Lithium-ion batteries are currently used in phones, laptop computers and, more recently, electric vehicles. Electrolyte additives are the most effective way to improve the calendar life and cycling performance of lithium-ion batteries.\(^1\)\(^-\)\(^3\) Vinylene carbonate (VC) is perhaps the most well-known additive for Li-ion batteries and has been shown to improve cycle and calendar life of Li-ion cells.\(^4\) Sinha et al.\(^5\) used storage studies to determine that VC was beneficial at the positive electrode by slowing the rate of electrolyte oxidation. Using high precision coulometry, Burns et al.\(^6\) determined that VC was beneficial at the positive electrode by reducing the rate of parasitic reactions. However, it has been shown that the performance of cells containing VC degrades at high temperatures due to electrolyte decomposition\(^6\) and at high voltages due to electrolyte oxidation.\(^7\) Sulfur-containing electrolyte additives have been studied in the hopes of overcoming the temperature sensitivity of VC.\(^8\)\(^-\)\(^10\) Prop-1-ene-1,3-sultone (PES) was found to have smaller irreversible capacity than VC-containing cells, and was suggested to be a stable SEI forming additive.\(^10\) Recently, Xia et al.\(^11\) studied the effects of VC and/or PES as electrolyte additives in Li[Ni\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)]O\(_2\) (NMC111)/graphite pouch cells up to concentrations as large as 3% by wt. They found that both PES and VC improved coulombic efficiency, reduced charge transfer resistance after formation, but reduced gas evolution. Additional cells were filled with control electrolyte containing 0.5, 1, 2, 4, and 6% of prop-1-ene-1,3-sultone (PES, Lianchuang Medicinal Chemistry Co., 98.20%) by weight and compared to cells containing 2% vinylene carbonate (VC, BASF, 99.97%). Pouch cells were vacuum sealed after electrolyte filling. All cells were part of one of two experiments. One set of cells were cycled using the Ultra High Precision Charger (UHPC) at Dalhousie University between 2.8 and 4.2 V at C/20 for 20 cycles. The second cells underwent a 500 hour storage period at 40.\(^\circ\)C while VC does not. This is the main advantage of PES over VC.

In this paper, the work of Xia et al.\(^11\) is extended to include studies of complete range of PES contents from 0.5% to 6.0% in Li[Ni\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)]O\(_2\) (NMC111)/graphite pouch cells. The chemical structure of PES is shown in Figure 1. The Ultra High Precision Charger (UHPC) at Dalhousie University was used to monitor the coulombic efficiency, charge end-point capacity slippage and discharge capacity versus time and cycle number of the cells. In addition, gas evolution measurements employing Archimedes principle and electrochemical impedance spectroscopy (EIS) measurements were performed. Improved UHPC methods, where storage was performed before UHPC, to help distinguish between additives with similar properties, are introduced here. Finally, the combination of PES with the additive Li[SiO\(_2\)C\(_2\)F\(_4\)]\(_2\) known to reduce gassing in combination with VC, is explored.

\(^{*}\)Electrochemical Society Student Member.
\(^{**}\)Electrochemical Society Fellow.
\(^{*}\)E-mail: jeff.dahn@dal.ca

Studies of the Effect of Varying Prop-1-ene-1,3-sultone Content in Lithium Ion Pouch Cells

K. J. Nelson, Jian Xia, and J. R. Dahn

Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia, Canada

Experimental

Machine made 220 mAh Li[Ni\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)]O\(_2\) (NMC111)/graphite wound pouch cells balanced for 4.4 V operation were obtained (no electrolyte added) from Whenergy (Shandong, China). Pouch cells were manufactured and vacuum sealed in a dry room before shipping to Dalhousie University. After heating at 80\(^\circ\)C for 14 hours under vacuum to remove any residual water, the pouch cells were filled with 0.90 g of 1M LiPF\(_6\) in ethylene carbonate (EC):ethylmethyl carbonate (EMC) (Novolyte Technologies, now BASF) in a ratio of 3:7 (by weight) as the control electrolyte. Additional cells were filled with control electrolyte containing 0.5, 1, 2, 4, and 6% of prop-1-ene-1,3-sultone (PES, Lianchuang Medicinal Chemistry Co., 98.20%) by weight and compared to cells containing 2% vinylene carbonate (VC, BASF, 99.97%). Cells were vacuum sealed using a compact vacuum sealer (MTI Corp.) after electrolyte filling. All cells did a formation cycle at 40\(^\circ\)C, consisting of a 24 hour hold at 1.5 V to ensure adequate electrolyte wetting followed by a C/20 charge to 4.2 V and a subsequent C/20 discharge to 3.8 V. After this step, cells were transferred into an argon-filled glove box, cut open just below the heat seal to release generated gas and then vacuum sealed again. After degassing, electrochemical impedance spectroscopy (EIS) was used to measure the charge transfer resistance of the cells at 3.8 V and 10.\(\pm\)0.1\(^\circ\)C. AC impedance spectra were collected from 100 kHz to 100 mHz with a signal amplitude of 10 mV.

All these cells were part of one of two experiments. One set of cells were cycled using the Ultra High Precision Charger (UHPC) at Dalhousie University between 2.8 and 4.2 V at 40.\(\pm\)0.1\(^\circ\)C and C/20 for 20 cycles. The second cells underwent a 500 hour storage period at 40.\(\pm\)0.1\(^\circ\)C where their open circuit voltage was monitored and recorded every 6 hours before being cycled using the UHPC similarly to the first set of cells. This was done to observe the effect and potential benefit of a storage period prior to cycling experiments.

High temperature storage cells.— To further understand the role of PES as an additive and its potential to overcome the temperature sensitivity that plagues VC, a 60\(^\circ\)C storage study was performed. The additives VC, PES, and lithium bis(trifluoromethanesulfonyl) imide (Li[NiSO\(_2\)CF\(_3\)]\(_2\) or Li-TFSI) were added singly to the control electrolyte at 2% by weight. Several binary combinations of either 1 or 2% by weight of these additives were also studied. After undergoing the same formation procedure described above, the cells were placed at 60.\(\pm\)0.1\(^\circ\)C where their open circuit voltage was monitored and recorded every 6 hours during a 500 hour storage period.

In addition, gas evolution measurements employing Archimedes principle were done on all cells before and after formation, storage, and cycling. This was done by weighing the cells in nanopure water with \(\rho = 0.998\) g/mL (20\(^\circ\)C), such that the change in mass, \(\Delta m\), is a
Figure 1. The chemical structure of the additive prop-1-ene-1,3-sultone (PES).

direct measure of the volume, $\Delta v$, of gas produced during formation, storage, or cycling as described by $\Delta v = \Delta m / \rho$. This procedure is discussed in depth in reference 14.

**Results and Discussion**

Figure 2 shows the gas evolution during formation at 40.0°C. Error bars are the standard deviation of data from four pair cells. Cells containing low concentrations of PES and the control electrolyte produce large amounts of gas, leading to bulging of the pouch and possible loss of contact between separators and electrodes. Cells containing 2, 4, or 6% PES were comparable to 2% VC. Figure 3 shows the EIS spectra of the cells collected after formation. The EIS data was collected at 3.8 V and 10.0°C. The diameter of the semicircle of each impedance spectra is made up of contributions from the charge transfer resistances of both positive and negative electrodes and also resistances associated with Li$^+$ transport through the SEI layers. For simplicity, we call the diameter of the semicircle, $R_{ct}$. This is labeled in Figure 3 for the 2% PES-containing cells. Figure 3 shows that increasing the PES content in the control electrolyte causes an increase in $R_{ct}$ after formation. All cells show good repeatability with four cells for each additive type.

Figure 4 summarizes the gas evolution and impedance measurements taken after 500 hours of storage at 40°C and UHPC cycling at 40°C. The error bars are the standard deviation of data from pair cells.

Figure 2. Gas evolution during formation at 40.0°C measured using Archimedes principle. The dotted blue line highlights that of 2% VC.

Figure 3. EIS spectra of the NMC111/graphite cells collected at 3.8 V and 10.0°C after formation. The diameter of the impedance spectra is called $R_{ct}$ here (see text).

Figure 4. Gas evolution during storage at 40°C (a) and during cycling at 40.0°C (b) and the charge transfer resistance measured using EIS at 3.8 V and 10°C after storage (c) and after cycling (d).
Figures 4a and 4b show that all combinations studied show low gas evolution after storage and cycling. Figures 4c and 4d again show that increasing the content of PES caused an increase in charge transfer impedance after both storage and cycling at 40.0°C. The charge transfer impedance of all cells containing VC or PES additives was reduced after storage and cycling compared to the impedance measured after formation.

Figure 5 shows a summary of the 40°C, 4.2 V storage experiment. The error bars are the standard deviation of data from pair cells. The top panel shows the total change in open circuit voltage (OCV) from 4.2 V during the 500 hour storage period. Cells containing low concentrations of PES and the control electrolyte led to a large voltage drop and cells containing 2, 4, or 6% PES are comparable to 2% VC. The bottom panel of Figure 5 shows the difference between the discharge capacity immediately before the storage period and the discharge capacity following a full charge after the storage period. This difference is the irreversible capacity loss of the cells resulting from parasitic reactions at the negative electrode which deplete the Li inventory. Although all cells exhibited low irreversible capacity loss, the PES-containing cells resulted in the smallest loss.

Figure 6 shows the results of UHPC cycling for cells that underwent cycling only (Figures 6a to 6c) or cycling after a 500 hour storage period (Figures 6d to 6f). Figures 6a and 6d show the normalized discharge capacity, Figures 6b and 6e show the normalized charge-end-point capacity, and Figures 6c and 6f show the coulombic efficiency (CE), all plotted versus cycle number. The true discharge capacity of the cycling-only cells ranged from 208–225 mAh, and that of the storage before cycling cells ranged from 208–218 mAh. During storage at a full state of charge, lithium in the graphite slowly migrates to the overhang region of the anode. After the storage period some of this lithium in the overhang, that above the average state of charge of the anode during 100% DOD cycling, is slowly made available during cycling, causing the increase in capacity and decrease in CE shown in Figures 6d and 6f, respectively. This is an interesting effect which needs further exploration. Cells containing 2, 4, or 6% PES or 2% VC display high CE, low discharge capacity fade and small slippage of the charge end-point capacity.

Figure 7 shows the charge end-point capacity for the best performing cells. The increasing trend, or slippage, of the charge end-point capacity is due to electrolyte oxidation at the positive electrode. Cells containing 4 and 6% PES are superior to 2% VC as shown by the small slippage and small slope. Figure 7 shows that UHPC cycling
after storage gives a similar ranking of the additives as direct UHPC cycling, except in the case of 2% PES and 2% VC. Cells with 2% PES performed better than 2% VC when cells were cycled directly (Figure 7a) but performed worse when cells were cycled after the storage period (Figure 7b). The electrolyte oxidation rate, and correspondingly the charge end-point capacity slippage, in cells with 2% VC decreases dramatically from one 500 h storage period to the next as has been shown by Burns et al. Therefore, we are not surprised that the 2% VC cells appear better than the 2% PES cells when cycled after storage. By contrast, 4% and 6% PES outperform 2% VC in both UHPC methods.

Figure 8 shows the CE versus time after formation for the best performing cells. The cells that were cycled only are shown on the left and those that had a storage period prior to cycling are on the right. Figure 8 shows the benefit of a storage period prior to UHPC cycling. A more stable value of CE can be observed in fewer cycles when a storage period precedes the cycling experiments, possibly due to the maturation of the negative electrode SEI during the storage period. There are several features in Figure 8 that are very interesting. First, the CE versus time data for the PES-containing cells appear to extrapolate well from the cycling only experiment to the store-before-cycling experiment as one might expect. However, the data for 2% VC–containing cells that were stored before cycling is clearly shifted upwards relative to the extrapolation of the cycling-only cells. This is consistent with the results from Figure 7. From the cycling and storage data at 40°C (Figures 5 and 7), the performance of 4 and 6% PES proves to be comparable to or better than 2% VC.

**Figure 7.** a) The normalized charge end-point capacity of the cycled-only cells and b) the stored–before-cycled cells, both versus cycle number. The cells were cycled at C/20 between 2.8 and 4.2 V at 40°C.

**Figure 8.** The coulombic efficiency of the cycled-only cells and the stored-before-cycled cells as a function of time. The zero of time marks the point after EIS was measured after formation for all the cells. The cells were cycled at C/20 between 2.8 and 4.2 V at 40°C.
High temperature storage cells.— Figure 9 summarizes the gas evolution and impedance measurements taken after formation at 40 °C and after 500 hours of storage at 60 °C. The error bars are the standard deviation of data from pair cells. Figure 9a shows that all additive types produced small amounts of gas during formation except for Li-TFSI alone. Figure 9b shows the EIS spectra after formation at 3.8 V and 10 °C. PES-containing cells have larger charge transfer resistances than cells without PES. Figure 9c shows the volume of gas evolved during the 500 hour storage period at 60 °C. This panel shows that cells with PES alone had only 10% of the gas produced compared to cells with VC alone. All the PES-containing cells exhibited a significant reduction in gas compared with cells that did not contain PES. Figure 9c demonstrates the superiority of PES over VC as an additive at high temperature. Figure 9d shows the EIS spectra after the 60 °C storage period measured at 3.8 V and 10 °C. Although all cells show low impedance, the impedance of PES-containing cells have been significantly reduced after the 60 °C storage period compared to after formation. The reasons for this are not understood. Figure 9c shows that combining Li-TFSI with VC caused a reduction in gas evolution compared to 2% VC alone. Although the difference is minor, it appears that adding Li-TFSI to 2% PES also caused a reduction in gas evolution compared to 2% PES alone. Clearly, combining PES with other additives may be beneficial to optimize battery performance.

Figure 10 shows the voltage change from 4.2 V during the 500 hour storage period at 60 °C. The error bars are the standard deviation of data from pair cells. Figure 10 shows that all additives and additive combinations except Li-TFSI alone exhibited a relatively small voltage drop during storage. Combining Li-TFSI with either 2% VC or 2% PES reduced the magnitude of the voltage drop compared to 2% VC or 2% PES alone, suggesting useful synergies.

Conclusions

Through the use of storage and UHPC cycling experiments, the effectiveness of PES as an additive was investigated. UHPC cycling
experiments showed that 4% or 6% PES outperformed 2% VC while 2% PES was comparable to 2% VC. However, the use of 4% or 6% PES comes at the expense of higher charge transfer impedance in the resulting cells. The voltage drop during storage in PES-containing cells was very similar to that for cells with 2% VC, however, gas evolution at high temperatures was dramatically reduced when PES was used. In storage experiments at 40°C, cells with PES showed less irreversible capacity loss than cells with VC. Finally the combination of Li-TFSI with either VC or PES reduced both gassing and voltage drop during 60°C storage. We are aware of no “showstoppers” that prevent PES from reaching the same “famous” status as VC as a general purpose additive, at least in NMC111/graphite cells.

Acknowledgments

The authors acknowledge the financial support of NSERC and 3M Canada under the auspices of the Industrial Research Chairs program. KJN thanks NSERC for scholarship support though the CREATE DREAMS program at Dalhousie University.

References

1. S. S. Zhang, J. Power Sources, 162, 1379 (2006).
2. K. Xu, Chem. Rev., 104, 4305 (2004).
3. J. C. Burns, G. Jain, A. J. Smith, K. W. Eberman, E. Scott, J. P. Gardner, and J. R. Dahn, J. Electrochem. Soc., 158, A255 (2011).
4. M. Broussely, P. Biensan, F. Bonhomme, P. Blanchard, S. Herreyre, K. Nechev, and R. J. Staniewicz, J. Power Sources, 146, 90 (2005).
5. 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).
6. H. M. Jung, S.-H. Park, J. Jeon, Y. Choi, S. Yoon, J.-J. Cho, S. Oh, S. Kang, Y.-K. Han, and H. Lee, J. Mater. Chem. A, 1, 11975 (2013).
7. J. Jeon, S. Yoon, T. Park, J.-J. Cho, S. Kang, Y.-K. Han, and H. Lee, J. Mater. Chem., 22, 21003 (2012).
8. J. Xia, N. N. Sinha, L. P. Chen, G. Y. Kim, D. J. Xiong, and J. R. Dahn, J. Electrochem. Soc., 161, A84 (2013).
9. B. Li, M. Xu, B. Li, Y. Liu, L. Yang, W. Li, and S. Hu, Electrochim. Acta, 105, 1 (2013).
10. B. Li, Y. Wang, H. Rong, Y. Wang, J. Liu, X. M. Xu, and W. Li, J. Mater. Chem. A, 1, 12954 (2013).
11. J. Xia, L. Ma, C. P. Aiken, K. J. Nelson, L. P. Chen, and J. R. Dahn, J. Electrochem. Soc., 161, A1634 (2014).
12. A. J. Smith, J. C. Burns, S. Trussler, and J. R. Dahn, J. Electrochem. Soc., 157, A196 (2010).
13. T. M. Bond, J. C. Burns, D. A. Stevens, H. M. Dahn, and J. R. Dahn, J. Electrochem. Soc., 160, A521 (2013).
14. C. P. Aiken, J. Xia, D. Y. Wang, D. A. Stevens, S. Trussler, and J. R. Dahn, J. Electrochem. Soc., 161, A1548 (2014).
15. J. C. Burns, N. N. Sinha, G. Jain, H. Ye, C. M. VanEleen, W. M. Lamanna, a. Xiao, E. Scott, J. Choi, and J. R. Dahn, J. Electrochem. Soc., 159, A1105 (2012).
16. J. C. Burns, a. Kassam, N. N. Sinha, L. E. Downie, L. Solnickova, B. M. Way, and J. R. Dahn, J. Electrochem. Soc., 160, A1451 (2013).