Studies of Gas Generation, Gas Consumption and Impedance Growth in Li-Ion Cells with Carbonate or Fluorinated Electrolytes Using the Pouch Bag Method

D. J. Xiong, a, L. D. Ellis, a,∗ Remi Petibon, a Toren Hynes, a Q. Q. Liu, b,c and J. R. Dahn a,b,∗,∗

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

CMIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, People’s Republic of China

Abstract

A pouch bag technique was used to study the interactions between negative electrodes and positive electrodes within a Li-ion cell.34–36 The lithiated NMC442 electrode and other novel electrolyte systems has been widely investigated to improve the electrochemical performance of high voltage Li-ion cells. The pouch bag experiment may be a rapid screening method to identify effective electrolyte systems for high voltage Li-ion cells. The best electrolyte may be the one which causes the smallest impedance growth of the positive electrode in a pouch bag during a storage experiment. Reference 40 also reported that CO2 generated by the delithiated NMC442 electrode can move to the lithiated graphite electrode and be reduced there resulting in limited CO2 generation in the cells. Even though GC-MS was used to identify the gas compositions in the pouch cells and pouch bags, CO and hydrogen were excluded in the gas composition analysis due to limitations of the GC-MS method. Metzger et al. found that the generation of hydrogen is through an interaction between negative and positive electrodes in Li-ion cells.41

In this report, the pouch cell and pouch bag method developed by Xiong et al.30 is used to study the effect of a conventional carbonate electrolyte and a fluorinated electrolyte on impedance growth of charged positive electrodes stored at elevated temperature. A gas chromatography method is used to identify gas compositions, including hydrogen and CO, to gain more insight about the interactions between the positive electrode and the negative electrode in the cells.

Experimental

Pouch cells and pouch bags.—Dry NMC442/graphite (240 mAh) pouch cells which can be operated up to 4.7 V were obtained from Li-Fun Technology (Xiinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000, China). These cells were sealed under vacuum in a dry room in China without electrolyte before shipping to Canada. In Canada, these cells were cut below the seal and vacuum dried at 80 °C for 14 h prior to filling electrolyte. The pouch cells were filled with 0.76 mL of 1 M LiPF6 in EC:EMC (BASF, USA, EC purity: 99.95%, EMC purity: 99.9%, water content <20 ppm) (control electrolyte) or 0.76 mL of 1 M LiPF6 in TFEC and FEC (1:1 by weight) + 1% PES (called TFEC/FEC) in an argon-filled
the chamber was then pushed down to puncture the pouch cells or bags. The chamber was then back-filled with ultra-pure Ar to a gauge pressure of 10 kPa. A gastight syringe was used to extract 200 ± 5 μL of gas from this chamber through a rubber GC-septum (Bruker). This 200 μL of sampled gas was then injected into the GC.

The GC-TCD consisted of a Bruker 436-GC equipped with a split/splitless injector (270 °C) and a thermal conductivity detector (Bruker) equipped with a custom-made capillary column. The column consisted of a 5A molecular sieve column (Bruker, 10 m, 0.32 mm ID, 30 μm coating), in parallel with a Q-PLOT column (Bruker, 50 m, 0.53 mm ID, 20 μm coating). This custom column allows for permanent gases (H₂, O₂, N₂, CO) and light hydrocarbons (CH₄, C₂H₆, C₂H₄, etc.) as well as CO₂ to be well-separated in a single injection. Argon was used as the carrier gas at a flow rate of 9 mL·min⁻¹. In order to maximize the sensitivity of the detector, the reference cell flow rate of the TCD was set to 30 mL·min⁻¹ and the make-up flow rate of the analytical cell was set to 5 mL·min⁻¹. The TCD temperature was set to 230 °C while the filament temperature was set to 370 °C.

To quantitatively analyze the gas compositions, a calibration gas mixture was purchased from Praxair for retention time determination and signal calibration. The gas mixture contained butane, carbon dioxide, carbon monoxide, ethene, ethylene, hydrogen, methane, propane, propylene and argon. Each gas was 10 mol% in the mixture. The pressure in the tank was supplied at only 13 bar (gauge pressure) to ensure that each species was entirely in the gas phase. Pure butane liquefies first of these gases at 3.5 bar at room temperature so, at a partial pressure of 1.3 bar (assuming the ideal gas law) in this tank, it would be entirely gaseous.

**XPS experimental method.**—Only the delithiated NMC442 samples taken from pouch cells and pouch bags stored at 60 °C were used for XPS analysis since there was a bigger difference in the impedance of electrodes stored in pouch cells and pouch bags at 60 °C. Delithiated NMC442 electrodes were rinsed with EMC several times in a glove box to remove the remaining electrolyte after they were taken from these pouch cells and pouch bags. The samples were then transferred to ultra-high vacuum. A specially designed air-tight apparatus was used to ensure that the delithiated NMC442 electrodes were not exposed to air during the process. The delithiated NMC442 electrodes were then left under ultra-high vacuum overnight prior to their introduction to the analysis chamber, which was maintained at a pressure below 2 × 10⁻⁹ mbar at all times. Analysis was performed with a SPECs spectrometer equipped with a Phoibos hemispherical analyzer using monochromatized Mg Kα radiation and a pass energy of 20 eV. Preliminary and final survey scans were compared to ensure that no photochemical degradation was induced during analysis. Calibration of the binding energy scale was deemed unnecessary because all peak positions remained constant while the X-ray flux was varied, indicating the absence of charging effects. XPS spectra were fit with a non-linear Shirley-type background. This background was subtracted from the signal to allow for qualitative comparison of atomic concentrations between samples using relative peak heights.

**Results and Discussion**

Figure 1 shows the gas evolution in the pouch cells and pouch bags with PES222 or TFEC/FEC during the 500 h storage period at 60 °C. No volume changes were detected for pouch bags containing lithiated graphite electrodes during the storage period at 60 °C, which is consistent with previous results. Pouch bags with delithiated NMC442 taken from pouch cells with PES222 produced much more gas than the corresponding pouch cells while pouch bags with delithiated NMC442 taken from pouch cells with TFEC/FEC produced less gas during the first 300 h. The large error bars for the gas volume in pouch bags with TFEC/FEC after approximately 300 h are based on 2 pair corresponded pouch cells and pouch bags determined using the GC-TCD method. Figure 2 shows that there is almost no CO₂ left in the pouch cells with PES222 while there is still a significant amount of CO₂ found in the pouch cells with TFEC/FEC.
This suggests that the modified SEI at the graphite electrode in pouch cells with TFEC/FEC suppresses CO₂ reduction at the graphite electrode and its removal from the gas. Interestingly, hydrogen was only found in pouch cells and not in pouch bags. This suggests that the generation of hydrogen is through species created at the positive electrode which travel to the negative electrode, react and produce hydrogen. Figure 2 shows that there is much more hydrogen generated in pouch cells with TFEC/FEC than in pouch cells with PES222. This explains why fluorinated electrolytes can cause severe gassing problems when used in Li-ion cells operated at elevated temperatures.

Figure 3 shows the gas volume in the pouch cells and pouch bags measured by GC-TCD and also by Archimedes principle. Figure 3
shows that gas volume measured by GC-TCD is consistently larger than that measured by Archimedes principle. This is expected since gaseous products can be dissolved in the electrolyte in the cells and bags according to Henry’s law.49,50

Figures 4a, 4b, 5a and 5b show the area-specific Nyquist plot of positive electrode symmetric cells reconstructed from NMC442/graphite pouch cells with PES222 or TFEC/FEC, respectively. Nelson et al. discovered that $R_{ct}$ changed quasi-reversibly at high voltage in NMC442/graphite pouch cells containing EC-based electrolytes which shows that $R_{ct}$ of the positive electrode varies with potential (vs Li/Li$^{+}$) in EC-based electrolytes.51 However, Xia et al. found that $R_{ct}$ did not change over the voltage range (3.8–4.5 V) in NMC442/graphite pouch cells containing fluorinated electrolyte indicating that $R_{ct}$ of the positive electrode does not vary strongly with potential (vs Li/Li$^{+}$) in the TFEC/FEC electrolyte. One must compare the impedance of the positive electrode at the same potential vs Li/Li$^{+}$ in EC-based electrolyte but there is no need to compare the impedance of the positive electrode at exactly the same potential vs Li/Li$^{+}$ in fluorinated electrolyte. After 500 h of storage at 40 °C, the potential of pouch cells with control + PES222 dropped from 4.40 to 4.27 V, as shown in Figure S1. Therefore, Nyquist plots of positive electrodes taken from pouch cells with control + PES222 before storage at both 4.4 V and 4.27 V are also included in these Figures 4 and 5 for comparison. Figure S2 shows the potential versus time of pouch cells containing TFEC/FEC electrolyte during storage for completeness.

Figures 4 and 5 show that $R_{ct}$ of the positive electrode in pouch cells does not change significantly as the storage temperature increases from 40 °C to 60 °C. Figure 4 shows that $R_{ct}$ of positive electrodes taken from pouch bags is larger than that of positive electrodes taken from pouch cells with PES222, especially at 60 °C. This is consistent with the results found by Xiong et al when an additive-free carbonate electrolyte was used.40 This suggests that the addition of PES222 does not suppress the oxidized species from reacting with the charged positive electrode material leading to a large increase in impedance. Figure 5 shows that $R_{ct}$ of positive electrodes taken from pouch bags with TFEC/FEC is slightly larger compared to $R_{ct}$ of positive electrodes taken from pouch cells with TFEC/FEC. Comparison of Figures 4d and 5d shows that $R_{ct}$ of the electrodes stored at 60 °C in pouch bags with PES222 is about an order of magnitude larger than those of electrodes stored with TFEC/FEC. This suggests that either the oxidized species from TFEC/FEC do not react with the positive electrode or that the passivating layer resulting from TFEC/FEC can prevent the oxidized species from reacting with the positive electrode resulting in less impedance growth for charged positive electrodes in contact with TFEC/FEC.

Figures 6 and 7 show the area-specific Nyquist plots of lithiated graphite electrode symmetric cells reconstructed from
Figure 5. Area-specific Nyquist plot of positive electrode symmetric cells where the electrodes were taken from NMC442/graphite pouch cells with TFEC/FEC after 500 h storage at 40 °C (a) and 60 °C (b) and from charged NMC442-containing pouch bags with TFEC/FEC after 500 h storage at 40 °C (c) and 60 °C (d).

NMC442/graphite pouch cells and pouch bags stored with PES222 or TFEC/FEC, respectively. Figures 6 and 7 show that $R_{ct}$ of the lithiated graphite electrodes harvested from the pouch cells is roughly the same as those from pouch bags. However, $R_{ct}$ of the lithiated graphite electrodes harvested from pouch cells and pouch bags with TFEC/FEC (Figure 7) is much larger compared to $R_{ct}$ of the lithiated graphite electrodes taken from pouch cells and pouch bags with PES222 (Figure 6). Large impedance at the graphite electrode is not desirable for high rate and low temperature applications. This suggests that TFEC/FEC will not be a good choice for Li-ion cells which need to operate at high rates and low temperatures.

Figure 8 shows the background-subtracted O1s spectra of positive electrodes stored at 60 °C for 500 h in PES 222 (Figure 8a) or TFEC/FEC (Figure 8b) containing pouch bags or pouch cells. The trends are roughly the same for both electrolytes. The peak at 529.5 eV, assigned to the NMC lattice oxygen, is larger for positive electrodes stored in pouch bags than for those stored in cells. The peaks at 531.5 eV and 533.3 eV, originating from SEI components containing ether and carbonyl-type environments, are smaller for the positive electrodes stored in bags than those stored in cells. Both observations indicate that the SEI is much thinner for the positive electrode stored in bags than stored in cells. This is unexpected as $R_{ct}$ of positive electrodes stored in bags containing conventional carbonate electrolyte is much larger than $R_{ct}$ of electrodes stored in cells and $R_{ct}$ of the positive electrode stored in bags containing fluorinated electrolyte was slightly larger than $R_{ct}$ of electrodes stored in cells. The thinned SEI of positive electrodes stored in bags gives evidence that a thin, non-organic, insulating phase is the main contributor to $R_{ct}$ growth. This insulating phase may be the reduced layer of rocksalt structure transition metal oxide described in several recent publications. No significant chemical differences were revealed in the C1s and F1s regions of the XPS spectra between positive electrodes stored in cells and bags containing PES222 and TFEC/FEC, other than the thinned SEI.

Figure 9a shows a schematic of possible reactions and crosstalk between negative and positive electrodes in the pouch cells and of reactions in the pouch bags containing conventional carbonate electrolyte suggested by the data presented here. Figure 9b shows a similar schematic for the cells and bags containing fluorinated electrolyte. In a pouch cell (left side of Figures 9a and 9b), both the conventional carbonate electrolyte and the fluorinated electrolyte are oxidized at the positive electrode at high voltage and elevated temperature generating gaseous or oxidized species as well as electrons. The oxidized species can be dissolved in the electrolyte to some extent. The solubility of the oxidized species depends on their chemical nature, temperature and the electrolyte composition. The lithium ions in the electrolyte combine with the generated electrons and insert into the positive electrode reducing the potential of the positive electrode vs $Li^+$/Li. The gaseous and dissolved oxidized species move to the negative electrode and are reduced there. CO2 is consumed at the negative electrode to
produce products that coat the graphite electrode surface. It is possible that released protic species react at the graphite electrode to produce hydrogen. Much more hydrogen is produced in cells containing TFEC/FEC electrolyte than PES222 electrolyte. In a pouch bag with conventional carbonate electrolyte, generated gases and other oxidized species which remain in the electrolyte or at the surface of the positive electrode can further react with the positive electrode leading to a more resistive passivating film, possibly a rock salt surface layer at the positive electrode. However, in a pouch bag with fluorinated electrolyte, the gaseous and other oxidized species are either unable to react with the positive electrode or there is a better passivating layer at the electrode which prevents reactions. Therefore a minimal impedance growth at the positive electrode is observed in pouch bags with TFEC/FEC.

Conclusions

EC-based and fluorinated electrolytes have been comparatively studied using NMC442/graphite pouch cells and pouch bags. The results show that the fluorinated electrolyte suppresses impedance growth of the charged NMC442 electrode but creates large initial negative electrode impedance. CO₂ is produced in pouch bags containing charged NMC442 and either electrolyte, but very little CO₂ is found in pouch cells with the EC-based electrolyte. This suggests that the SEI at the graphite electrode created by the fluorinated electrolyte limits CO₂ consumption compared to the carbonate electrolyte.

Virtually no gas was produced in pouch bags containing charged graphite and either electrolyte. Virtually no hydrogen was produced in pouch bags containing charged NMC442 and either electrolyte. However, hydrogen was found in pouch cells containing either electrolyte and the amount of hydrogen in the pouch cells containing the fluorinated electrolyte was very large. Therefore, the generation of hydrogen must be caused by the crosstalk between the negative electrode and the positive electrode in a cell. Metzger et al. proposed that protic species were responsible for the generation of hydrogen. If these species are generated at the positive electrode, they will simply accumulate in the pouch bags and hydrogen will not be created. Therefore, in future experiments, liquid phase GC-MS will be employed to hopefully identify these oxidized species in pouch bags containing charged positive electrodes to understand exactly how hydrogen is generated in pouch cells.

Acknowledgments

The authors thank NSERC, 3M Canada and Tesla Motors for funding of this work under the auspices of the two successive Industrial Research Chair programs. The authors thank Dr. Jing Li of BASF for providing some of the solvents and salts used in his work. The authors thank David Yaohui Wang and Yong-Shou Lin of CATL for providing...
Figure 7. Area-specific Nyquist plot of lithiated graphite electrode symmetric cells where the electrodes were taken from NMC442/graphite pouch cells with TFEC/FEC after 500 storage at 40°C (a) and 60°C (c) and from the corresponding pouch bags after 500 h storage at 40°C (b) and 60°C (d).

Figure 8. XPS O1s spectra of positive electrodes stored (500 h at 60°C) in cells (black) and in bags (red) with PES222 (a) and TFEC/FEC (b).
the pouch bag material used in this work. Remi Petibon and Leah Ellis thank NSERC and the Walter C. Sumner Memorial Foundation for scholarship support.

References

1. Z. Lu, D. D. MacNeil, and J. R. Dahn, Electrochim. Solid-State Lett., 4, A200 (2001).
2. T. Ohzuku and Y. Makimura, Chem. Lett., 30, 642 (2001).
3. J. Li, L. E. Downie, L. Ma, W. Qiu, and J. R. Dahn, J. Electrochem. Soc., 162, A1401 (2015).
4. H. Cao, Y. Zhang, J. Zhang, and B. Xia, Solid State Ion., 176, 1207 (2005).
5. A. Park et al., J. Electrochem. Soc., 154, A520 (2007).
6. P. Y. Liao, J. G. Duh, and S. R. Sheen, J. Electrochem. Soc., 152, A1695 (2005).
7. D. D. MacNeil, Z. Lu, and J. R. Dahn, J. Electrochem. Soc., 149, A1332 (2002).
8. J. Jiang, K. W. Eberman, L. J. Krause, and J. R. Dahn, J. Electrochem. Soc., 152, A566 (2005).
9. J. Jiang, K. W. Eberman, L. J. Krause, and J. R. Dahn, J. Electrochem. Soc., 152, A1874 (2005).
10. S. Jouanneau et al., J. Electrochem. Soc., 150, A1299 (2003).
11. J. Li et al., Electrochimica Acta, 150, 234 (2015).
12. J. Li, R. Shumuggasundaram, R. Doig, and J. R. Dahn, Chem. Mater., 28, 162 (2016).
13. J. M. Paulsen, L. Y. Kieu, and B. G. Ammundsen, US6660432, 2003.
14. Z. Lu et al., J. Electrochem. Soc., 158, A516 (2011).
15. L. Ma, M. Nie, J. Xia, and J. R. Dahn, J. Power Sources, 327, 145 (2016).
16. L. Xue, S.-Y. Lee, Z. Zhao, and C. A. Angell, J. Power Sources, 295, 190 (2015).
17. L. Xue, K. Ueno, S.-Y. Lee, and C. A. Angell, J. Power Sources, 262, 123 (2014).
18. L. Xu, D. Lu, A. Garsuch, and B. L. Lucht, J. Electrochem. Soc., 159, A2130 (2012).
19. M. Xu et al., J. Electrochem. Soc., 160, A2005 (2013).
20. A. von Cresce and K. Xu, J. Electrochem. Soc., 158, A337 (2011).
21. C.-C. Su et al., ChemElectroChem, 3, 790 (2016).
22. S. R. Li, N. N. Sinha, C. H. Chen, K. Xu, and J. R. Dahn, J. Electrochem. Soc., 160, A2014 (2013).
23. R. Luo et al., J. Electrochem. Soc., 163, A272 (2016).
24. S. H. Bae, W.-K. Shin, and D.-W. Kim, Electrochimica Acta, 150, A347 (2015).
25. J. Xia, L. Ma, and J. R. Dahn, J. Electrochem. Soc., 150, A330 (2011).
26. J. Xia et al., J. Electrochem. Soc., 159, A324 (2012).
27. S. H. Bae, W.-K. Shin, and D.-W. Kim, Electrochimica Acta, 150, A347 (2015).
28. M. Xu et al., J. Electrochem. Soc., 160, A1170 (2013).
29. M. Xu et al., J. Electrochem. Soc., 160, A1130 (2013).
30. A. von Cresce and K. Xu, J. Electrochem. Soc., 158, A337 (2011).
31. C.-C. Su et al., ChemElectroChem, 3, 790 (2016).
32. S. R. Li, N. N. Sinha, C. H. Chen, K. Xu, and J. R. Dahn, J. Electrochem. Soc., 160, A2014 (2013).
33. R. Luo et al., J. Electrochem. Soc., 163, A272 (2016).
34. J. Xia, L. Ma, and J. R. Dahn, J. Electrochem. Soc., 161, A2250 (2014).
35. J. Xia et al., J. Electrochem. Soc., 162, A1046 (2015).
36. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
37. J. Xia et al., J. Electrochem. Soc., 162, A307 (2016).
38. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
39. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
40. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
41. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
42. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
43. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
44. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
45. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
46. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
47. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
48. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
49. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
50. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
51. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
52. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
53. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
54. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).
55. J. Xia et al., J. Electrochem. Soc., 162, A1424 (2015).