therefore not all due to parasitic reactions, but also a portion was due to decay from the higher heat flow associated with the polarization and entropy terms at the higher current. Only the first $\sim$0.02 V of the charge of protocol step 1 to 4.2 V exhibited this feature for each cell, as all other protocol steps were at 1 mA (C/200). The voltage ranges chosen in this work take place on the last voltage plateau (stage 1 – stage 2) of the graphite negative electrode. This consideration avoids structural changes which are responsible for large heat flow signatures as a result of entropy, as seen in other thermal measurements.

Figures 4a and 4b show the parasitic heat flow during protocol steps 1 (4.2 V) and 2 (4.3 V) respectively. Pairs of cells with each electrolyte were measured and were almost identical. For simplicity, data for one cell from each pair is shown. The EC-containing control cell exhibited the lowest parasitic heat flow for both protocol steps to 4.2 V and 4.3 V. However, EMC:VC + PPF performed closely to control in step 1 and step 2. The bottom panels in Figures 4a and 4b show the differences in parasitic heat flow between each cell and the control cell. EMC:VC + TAP had comparable heat flow to control from 3.9 V to 4.0 V and showed the highest amount of parasitic heat flow above $\sim$4.1 V. However, Figure 2 showed EMC:VC + TAP performed better than both control and EMC:VC with no additives during 4.5 V barn cycling. This may be explained by TAP creating a positive electrode solid electrolyte interphase (SEI) as seen by Xia et al., which may be slightly less stable than other additives at 4.2 V and more stable than others at 4.5 V.

It is important to note that parasitic reactions decay with time, however at different rates depending on the electrolyte chemistry. In Figures 4a and 4b, the order of electrolytes ranked by heat flow did not change during the first two protocol steps, and heat flow decay appeared relatively equal between electrolytes. However, if exposure to higher voltage changes the severity or types of parasitic reactions in a cell, in subsequent cycles the differences in heat flow decay would become more pronounced. Therefore for protocol steps 3 and 4, cells were charged twice from 3.9 V to 4.4 V and 4.5 V, respectively. This allowed for the effects of exposure to high potential to be observed before introducing the cell to even higher potential.

Figures 5a and 5b show the parasitic heat flow during the two charges to 4.4 V in step 3. Figures 5c and 5d show the heat flow for the two charges to 4.5 V in step 4. The first charge to 4.4 V in Figure 5a yields very similar performance between all electrolytes, however this suggests major changes in parasitic reactions had occurred from steps 2 and 3, where clear differences in parasitic heat flow were visible. The new ordering of each curve in Figure 5b demonstrates the effect of exposure to 4.4 V. EMC:VC + TAP seemingly performed equally with all electrolytes during the first exposure to 4.4 V, however had the lowest heat flow during the second charge to 4.4 V, indicating TAP improved the resistance to high voltage parasitic reactions only above 4.5 V. This explained the trend seen in UHPC data shown in Figure 2, as in the high heat flow in Figure 4. During the second charge to 4.4 V in Figure 5b, the EC-containing control cell began to exhibit the highest heat flow above 4.2 V, even though up to 4.3 V in step 3 (Figure 4b) it had the lowest heat flow. This trend is seen to continue at

Figure 3. Extracted parasitic heat flow of an example NMC442/graphite pouch cell from 1 mA (C/200) cycling between 3.9 V and 4.2 V at 40 °C. Extracted parasitic heat flow was calculated as the average between charge and discharge heat flows (solid black and dotted black, respectively) minus the average of overpotential heat flow during charge (blue) and discharge (green). The blue and green lines almost entirely overlap in this example.

Figure 4. Parasitic heat flow at low potential 1 mA (C/200) cycling. a) shows 3.9 V to 4.2 V and b) shows 3.9 V to 4.3 V. Cells with EC-free electrolytes exhibit higher parasitic heat flow during low voltage operation. The bottom panels show the differences in parasitic heat of the EC-free cells to one of the control cells.
4.5 V in Figures 5c and 5d. EC-free electrolytes showed significantly fewer parasitic reactions than control after exposure to 4.5 V, and the difference in parasitic heat flow between EC-containing and EC-free electrolytes continued to increase during the second charge to 4.5 V (Figure 5d), indicating that the EC-free electrolyte was not able to recover from the high potential exposure.

The final high potential step (protocol step 5) to 4.6 V is shown in Figure 6a. Once again, all EC-free electrolytes performed well in comparison to control. During the 4.5 V and 4.6 V steps, the EC-free cells with additives performed relatively equally in terms of parasitic heat flow. Therefore these electrolytes could be selected based on other qualities such as low gas production or impedance, without having an effect on limited lifetime due to parasitic reactions. After step 5 to 4.6 V, cells were cycled to 4.2 V twice (first cycle shown in Figure 6b) in order to observe the performance at low potential after long times at high potential. The dotted lines in Figure 6b correspond to the first protocol step shown in Figure 4a. Since parasitic heat flow decays with time and is voltage dependent, the heat flow of solid lines (step 7) should ideally be lower at each voltage than the dotted lines (step 1). The control cell showed higher heat flow for most of step 7, indicating the electrolyte had been irreversibly damaged and high voltage exposure had caused more parasitic reactions than were decaying with time.

Figure 7 shows an overview of all protocol steps (labelled by the maximum potential of each step in Figure 7a). Figure 7a shows the heat flow at the maximum potential of each step, and Figure 7b shows the average heat flow during each step. Step 3 (4.4 V) clearly shows that EC-free electrolytes begin to show an advantage above 4.4 V. The last two points in Figure 7b show that control cells had much higher parasitic heat flow after high potential exposure. One topic of future work should be to optimize the low voltage (<4.4 V) performance of EC-free electrolytes by exploring different additive

Figure 5. Parasitic heat flow for high potential 1 mA cycling. a) and b) show the first and second cycles to 4.4 V respectively, and c) and d) show the first and second cycles to 4.5 V respectively. Cells with EC-free electrolytes become more stable at high potential. The bottom panels show the differences in parasitic heat of the EC-free cells to one of the control cells.

Figure 6. a) Parasitic heat flow up to 4.6 V and b) from 3.9 V to 4.2 V after exposure to all voltage ranges (solid). The dotted lines correspond to the heat flow from the first 3.9 V to 4.2 V section from Figure 4a. The bottom panels show the differences in parasitic heat of the EC-free cells to one of the control cells.

Figure 7. a) Maximum, and b) average parasitic heat flow during each experimental step in the 1 mA (C/200) protocol. The upper potential cut off of each step is shown in a).
concentrations. It is possible that the observed differences in parasitic heat flow may have occurred due to capacity loss above 4.4 V in EC-free electrolyte containing cells. Figures 8a, 8b, and 8c show the cell voltage vs capacity of the control, EMC:VC, and EMC:VC + PPF cells, respectively, during all repeated protocol steps (step 3 to 4.4 V, step 4 to 4.5 V and step 8 to 4.2 V). Figure 8 demonstrates that no noticeable discharge capacity loss can be seen between cells or subsequent cycles to voltages, although irreversible capacity due to parasitic reactions (end point slippage) can be seen during the first charge to each voltage range. Therefore, the differences in parasitic heat flow were not affected by any capacity loss in cells.

Figure 9a shows the electrochemical impedance spectroscopy spectra of each pair of cells after cycling in the calorimeter. Figure 9b summarizes the Rct values (taken here to be the diameter of the “semicircle” in the Nyquist plots) for each electrolyte type. Other than EMC:VC + TAP, the EC-free cells showed a lower charge transfer resistance (Rct) than control. The TAP-containing cells had very high impedance similar to work by Xia et al. who showed TAP significantly increases the impedance of both electrodes in loadings of >1% wt.\textsuperscript{14} Gas production during formation and cycling in the calorimeter is shown in Figure 9c. Cells containing EMC:VC + PPF produced the most gas during formation while cells containing EMC:VC + TAP produced the least gas during formation. Cells containing control and EMC:VC + TAP had the least amount of gas during cycling while cells containing EMC:VC + TTSP produced the most. Figure 9d shows the positive electrode side of the pouch cell separators after complete discharge and disassembly of one cell from each pair. Observing the deposits on a pouch cell separator can give a qualitative idea of the severity of internal reactions during operation. In this case, the quality of each separator correlated well with the results of electrochemical testing and parasitic heat flow. The control cell separator contained dark deposits and a brown product over the surface while EC-free cells contained little deposits.

EMC:VC + TAP showed some of the lowest parasitic heat flow at high voltage, good cycling performance, improved safety\textsuperscript{7} and cells containing this electrolyte produced low gas volumes during the aggressive high potential protocol and formation; however the cells showed large values of Rct. Cells with EMC:VC with or without TTSP had very low Rct, but produced the largest amounts of gas when cycling. It is clear from calorimetry and coulometry studies that EC-free electrolytes greatly improve cycle life during high voltage operation. However, much more work is needed to develop optimal additives or additive combinations to improve aspects such as impedance and gas production. This high potential solvent system will create many new opportunities for both new and existing additives and solvent blends to be explored.

Conclusions

Isothermal microcalorimetry was used to measure the parasitic heat flow in NMC442/graphite cells with “EC-free” electrolytes, such as EMC:VC (98:2) with and without additives, compared to cells with a control EC:EMC (3:7) electrolyte containing additives. Ultra-high precision coulometry was used to investigate high voltage cycling performance with extensive time spent at high potential. All cells with EC-free electrolytes showed lower parasitic heat flow than cells with control at 4.4 V and above, as well as higher coulombic efficiency and lower charge end point slippage during UHPC cycling to 4.5 V. Additives were shown to slightly lower parasitic heat flow in cells in the high potential ranges (above 4.4 V) compared to cells with control or EMC:VC with no additives. No significant differences in heat flow between cells with EC-free electrolytes containing additives were observed. However, additives were found to significantly affect gas production during formation and cycling, as well as cell impedance. This work suggests EC-free electrolytes for high potential operation should be investigated in great detail, with specific focus on improving low potential performance and developing additive combinations which address all aspects of performance.

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Figure 9. a) Area normalized negative imaginary vs. real impedance of cells after the experimental protocol. b) $R_{ct}$ values from a) for each cell type. c) Gas production during cell formation prior to degassing (gray) and post experiment (red). d) Photograph of pouch cell separators after the microcalorimetry experiments taken after full discharge, in the same order as panels b) and c).

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