Lithium-ion cells used in electrified vehicles require longer calendar and cycle lifetime than those used in portable electronics (e.g., laptops and cell phones). In addition, cell used in electrified vehicles can reach high temperatures, so improved tolerance of Li-ion cells to high temperature exposure is also desired. One method of extending lifetime and temperature tolerance of Li-ion cells is to use electrolyte additives in order to suppress parasitic reactions between charged electrodes and electrolyte.\textsuperscript{1,2} Vinylicene carbonate (VC), a popular electrolyte additive, has been shown to improve Li-ion cell performance.\textsuperscript{3,4} Recently, some novel sulfur-containing and phosphorous-containing electrolyte additives have also been shown to be able to increase lifetime, control impedance growth and suppress gas production, etc. for Li-ion cells. Xia et al.\textsuperscript{5} showed that the addition of ethylene sulfate (DTD) or trimethylene sulfate (TMS) to Li[Ni\textsubscript{0.5}Mn\textsubscript{0.2}Co\textsubscript{0.3}]O\textsubscript{2} (NMC111)/graphite pouch cells could increase coulombic efficiency (CE) and decrease impedance after cycling compared to cells without additives. Methylenedihalosulfonate (MMDMS) has been shown to be able to greatly decrease the impedance of NMC111/graphite cells after cycling and slow the rate of parasitic reactions at the Li\textsubscript{4}Mn\textsubscript{5}O\textsubscript{12} electrode according to storage results.\textsuperscript{6} Xia et al.\textsuperscript{6} also showed that prop-1-ene-1,3-sultone (PES) could increase CE, decrease charge end point capacity slippage and suppress gas production during cycling for NMC111/graphite pouch cells. Sinha et al.\textsuperscript{7} showed that the CE of NMC111/graphite pouch cells was improved and impedance was reduced when tris(trimethylsilyl) phosphate (TTSPi) was added to the electrolyte. In a massive study of over 110 electrolyte additive combinations tested in NMC111/graphite pouch cells, Wang et al. showed that ternary electrolyte additive blends containing one or more of VC or PES, one or more of DTD, MMDMS, ES or TMS and one or more of TTSP or TTSPi led to cells with excellent performance.\textsuperscript{8}

Electrolyte additives improve cell performance because they can modify the solid electrolyte interphase (SEI) at the negative electrode or the passivation layer formed on the positive electrode.\textsuperscript{9-12} Zuo et al.\textsuperscript{13} showed that the introduction of MMDMS modified the components of the passivation layer on the positive electrodes in LiCoO\textsubscript{2}/graphite cells, which suppressed electrolyte oxidation. Using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR), Li et al.\textsuperscript{14} found sulfur-containing species in the SEI on the graphite electrode, which indicated the importance of PES in forming the protective SEI. Sano et al.\textsuperscript{15} showed that the electrolyte additive in cells with DTD contained a polyethylen oxide (PEO) like polymer and Li\textsubscript{4}S\textsubscript{4} like compounds. Yang et al.\textsuperscript{16} showed that TTSPi could impact the passivation layer on the surface of the positive electrode in LiNi\textsubscript{0.5}Mn\textsubscript{0.2}Co\textsubscript{0.3}O\textsubscript{2}/Li cells, which apparently helped protect the electrode material from HF.

Since electrolyte additives modify the interphase between charged electrode materials and electrolytes, electrolyte additives may strongly affect the safety of Li-ion cells at elevated temperatures.\textsuperscript{17} Accelerating rate calorimetry (ARC) has proved to be able to distinguish the effects of different electrolyte additives on the reactivity between charged electrodes and electrolytes at elevated temperatures.\textsuperscript{18} In this work, the reactivity of lithiated graphite or delithiated NMC111 with electrolytes containing various sulfur-containing or phosphorous-containing electrolyte additives at a level of 2 wt% was systematically studied using ARC. Electrolytes with the ternary electrolyte additive blends VC + MMDMS + TTSPi and PES + MMDMS + TTSPi were also studied using ARC and are shown to dramatically reduce negative electrode reactivity with electrolyte. These results should be of interest to researchers looking to develop Li-ion cells with longer lifetime and better safety.

**Experimental**

1.0 M LiPF\textsubscript{6} in ethylene carbonate (EC):ethyl methyl carbonate (EMC) (3:7 by weight, from BASF, water content was 12.1 ppm) was used as the control electrolyte. Electrolytes with additives were formulated by dissolving 2 wt% VC (from BASF, 99.97%), DTD (Sigma-Aldrich, 98%), TMS (Sigma-Aldrich, 99%), propylene sulfinate (PLS) (Sigma-Aldrich, 99%), MMDMS (Tinci Materials Technology, 98.7%), TTSP (Sigma-Aldrich, > 98%), TTSPi (Sigma-Aldrich, > 95%) or PES (Lian Chuang Pharmaceutical, 98.2%) into the electrolyte. Electrolytes with 2% VC + 1% MMDMS + 1% TTSPi (“VC-211”) and 2% PES + 1% MMDMS + 1% TTSPi (“PES-211”) were also studied in this work. Figure 1 shows the chemical structures of the electrolyte additives used in this work.

**Pouch cells**—Dry (no electrolyte) NMC111/graphite pouch cells (240 mAh) balanced for 4.4 V operation and NMC442/graphite pouch cells (240 mAh) balanced for 4.7 V operation were obtained from...
Li-Fun Technology (Xinxian Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000). SEM images of the NMC111 and graphite electrode surfaces can be found in reference.5 SEM images of the materials used for the ARC studies can be found in reference.18

All pouch cells were vacuum sealed without electrolyte in a dry room in China and then shipped to our laboratory in Canada. Before electrolyte filling, the cells were cut just below the heat seal and dried at 80°C under vacuum for 12 hours to remove any residual water. Then the cells were transferred immediately to an argon-filled glove box for filling and vacuum sealing. The NMC111/graphite and NMC442/graphite pouch cells were filled with 0.9 g of electrolyte and dried at 80°C. The cells were charged and discharged at 0.1 C for NMC and graphite (MCMB), respectively. ARC tests were tracked under adiabatic conditions when 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. To test the reproducibility of the ARC sample construction and measurements, two identical ARC samples were made and tested for every condition.

Some researchers have questioned the ARC protocol described above and wonder if the SEI created on the electrodes during the lithiation of the electrodes at 30°C in control electrolyte dominates the response in the ARC even when additives are subsequently added for the ARC testing. After the first lithiation, the SEI on either electrode is not mature and it continues to grow and thicken over time as has been shown by many researchers.12–24 Therefore, when the charged electrode material is heated in the ARC experiment during the heat-wait-search segments beginning at 70°C or 50°C, the SEI grows substantially in the presence of the additives and hence the additives strongly affect the ARC response.

**Results and Discussion**

Some promising VC-based and PES-based additive combinations9 were selected for evaluation during long-term cycle testing at 55°C between 2.8 and 4.2 V with a current of 80 mA (C/3) and compared to additives used alone. Figure 2(a) shows capacity versus cycle number for NMC111/graphite pouch cells with the selected additives or additive blends: 2% VC, 2% PES, 2% DTD, 2% PES + 1% MMDs, 2% PES + 1% TTSP, “VC-211”, and “PES-211”. The binary additive blends do not show any advantages during the long term cycling test compared to 2% PES used alone. However, the ternary blends, especially “PES-211”, could impart excellent capacity retention compared to the additives used alone or in pairs. Cells with “PES-211” still retain more than 80% of their initial capacity after ~900 cycles at 55°C.

**Cycling tests.** All the type-A cells were prepared for long-term cycling at 55 ± 0.1°C. The cells were charged and discharged at 80 mA (C/3) between 2.8 and 4.2 V using a Neware (Shenzhen, China) charger system. All the type-B cells were prepared for long-term cycling at 45 ± 0.1°C. The cells were charged and discharged at 100 mA (C/2.5) between 3.0 and 4.4 V using a Maccor Series 4000 (Tulsa, US) charger system. All pouch cells were cycled without applied pressure, that is, external clamps were not used on the cells.

**ARC tests.** NMC111 and graphite (MCMB) were obtained from 3M Company (St. Paul, MN, USA) and E-One Moli/Energy Canada Ltd. (Maple Ridge, BC), respectively. The MCMB (heated to 2650°C) used was produced by Osaka Gas (Chuo-ku, Osaka, Japan), and had a probability of turbostratic misalignment of P = 0.19.20 The single-point BET surface areas of the graphite (MCMB) and NMC powders were 0.30 ± 0.01 m²/g and 0.48 ± 0.01 m²/g, respectively, as measured with a Micromeritics Flowtsorb 2300 instrument. Pellet type electrodes were made with a weight ratio of active material, Super C45 (Timcal) and polyvinylidene fluoride (PVDF) binder (Kynar 301F; obtained from Elf-Atochem) of 92.4:4 and 86:7:7 for NMC and graphite (MCMB), respectively.

ARC sample preparation followed the procedure shown in Jiang’s earlier work.21 Pellet-electrode coin cells were made using control electrolyte and charged to 4.2 V for the NMC electrodes or discharged to 0.0 V for the graphite (MCMB) electrodes using the protocol described in Reference 21. Then the coin cells were opened in an argon-filled glove box to recover the electrode. The electrode was lightly ground and rinsed four times using dimethyl carbonate (DMC, from Sigma-Aldrich, ≥ 99.00%) to remove the residual electrolyte. The powder was then dried in the vacuum antechamber of the glove box overnight before it was used for the ARC tests. The electrode:electrolyte mass ratios were 94 mg delithiated NMC with 30 mg electrolyte and 140 mg lithiated graphite (MCMB) with 140 mg electrolyte, respectively. The ARC starting temperature was set at 70°C and 50°C for NMC and graphite (MCMB), respectively. ARC tests were tracked under adiabatic conditions when 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. To test the reproducibility of the ARC sample construction and measurements, two identical ARC samples were made and tested for every condition.
Figure 2. (a) Capacity versus cycle number for NMC111/graphite pouch cells (unclamped) containing selected additives or additive blends. The cycling was done between 2.8 and 4.2 V at 55 °C and at 80 mA. (b) Capacity versus cycle number for NMC442/graphite pouch cells (unclamped) containing selected additives or additive blends. The cycling was done between 3.0 and 4.4 V at 45 °C and at 100 mA. 

decreases dramatically, which indicates that VC alone is not suitable for NMC442/graphite pouch cells charged to 4.4 V. When 2% PES is used, the capacity is greater than 80% until ~350 cycles while cells with “PES-211” show better capacity retention than those with 2% VC or 2% PES.

Figure 3 shows the results of ARC experiments on 94 mg delithiated NMC reacting with 30 mg electrolyte containing 2 wt% of selected electrolyte additives. Each experiment was repeated and the results are highly reproducible. Figure 3(a) shows that 2% VC caused the self-heating rate (SHR) to be slightly higher than that of control electrolyte between 200 and 250 °C. Figures 3(d), 3(e), 3(f) and 3(g) show that some of the selected electrolyte additives (DTD, TMS, PLS and TTSP) and control electrolyte have virtually the same response for the reaction between delithiated NMC and electrolyte. Figures 3(b), 3(c) and 3(h) show that MMDS, PES and TTSPi at a level of 2 wt% yield a small improvement in thermal stability compared to control by decreasing the SHR after 250 °C and increasing the thermal runaway temperature by ~10 °C compared to the control electrolyte.

Figure 4 shows the results of ARC experiments on 140 mg lithiated graphite reacting with 140 mg electrolyte containing 2 wt% of selected electrolyte additives compared to the results for control electrolyte. Except for PES, other selected electrolyte additives decreased the SHR compared to the control sample over almost the entire testing range as shown in Figures 4(a), 4(c) – 4(h). The most striking feature of Figure 4 is that the sample with 2% MMDS showed no exothermic feature at around 100 °C thought to be caused by the decomposition of the metastable SEI on the lithiated graphite, which suggests a very thermally stable surface film on the negative electrode. Furthermore, the addition of 2% TTSPi dramatically decreased the SHR between ~150 °C and ~200 °C compared to the control sample. However, Figure 4(b) shows that when 2% PES alone is used, there is a small exothermic reaction near 50 °C which is much lower than that of the control electrolyte. In addition, 2% PES demonstrated a higher SHR between ~100 °C and ~150 °C compared to control electrolyte but 2% PES also decreased the SHR between ~150 °C and ~260 °C compared to control electrolyte.

Figure 5 shows the results of ARC experiments on 140 mg lithiated graphite reacting with 140 mg electrolyte containing selected electrolyte additive combinations compared to the results for control electrolyte. “VC-211” and “PES-211” blends dramatically decrease the exothermic feature at around 100 °C thought to be caused by the decomposition of the metastable components of the SEI on the lithiated graphite, which indicates the formation of a robust SEI on the graphite electrode. This may be a partial reason for the excellent...
capacity retention of NMC/graphite cells during long-term cycling test with addition of these additive blends. Additionally, the SHR versus temperature is lower than that of the control sample over almost the entire testing range. As a note in passing, it was not possible to measure the SHR versus temperature for these blends reacting with delithiated NMC due to corrosion of the thin walled stainless steel ARC tube at the welded ends (reasons for this are unknown, but happens every time) at elevated temperatures (>200°C). However, this feature of these blends will not be problematic in pouch cells which contain no ferrous metals.

Conclusions

Using long-term cycling tests at elevated temperature, the utility of the ternary electrolyte additive blends “VC-211” and “PES-211” have been demonstrated. “PES-211” is especially useful for NMC442/graphite pouch cells operated at 4.4 V.

Most of the selected additives do not have a dramatic effect on the reaction between delithiated NMC and electrolyte compared to control sample, except for PES, MMDS and TTSPi. These three additives decreased the SHR above ~250°C compared to control sample.

Unlike delithiated NMC, the reactivity between lithiated graphite and electrolyte was affected more or less by all the additives used in this work. The most interesting are the effects of MMDS and TTSPi at a level of 2 wt%; MMDS suppressed obvious exothermic reactions up to ~200°C while TTSPi dramatically decreased the SHR in the temperature range between ~150°C and ~200°C. In cases of DTD, TMS and TTSP, the SHR decreased slightly during almost the entire test temperature range. It is unfortunate that 2 wt% PES used alone does not give a beneficial effect on the reaction between lithiated graphite and electrolyte. In addition, when PES is used, there was a small exothermic reaction with an onset temperature of 50°C which the control electrolyte did not show. Almost no exothermic reaction between lithiated graphite and electrolyte could be detected up to 200°C with the addition of “VC-211” or “PES-211”. The work in this paper focused on the effect of additives or additive blends on the reactivity of charged electrodes with electrolytes at elevated temperatures. The additive blend, “PES-211”, can yield significant cycle life improvements for NMC/graphite cells operating at both 4.2 V and 4.4 V and lower thermal reactivity for the charged graphite electrode. We encourage Li-ion battery manufacturers and researchers studying NMC-based Li-ion cells to try “PES211” in their experiments.

Acknowledgments

The authors thank NSERC, 3M Canada for the funding of this work under the auspices of the Industrial Research Chairs program.

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