Interactions between Positive and Negative Electrodes in Li-Ion Cells Operated at High Temperature and High Voltage

D. J. Xiong,†,* R. Petibon,†,* M. Nie,‡† L. Ma,‡† J. Xia,‡†* and J. R. Dahn†,*‡‡

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

When NMC/graphite Li-ion cells are operated at elevated temperature or at a cutoff potential above 4.2 V, electrolyte oxidation becomes increasingly severe leading to gas product generation and other oxidized species. These produced gas products and oxidized species can migrate to, and then interact with, the negative electrode. A variety of cell formats (pouch cells, symmetric cells and coin cells) as well as pouch bags, containing only a delithiated positive electrode or a lithiated negative electrode, were used to investigate electrode/electrode interactions. Open circuit potential measurements during high temperature storage, ex-situ measurements of gas volume produced versus time, gas chromatography-mass spectrometry (GC-MS) of the gases produced and electrochemical impedance spectroscopy (EIS) of the electrodes versus time were performed. During storage at 60°C, pouch bags containing only a delithiated positive electrode and electrolyte produced no gas while charged full pouch cells produced some gas and pouch bags containing only a delithiated positive electrode and electrolyte produced a significant amount of gas. The predominant gas produced in the positive electrode pouch bags was CO2 while virtually no CO2 was detected in the gases evolved in the charged full cell, suggesting that the negative electrode in the full cell consumes CO2 generated at the charged positive electrode. In addition, the impedance of the surface film on the charged positive electrodes in the pouch bags increased at least three times more than the positive electrodes in the charged pouch cells, even though they were both in contact with electrolyte for the same period of time. These impedance results suggest that oxidized species created at the positive electrode in the pouch bag remain in the vicinity of the positive electrode and create a high impedance film possibly a rock salt surface layer, while the same species migrate to the negative and are “consumed” in the pouch cell where the impedance of the positive electrode remains small. These interactions are apparently essential for the health of a NMC/graphite Li-ion pouch cell when operated at an elevated temperature or at a cutoff voltage above 4.2 V.

Increasing evidence show that interactions between positive and negative electrodes exist in full Li-ion cells. A well-known example is Mn dissolution from the positive electrode and its subsequent deposition at the negative electrode. This interaction has been shown to be detrimental to cell performance. Another proposed example is CO2 generation at the positive electrode followed by reduction at the negative electrode. This “dialog” between both electrodes was proposed as creating a “shuttle” which could damage cell performance. Li et al. recently found that oxidized species from LiNi0.5Mn1.5O4 caused severe parasitic reactions on the Li4Ti5O12 electrode using an Li+ electrolyte. This interaction has been shown to cause severe parasitic reactions on the Li4Ti5O12 electrode using an Li+ electrolyte. This “dialog” between both electrodes was proposed as creating a “shuttle” which could damage cell performance. Li et al. recently found that oxidized species from LiNi0.5Mn1.5O4 caused severe parasitic reactions on the Li4Ti5O12 electrode using an innovative “pseudo-full cell” configuration.

When NMC/graphite Li-ion cells are operated at a cutoff potential higher than 4.2 V, severe impedance increase can be the main contributor to cell failure instead of conventional mechanisms, like loss of Li inventory, that dominate in low voltage cells. It is our opinion that the precipitation of oxidized species generated and a rock salt surface layer generated at the positive electrode are the two main sources of impedance increase when cells are cycled at high voltage. In principle, generated gas products and oxidized species which could passivate the positive electrode and/or dissolve in the bulk electrolyte could reach the negative electrode and be reduced there.

Petibon et al. found that the impedance of LiCoO2 positive electrode symmetric coin cells increased rapidly with time while the impedance of reconstructed full coin cells changed slowly with time and that of negative electrode symmetric cells did not change at all over time. In order to study electrode/electrode interactions further, pouch bags were used to isolate the charged positive electrode from the lithiated negative electrode, so that interactions between two electrodes would be impossible. Pouch bags containing only the charged positive electrode and electrolyte can be used as a simple tool to obtain valuable information concerning the consequences of the absence of an interaction with the negative electrode. In addition, use of pouch bags containing a charged positive electrode and electrolyte may be a convenient and rapid way to screen novel electrolytes and electrolyte additives for effectiveness in allowing NMC/graphite cells to operate to high potential.

In this report, pouch bags containing only delithiated Li[Ni0.2Mn0.2Co0.6O2]0.5 (NMC111) plus electrolyte or delithiated Li[Ni0.42Mn0.42Co0.16]O2 (NMC442) positive electrodes plus electrolyte and NMC111/graphite or NMC442/graphite pouch cells were comparatively studied. Pouch bags containing lithiated graphite and electrolyte were also studied for comparison. The volume of gas produced in the pouch bags, the composition of that gas, the charge transfer resistance of electrodes recovered from pouch bags and the potential change of the charged positive electrodes, during storage, from the pouch bags vs Li/Li+ were measured and compared to electrodes from pouch cells. The results obtained demonstrate that when the CO2 and other oxidized species generated by the positive electrode are removed by the graphite electrode then gas production can be minimized and impedance can be kept under control. This suggests such interactions are essential to allow a NMC/graphite Li-ion cell to function well in a current carbonate-based electrolyte system when operated at elevated temperature and a cutoff potential higher than 4.2 V.

Experimental

Pouch cells and pouch bags.—Dry (no electrolyte) NMC111/graphite (220 mAh) pouch cells balanced for 4.4 V operation and NMC442/graphite (240 mAh) pouch cells balanced for 4.7 V operation were obtained from Li-Fun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000, China). Prior to shipping, these cells were vacuum sealed in a dry room in China without electrolyte. In Canada, before electrolyte filling, these cells were cut below the seal and vacuum dried at 80°C for 14 h. The pouch cells were filled with 0.9 g of 1 M LiPF6 in EC:EMC (BASF, USA, EC purity: 99.95%, EMC purity: 99.9%, water content < 20 ppm) (3:7 by weight) (control electrolyte) in an argon-filled glove box and vacuum sealed in the same glove box. After electrolyte filling, cells were placed in a temperature box at 40 ± 0.1°C and held at 1.5 V for 24 h. They were then charged to 3.8 V at C/20, and transferred to a glove box for degassing (cut open below the seal and re-sealed under vacuum).
After degassing, they were charged to either 4.2 or 4.4 V, then discharged to 2.8 V and charged back to the same charge cutoff voltage until the current for NMC111/graphite dropped below C/1000 and the until the holding period for the NMC442/graphite cells reached 30 hours.

For the NMC111/graphite cells, two cells of each cell category (charged to either 4.2 V or 4.4 V), were moved to a 60 °C temperature box for storage. The other cells were transferred to the glove box and dissembled there. The delithiated NMC111 electrodes collected from the full cells were inserted into different pouch bags (made of the same material as the pouch cells) with 0.7 g of control electrolyte. In addition, the lithiated graphite electrodes were inserted into separate pouch bags with 0.7 g of electrolyte. In order to study the effect of the LiPF6 on gas evolution at elevated temperature, some delithiated NMC111 electrodes and the lithiated graphite electrodes collected from the full cells were first washed with DMC three times and then inserted into different pouch bags with 0.7 g of EC/EMC (no LiPF6). The pouch bags were then vacuum sealed and transferred to the same temperature box as their parent cells for storage. Figure 1 shows photographs to illustrate how the pouch cells were disassembled, the pouch bags were created and how the pouch cells and pouch bags were then used.

For NMC442/graphite pouch cells, six cells at 4.4 V were moved to either a 40 °C or 60 °C temperature box for storage. The other cells were transferred to the glove box and dissembled there. The delithiated NMC442 electrodes collected from the pouch cell were inserted into pouch bags with 0.3 g EMC. The addition of 0.3 g EMC to pouch bags created a similar electrolyte environment as in the original pouch cells, because EC and LiPF6 were still left in the electrode and only about 0.3 g of EMC evaporated from the positive electrodes.

The volume of all the pouch bags and pouch cells during the 500 h storage period were measured from time to time using Archimedes’ method and the ex-situ gas equipment described in reference. The potential change of NMC111/graphite and NMC442/graphite symmetrical cells were measured using a voltmeter and an automated voltage measurement system, respectively. 50

Results and Discussion

Figure 2a shows the volume change versus time for full pouch cells, pouch bags containing the charged positive electrode plus electrolyte or solvent and pouch bags containing delithiated graphite plus electrolyte or solvent during a 500 h storage period at 60 °C. Figure 2a shows that the volume of the pouch cells and pouch bags containing the charged positive electrodes increased with time while the pouch bags containing delithiated graphite showed no volume change at all. Figure 2a also shows that the pouch bags containing the delithiated NMC111 electrodes plus electrolyte or solvent produced almost two times more gas than the corresponding pouch cells during the storage period. This suggests that some gaseous products generated at the positive electrode are consumed at the negative electrode in a full cell or that their production is somehow inhibited by its presence. This

Analysis of the gas composition in NMC111/graphite pouch cells and NMC111-containing pouch bags.—For NMC111/graphite pouch cells and NMC111-containing pouch bags, GC-MS was used to analyze the gases other than H2 and CO. The gas extraction procedure followed that described by Petibon et al. Interested readers can read the detailed procedure there. 50 μL of the gas was injected into the GC-MS for analysis. The GC-MS used was a Bruker 436-GC and a Bruker Scion single-quadrupole mass spectrometer and operating parameters are also described in Reference 20.

Symmetric cells and coin cells.—The NMC442/graphite pouch cells and NMC442-containing pouch bags were opened in an argon-filled glove box after they were stored for 500 h. For pouch cells, at least 3 full Li/graphite, Li/NMC442 coin cells and NMC442/NMC442 symmetrical cells were assembled using one Celgard 2320 (Celgard) separator for coin cells or one polypropylene blown microfiber separator (BMF – available from 3 M Co. 0.275 mm thickness, 3.2 mg/cm2) for the symmetric cells. Control electrolyte was used for these cells. For electrodes from the pouch bags, at least 3 Li/NMC442 coin cells and NMC442/NMC442 symmetric cells were made. A voltmeter was used to measure the potential of the assembled full coin cells once their voltage stabilized after a few minutes. EIS measurements were conducted on the assembled symmetric cells. AC impedance spectra were collected using a Biologic VMP-3 with ten points per decade from 100 kHz to 10 mHz and a 10 mV input signal amplitude. All EIS spectra were collected at 10. ± 0.1 °C. This temperature was chosen to amplify the differences between the electrodes.
Figure 2. (a) Gas volume versus time for: pouch cells having an initial voltage of 4.2 V (black crosses) and 4.4 V (black diamonds), pouch bags containing the delithiated NMC111 electrode taken from pouch cells having an initial voltage of 4.2 V (red crosses) and 4.4 V (red diamonds) and pouch bags containing the delithiated NMC111 plus solvent (with DMC washing) taken from pouch cells having an initial voltage of 4.2 V (blue crosses) and 4.4 V (blue diamonds); (b) Open circuit voltage versus time for pouch cells with control electrolyte.

is of great importance since this interaction apparently helps a Li-ion pouch cell limit gas production. Pouch bags with the delithiated NMC111 electrode taken from pouch cells at 4.4 V produced more gas than those taken from pouch cells at 4.2 V. This means, unsurprisingly, that delithiated NMC111 electrodes at a higher potential oxidize electrolyte at a higher rate. Pouch bags containing the washed charged NMC111 electrode (DMC washing) + EC/EMC produced gas at a slightly lower rate than those with control electrolyte. This suggests that the presence of LiPF6 does not strongly affect the parasitic reactions at the positive electrode that cause gaseous products.

Figure 3 shows chromatograms of the major gaseous products from NMC111/graphite pouch cells and pouch bags that contained charged NMC111 electrodes. A logarithmic scale on the y-axis is used for clarity. DMC and DEC come from the trans-esterification of EMC. In full cells, the main gaseous products include CH₂=CH₂, C₃H₆, CH₃OCH₃ and CH₃OCH₂CH₃. These compounds are very similar to the ones found in NMC(111)/graphite cells formed to 3.5 V as introduced by Petibon et al. These compounds could be traced back to the reduction of both EC (CH₂=CH₂), and reduction as well as nucleophilic substitution from reduction by-products of EMC (CH₃CH₂, CH₃OCH₂CH₃). A detailed reaction mechanism can be found in Reference 19. The presence of these compounds could come from an incomplete degassing step or the continuous growth of the SEI at the negative electrode. Fluorinated alkanes such as CH₃CH₂F were also detected which indicates the participation of LiPF6 in the oxidation mechanism of the electrolyte. Most of the gaseous products in the full cells could also be found in the corresponding pouch bags except for ethane (the main gaseous product in the full cells). In the pouch bags containing the delithiated NMC111 electrodes, a significant amount of CO₂ was identified while almost no CO₂ was found in the pouch cells. This means that CO₂ has almost been consumed completely by the lithiated graphite in a full cell, which explains why pouch cells produced much less gas than the corresponding pouch bags with the positive electrode by itself. This suggests that this interaction between the positive electrode and negative electrode helps to limit gassing during high temperature operation.

Sloop et al. suggest a mechanism whereby CO₂ generated at the positive electrode diffuses to the negative electrode and reacts with intercalated lithium to form lithium oxalate. This formed lithium oxalate would decrease the lithium inventory and create irreversible capacity loss. Although lithium oxalate has limited solubility, Sloop et al. suggest the formed lithium oxalate can diffuse back to the positive
electrode and be oxidized to CO$_2$ again with corresponding insertion of Li (as Li$^+ + e^-$) into the positive electrode, causing self-discharge and reversible capacity loss. The lack of significant CO$_2$ found in the NMC/graphite full cells compared to the pouch bags suggests that the recreation of CO$_2$ from lithium oxalate at the positive electrode must be very slow, compared to the rate of capture of CO$_2$ at the negative electrode under the conditions explored here.

Figure 4 shows the area-specific Nyquist plot of positive electrode symmetric cells reconstructed from NMC442/graphite pouch cells stored at 40$^\circ$C (4a) and 60$^\circ$C (4b) and from NMC442-containing pouch bags stored at 40$^\circ$C (4c) and 60$^\circ$C (4d). The impedance spectrum of a positive electrode symmetric cell assembled from a pouch cell before storage is also shown in Figure 4a for comparison. The high frequency semicircle is caused by contact resistance between the double sided electrodes and the coin cell hardware as has been demonstrated in Reference 16. The low frequency semicircle originates from the charge transfer impedance, $R_{ct}$, of the positive electrode as demonstrated in Reference 16. $R_{ct}$ of the positive electrode from the pouch cells decreases slightly as the storage temperature increases from 40$^\circ$C to 60$^\circ$C. This slight decrease could be due to the lower time-averaged potential of the positive electrode at 60$^\circ$C compared to cells stored at 40$^\circ$C as shown in Figures 5a and 5d. Figure 4 shows that $R_{ct}$ of positive electrodes taken from pouch bags is significantly larger than that of positive electrodes taken from pouch cells. This suggests that in the absence of lithiated graphite, the impedance of the full cell would increase tremendously. When an NMC/graphite Li-ion cell with carbonate-based electrolyte is operated above 4.2 V, impedance growth can be the main reason for cell failure.8,9 This suggests that the “clean-up” of the oxidized species by the negative electrode is essential for maintaining reasonable impedance even though species transported to the negative and reduced there can partially block Li-ion pathways to the graphite electrode.15

Figure 5 shows the open circuit voltage versus time for NMC442/graphite pouch cells as well as charged NMC442 and lithiated graphite electrodes taken from pouch bags stored at either 40$^\circ$C or 60$^\circ$C. The OCV of the lithiated graphite and charged NMC442 electrodes from the pouch cells and pouch bags were measured by assembling Li/NMC442 and Li/graphite coin cells with the electrodes from the pouch cells and the pouch bags at different time periods. Figure 5 shows that the potential of the charged positive electrode in a pouch bag drops only slightly while the potential of the positive electrode in a full cell decreases more significantly. This could be due to the formation of a high resistance rock salt layer on the positive electrode in the pouch bags which then slows electrolyte oxidation.19 The potential of the lithiated graphite electrode in the pouch cell stored at 40$^\circ$C remained virtually unchanged while the potential of the lithiated graphite electrode in the cell stored at 60$^\circ$C increased around 0.02 V. This is most likely caused by an increase in the rate of SEI
Figure 4. The area-specific Nyquist plot of positive electrode symmetric cells from NMC442/graphite pouch cells stored at 40°C (a) and 60°C (b) and from charged NMC442-containing pouch bags stored at 40°C (c) and 60°C (d). Data for a positive electrode symmetric cell constructed from a fresh pouch cell (after formation) is also shown in panel a). Note that the x-axis and y-axis scales in Figures 4a and 4b are different from those in Figures 4c and 4d.

Figure 5. Open circuit voltage versus time for NMC442/graphite pouch cells during storage (a, d), as well as Li/NMC442 (b, e) and Li/graphite (c, f) coin cells where the electrodes were taken out of the pouch cells and pouch bags at the times indicated.
thickening reactions, which consume intercalated lithium, at the higher temperature.\textsuperscript{22}

Figure 6 shows a schematic of negative/positive electrode interactions suggested by the data presented here. In a pouch cell, electrolyte is oxidized at the positive electrode and gaseous or oxidized species as well as electrons are generated. The generated electrons combine with lithium ions and insert into the positive electrode. The released gaseous and oxidized species move to the negative electrode and are reduced there. This leads to lower cell volume increase and lower full cell impedance growth even though it can thicken the negative electrode SEI film leading to partial blocking of the pathway for lithium ions to insert into graphite.\textsuperscript{15} In a pouch bag, generated gases such as CO\textsubscript{2} remain, other oxidized species accumulate and can react at the positive electrode again. This may produce a more resistive passivating film possibly a rock salt surface layer at the positive electrode. These phenomena would explain the larger gas volume production and larger impedance in pouch bags compared to full pouch cells.

Conclusions

In this report, NMC111/graphite, NMC442/graphite pouch cells, pouch bags containing charged positive electrodes plus electrolyte or solvent and pouch bags containing only lithiated graphite plus electrolyte or solvent were studied after storage at 40°C or 60°C. No gas was generated in the pouch bags containing lithiated graphite plus electrolyte. However, large amounts of CO\textsubscript{2} were generated at the positive electrode side and the generated CO\textsubscript{2} could apparently be reduced at the negative side leading to a smaller volume expansion in pouch cells than pouch bags. The experiments also suggest that other oxidized species (Such as those suggested by Jarry et al.\textsuperscript{23}) can be produced at the positive electrode and consumed at the negative electrode as well, leading to a lower rate of impedance increase at the positive electrode. Without the “clean-up” of these generated gas products and oxidized species by the lithiated graphite electrode, NMC/graphite Li-ion pouch cells could experience rapid failure due to gas production and impedance growth at the positive electrode when they are cycled at an elevated temperature or a higher cutoff voltage.

Further work is needed in order to identify which and how oxidized species are reduced at the negative side. The same method should be systematically used in order to study the effects of additives and additive blends on these electrode/electrode interactions. It is our opinion that the most rapid experiments to identify effective electrolutes for high voltage Li-ion cells may be those involving storage experiments on charged positive electrodes placed in pouch bags. The best electrolytes may be those which produce the least gas volume in the pouch bag and the smallest impedance change of the positive electrode when measured after storage in a symmetric cell.

Acknowledgments

The authors thank NSERC and 3 M Canada for the funding of this work under the auspices of the Industrial Research Chairs program. The authors thank Dr. Jing Li of BASF for providing some of the solvents and salts used in his work. RP thanks NSERC and the Walter C. Sumner Memorial Foundation for scholarship support.

References

1. K. Xu, Chem. Rev., 114, 11503 (2014).
2. S. Komaba, N. Kumagai, and Y. Kataoka, Electrochimica Acta, 47, 1229 (2002).
3. C. Delacourt, A. Kwong, X. Liu, R. Qiao, W. L. Yang, P. Lu, S. J. Harris, and V. Srinivasan, J. Electrochem. Soc., 160, A1099 (2013).
4. C. Zhan, J. Lu, A. Jeremy Kropl, T. Wu, A. N. Jansen, Y.-K. Sun, X. Qiu, and K. Amine, Nat. Commun., 4 (2013).
5. N. Mahootian, E. Asl, J.-H. Kim, N. P. W. Pieczonka, Z. Liu, and Y. Kim, Electrochim. Commun., 32, 1 (2013).
6. S. E. Sloop, J. B. Kerr, and K. Kinoshita, J. Power Sources, 119–121, 330 (2003).
7. S. R. Li, C. H. Chen, X. Xia, and J. R. Dahn, J. Electrochem. Soc., 160, A1524 (2013).
8. K. J. Nelson, G. L. d’Eon, A. T. B. Wright, L. Mu, J. Xia, and J. R. Dahn, J. Electrochem. Soc., 162, A1046 (2015).
9. L. Ma, J. Xia, and J. R. Dahn, J. Electrochem. Soc., 161, A2250 (2014).
10. C. P. Aiken, J. Self, R. Petibon, X. Xia, J. M. Paulsen, and J. R. Dahn, J. Electrochem. Soc., 162, A760 (2015).
11. J. Self, C. P. Aiken, R. Petibon, and J. R. Dahn, J. Electrochem. Soc., 162, A796 (2015).
12. J. Camarella and C. B. Arnold, J. Power Sources, 245, 745 (2014).
13. J. Self, D. S. Hall, L. Madsen, and J. R. Dahn, J. Power Sources, 298, 369 (2015).
14. F. Lin, I. M. Markus, D. Nordlund, T.-C. Weng, M. D. Asta, H. L. Xin, and M. M. Doeff, Nat. Commun., 5, 3529 (2014).
15. 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).
16. R. Petibon, C. P. Aiken, N. N. Sinha, J. C. Burns, H. Ye, C. M. VanElzen, G. Jain, S. Trussler, and J. R. Dahn, J. Electrochem. Soc., 160, A1117 (2013).
17. C. P. Aiken, J. Xia, Y. D. Wang, D. A. Stevens, S. Trussler, and J. R. Dahn, J. Electrochem. Soc., 161, A1548 (2014).
18. 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).
19. R. Petibon, L. Rotermund, K. J. Nelson, A. S. Goudz, J. Xia, and J. R. Dahn, J. Electrochem. Soc., 161, A1167 (2014).
20. R. Petibon, L. M. Rotermund, and J. R. Dahn, J. Power Sources, 287, 184 (2015).
21. D. Abraham, J. Bare˜no, J. Wen, and I. Petrov, Microsc. Microanal., 17, 1577 (2011).
22. D. Xiong, J. C. Burns, A. J. Smith, N. Sinha, and J. R. Dahn, J. Electrochem. Soc., 158, A1431 (2011).
23. A. Jarry, S. Gotty, Y.-S. Yu, J. Roque-Rosell, C. Kim, J. Cabana, J. Kerr, and R. Kostecki, J. Am. Chem. Soc., 137, 3553 (2015).