Hindering Rollover Failure of Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O_{2}/Graphite Pouch Cells during Long-Term Cycling

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Eventual rapid capacity loss or “rollover” failure of lithium-ion cells during long-term cycling (>3000 cycles in many cases) at room temperature was studied with Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O_{2}/graphite pouch cells. The effects of positive electrode material coating, electrolyte additives, upper cutoff voltage, LiPF_6 concentration, cell rest periods, electrode thickness, graphite type and electrolyte solvent formulation were probed. Cells were tested under 1C charge and discharge with “rate maps” (discharges at C/20, C/2, 1C, 2C, 3C) applied every 100 cycles. The loss of high rate capability (3C) is shown to be an early warning of impending rollover failure. Electrochemical impedance spectroscopy (EIS) and studies of symmetric cells made using electrodes from disassembled cells demonstrate that impedance growth at the positive electrode and associated DC resistance growth is responsible for rollover failure in these cells. Ultra-high precision coulometry (UHPC) shows that cells that were charged to higher voltages, which increase the rate of electrolyte oxidation, or show higher rates of electrolyte oxidation at the same cutoff potential due to changes in electrolyte formulation, normally are more prone to eventual rollover failure. In order to avoid rollover and extend the cycling life of Li-ion cells, it is important to choose optimal cell chemistries, some of which are enumerated in this report.

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Figure 1. Long-term cycling of coated NMC532/AG (type I) pouch cells containing 2% FEC or 2% FEC + 1% DTD with 0%, 20% or 40% MA as co-solvent with EC:EMC at 20°C. (a) Normalized capacity versus cycle number; (b) ΔV versus cycle number. Cells were cycled between 3.0 and 4.2 V with a constant current corresponding to C/3 and the voltage was held at TOC until the current dropped to C/20 (denoted as CCCV).
impedance spectra for negative vs. negative cells (see the insets for better view), and their small $R_{ct}$ values indicate a negligible contribution from the negative electrode side to the full cell impedance. Figure 2 shows that the cell which displayed capacity rollover (2% FEC, Figure 1b) and large positive electrode charge transfer resistance as cells near rollover. We believe this may be the cause of rollover failure as is outlined in this report.

Due to the complexity of rollover failure, many factors, not only cell chemistry but cell design, may potentially impact the occurrence of rollover. In this work, rollover failure of Li[Ni$_{0.5}$Mn$_{0.3}$Co$_{0.2}$]O$_2$/graphite pouch cells with different electrolytes, electrolyte additives, electrode loadings, salt concentrations, upper cutoff potential and testing protocols was probed. Additional variables included cells with and without a positive electrode material coating and cells using artificial or natural graphite negative electrodes. Due to the possible long cycling period before rollover failure, cells were charged and discharged with a current corresponding to 1C. Rate maps at discharge currents of C/20, C/2, 1C, 2C and 3C were also collected after every 100 1C/1C cycles.

The pouch cells were disassembled at 3.8 V.

**Experimental**

**Preparation and formation of pouch cells.**—Chemicals were used as received: LiPF$_6$ (purity $> 99.9\%$, water content 14 ppm, BASF), ethylene carbonate (EC); ethyl methyl carbonate (EMC): dimethyl carbonate (DMC) (25:5:70 vol.%, water content 19.7 ppm, BASF) and methyl acetate (MA, purity $> 99\%$, water content 5.2 ppm, BASF) were used in formulating electrolytes. Vinylene carbonate (VC, purity $> 99.8\%$, BASF), fluoroethylene carbonate (FEC, purity $> 99.9\%$, BASF), 1,3,2-dioxathiolane-2,2-dioxide (DTD, purity $> 99.8\%$, BASF), 1,3,2-dioxathiolane-2,2-dioxide (DTD, purity $> 99.8\%$, BASF) and methyl acetate (MA, purity $> 99\%$, BASF) were used in formulating electrolytes. Vinylene sulfite (ES, purity $> 99\%$, Sigma Aldrich) and LiPO$_2$F$_2$ (LFO, Purity $> 99.8\%$, Shenzhen Capchem, China) were used as electrolyte additives. We note that LiPO$_2$F$_2$ is abbreviated as LFO in this report.

Four types of dry and sealed Li[Ni$_{0.5}$Mn$_{0.3}$Co$_{0.2}$]O$_2$(NMC532)/graphite pouch cells were obtained from Li-FUN Technology (Xinxia Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, China, 412000). These were coated NMC532/artificial graphite (AG) (type I, 230 mAh at 4.3 V), uncoated NMC532/AG (type II, 230 mAh at 4.3 V), coated NMC532/natural graphite (NG) (type III, 230 mAh at 4.3 V) and coated NMC532/AG (type IV, 210 mAh at 4.3 V, with a lower loading of both positive and negative electrode active materials). The NMC532 used in these cells was single crystal NMC532 as described in reference 8 both with a Ti-based coating and without a coating. The performance of the coated and uncoated materials has been detailed in Ref. 9. The artificial graphite used was Kajin AML-400 from Kajin, China. The natural graphite used was grade BTR-918 from BTR New Materials Technology, China. The relative performance and physical properties of these graphite materials has been reported in the recent paper by Glazier et al. The single side active material electrode loadings were 21.1 mg/cm$^2$ for the positive electrode and 12.4 mg/cm$^2$ for the graphite negative electrode for cell types I, II and III. The single side active material electrode loadings were 14.4 mg/cm$^2$ for the positive electrode and 10.2 mg/cm$^2$ for the graphite negative electrode for cell type IV. The capacities of the types I, II, III and IV cells were all approximately the same since the electrode lengths incorporated into the type IV cells were longer. Thus all cell types required the approximately the same amount of electrolyte. The positive and negative electrodes consisted of 94 wt% and 95.4 wt% active materials, respectively. The positive electrode was compressed to 3.5 g/cm$^3$ and negative electrode was compressed to 1.55 g/cm$^3$. All types of cells were balanced for 4.4 V and were received without electrolyte. Prior to filling with the designed electrolyte, pouch cells were cut open and dried at 100°C under vacuum for 14 h to remove residual moisture. Afterwards, pouch cells were filled with 0.85 mL electrolyte in an Ar-filled glove box and sealed with a pouch sealer (MSK-115A Vacuum Sealing Machine) under vacuum at a pressure of $\sim$90 kPa (relative to the atmosphere) and sealed in a filled glove box and sealed with a pouch sealer (MSK-115A Vacuum Sealing Machine) under vacuum at a pressure of $\sim$90 kPa (relative to the atmosphere) and sealed in a filled glove box.

**Figure 2.** Nyquist plots (10°C) of symmetric coin cells prepared from disassembled coated NMC532/AG (type I) pouch cells after long-term cycling as shown in Figure 1. (a1-3) cell with 2% FEC; (b1-3) cell with 2% FEC and 20%MA; (c1-3) cell with 2% FEC and 40%MA; (d1-3) cell with 2% FEC + 1% DTD and 20%MA. Top panels: positive/negative cells; middle panels: positive/positive symmetric cells; bottom panels: negative/negative symmetric cells. The pouch cells were disassembled at 3.8 V.
atmospheric pressure). The electrolytes contained 1.2M or 1.5M LiPF₆ in EC:EMC:DMC (25:5:70 vol. %) or 80 wt% EC:EMC:DMC + 20 wt% MA. Solutions were prepared with the electrolyte additive blends: 2% VC + 1% DTD, 1% VC + 1% DTD, 2% FEC + 1% DTD, 2% VC + 1% DTD + 1% ES, 2% FEC + 1% DTD + 1% ES, 1% LFO, 1% LFO + 2% FEC or 1% LFO + 1% ES (all in wt%). Most cell electrolytes contained 1.2M LiPF₆ but several contained 1.5M LiPF₆ as will be indicated. DTD and LFO have been reported to be promising electrolyte additives in NMC532/AG cells recently.⁶⁻¹⁴ ES was also found to be an effective additive to help passivate graphite electrodes with SEI layers having reduced impedance in Li[Ni₀·₄₂Mn₀·₄₂Co₀·₁₆]O₂/graphite pouch cells.¹⁵ Table I summarizes the information of the four cell types tested under various testing protocols.

After filling, cells were held at 1.5 V for 24 h to promote wetting and prevent dissolution of the negative electrode copper current collector. Subsequently cells were moved to a 40°C box connected to a Maccor 4000 series charger. Cells were charged to 4.1 V, 4.2 V or 4.3 V at currents corresponding to C/20, held at top of charge (i.e. 4.1 V, 4.2 V or 4.3 V, respectively) for 1 h, and then discharged to 3.8 V at C/20. The various upper cutoff potentials were chosen to match the intended upper cutoff potential in long-term testing. In order to remove the gas produced during charging and discharging processes, the pouch cells were cut open and resealed under vacuum in an Ar-filled glove box. Electrochemical impedance spectroscopy (EIS) measurements were then made.

**Electrochemical impedance spectroscopy (EIS).**—Electrochemical impedance spectra of the pouch cells were collected after formation and after cycling using a BioLogic VMP3 equipped with 3 EIS boards. All the measurements were performed at 10.0 ± 0.1°C from 100 kHz to 10 mHz (10 mV sinusoidal amplitude input). A temperature of 10°C was selected to amplify the differences between cells with different ester and additive contents. The data for both pouch cells and symmetric coin cells have been normalized based on their corresponding positive electrode areas, so that area-specific impedance is reported.

**Gas volume measurement.**—The gas production in pouch cells during formation and cycling was measured using Archimedes’ principle. Each cell was suspended underneath a Shimadzu analytical balance (AUW200D) and weighed while submerged in nano-purified deionized (DI) water (18.2 MΩ·cm). The produced gas (Δv) in each cell is proportional to the change in apparent cell weight (Δw) that was caused by the buoyant force, as Equation 1:

\[
\Delta v = -\Delta w / \rho
\]

[1]

where ρ is the density of DI water.

**Long-term cycling and the ultra high precision coulometry (UHPC) cycling.**—Long-term cycling was performed on a Neware testing system (Shenzhen, China) at ambient temperature (20 ± 1°C) with upper cutoff voltages of 4.1 V, 4.2 V or 4.3 V, respectively. The cells were charged and discharged with a current corresponding to 1C between 3.0 and 4.1 V, 4.2 V or 4.3 V and the voltage was held at the top of charge (TOC) until the current dropped below C/20. After every 100 cycles at 1C/1C, each cell was charged and discharged at C/20 for 1.5 cycles. Subsequently, cells were cycled for one cycle each with sequentially increasing discharge rates of C/2, 1C, 2C and 3C, respectively, and the charging rate was set at 1C. Cells cycling with rest followed a similar protocol as discussed above with the addition of resting at open circuit for 30 minutes at TOC and bottom of discharge (BOD), respectively, during each 1C/1C cycle.

Ultra-high precision coulometry (UHPC) studies of the coated NMC532/AG pouch cells (type I) were performed at 40.0 ± 0.1°C using the UHPC charger at Dalhousie University. A detailed description on the method can be found in reference.¹⁵ Cells were charged and discharged with a current corresponding to C/20 between 3.0 and 4.3 V.

**Post-cycling disassembly of pouch cells.**—Certain pouch cells were disassembled in an Ar-filled glove box to extract both positive and negative electrodes after a sufficient number of cycles. After a visual examination for Li plating on the graphite negative electrode (some of them were imaged), both positive and negative electrodes were punched into standard electrodes (1.25 cm diameter) for positive vs. negative full coin cells, positive vs. positive symmetric coin cells and negative vs. negative symmetric coin cells. The preparation of symmetric cells followed the procedure as discussed by Petibon et al. EIS measurements were performed at 10.0 ± 0.1°C from 100 kHz to 10 mHz (10 mV sinusoidal amplitude input).

**Results and Discussion**

Figure 3 summarizes Rₓ of the three types of NMC532/graphite pouch cells containing different additive blends with upper cutoff voltages at 4.1 V, 4.2 V and 4.3 V after formation. These cells have the normal electrode loadings. The top, middle and bottom panels show results for type I, II and III cells, respectively. Most of the cells show smaller Rₓ values after formation to higher upper cutoff voltages. A similar trend was also observed in Li[Ni₀·₄₂Mn₀·₄₂Co₀·₁₆]O₂/NMC442/graphite pouch cells.¹⁸ This may be due to a more complete passivation of the graphite electrode during formation. For coated NMC532/AG cells containing 1%LFO, Rₓ does not show a similar trend. Liu et al. showed that LFO dramatically decreased the negative electrode charge transfer impedance after formation,¹⁹ which is presumably the reason why the cells with LFO

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**Table I.** Matrix for all uncoated or coated NMC532/graphite pouch cells with different positive electrode loadings, additives, graphite types, LiPF₆ concentrations and upper cutoff voltages, that were measured for 1C/1C cycling at 20°C (“×” marks the tests performed).

|          | Rest (TOC& BOD) | Coated Type I (Normal loading) | Coated Type IV (low loading) | Uncoated Type II (Normal loading) | Additives | LiPF₆ | 3V-4.1V | 3V-4.2V | 3V-4.3V |
|----------|----------------|-------------------------------|---------------------------|---------------------------------|-----------|------|---------|---------|---------|
| **NMC 532/AG** |                |                               |                           |                                 | LiPF₆     |      |         |         |         |
| No       | ×              | ×                             | ×                         | ×                               | 2%VC+1%DTC | ×    | ×       | ×       | ×       |
| Yes      | ×              | ×                             | ×                         | ×                               | 1%LFO     | ×    | ×       | ×       | ×       |
| No       | ×              | ×                             | ×                         | ×                               | 1%LFO     | ×    | ×       | ×       | ×       |
| No       | ×              | ×                             | ×                         | ×                               | 1%LFO     | ×    | ×       | ×       | ×       |
| No       | ×              | ×                             | ×                         | ×                               | 1%LFO     | ×    | ×       | ×       | ×       |
| No       | ×              | ×                             | ×                         | ×                               | 1%LFO     | ×    | ×       | ×       | ×       |
| No       | ×              | ×                             | ×                         | ×                               | 1%LFO     | ×    | ×       | ×       | ×       |
| No       | ×              | ×                             | ×                         | ×                               | 1%LFO     | ×    | ×       | ×       | ×       |
| No       | ×              | ×                             | ×                         | ×                               | 1%LFO     | ×    | ×       | ×       | ×       |
| NMC 532/NG (Type III) | No       | ×                             | ×                         | ×                               | 1%LFO     | ×    | ×       | ×       | ×       |

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**Note:** Table I contains the matrix for all uncoated or coated NMC532/graphite pouch cells with different positive electrode loadings, additives, graphite types, LiPF₆ concentrations and upper cutoff voltages, that were measured for 1C/1C cycling at 20°C. **“×” marks the tests performed.**
Figure 3. Summary of $R_{ct}$ values after formation for NMC532/graphite pouch cells containing different additive blends with different upper cutoff voltages. (a) Coated NMC532/AG cells (type I), (b) uncoated NMC532/AG cells (type II) and (c) coated NMC532/NG cells (type III). “2VC+1DTD, 4.1V” represents the cell containing 2% VC + 1% DTD with an upper cutoff voltage of 4.1 V.

have the lowest $R_{ct}$ in Figure 3 and could be the reason they do not show the same trend with increasing potential of formation.

Figure 3a shows that for coated NMC532/AG cells with 2% VC + 1% DTD, higher LiPF$_6$ concentration (1.5M) led to slightly larger $R_{ct}$. Comparing 2% VC + 1% DTD vs. 1% LFO in both coated and uncoated NMC532/AG cells, 2% VC + 1% DTD induced larger $R_{ct}$ than 1% LFO. Figures 3a and 3b show that the coating on the positive electrode played a distinct role in lowering the impedance, irrespective of additive compositions. Figures 3a and 3c show that coated NMC532/NG cells have lower $R_{ct}$ than coated NMC532/AG cells. Adding 1% ES in both coated and uncoated NMC532/AG cells led to higher $R_{ct}$ for cells with 2% VC + 1% DTD, 2% FEC + 1% DTD and 1% LFO, respectively. As an aside, we mention that this is opposite to the reduced $R_{ct}$ values of uncoated NMC442/graphite pouch cells with 2% VC only. This highlights the complexities of Li-ion cell research.

Figure 4 shows the capacity, normalized capacity and $\Delta V$ vs. cycle number of uncoated (Type II) and coated (Type I) NMC532/AG cells containing 2% VC + 1% DTD, 2% FEC + 1% DTD and 1% LFO. $\Delta V$ is the difference between the average 1C charge and discharge voltages measured during each cycle. The cycling data were collected at 20°C (1C:1C CCCV) with upper cutoff voltages of 4.1 V (left column), 4.2 V (middle column) and 4.3 V (right column), respectively. Figure 4 shows that uncoated cells show worse capacity retention and more rapid impedance growth compared to coated cells. This should not be surprising based on the large body of literature promoting the use of coated positive electrode materials. Uncoated cells with 1% LFO show better cycling performance with slower $\Delta V$ growth than the uncoated cells with the other electrolytes.

Figure 4 also shows that the cell longevity decreases as the upper cutoff potential increases for all cell types and all electrolytes. This is evidenced by more rapid capacity loss and more rapid $\Delta V$ growth as the upper cutoff potential increases. At 4.3 V, the coated cell containing 2% FEC + 1% DTD shows rollover failure after about 2000 cycles, with an obvious increase in $\Delta V$ observed after 1000 cycles. Similarly, the uncoated cell with 1% LFO shows rollover failure beginning around 700 cycles with an obvious increase in $\Delta V$ beginning around 4000 cycles. The coated cell with 2% VC + 1% DTD testing to 4.3 V shows rollover failure after 2500 cycles with an obvious increase in $\Delta V$ while the coated cell with 1% LFO testing to 4.3 V still cycles normally after about 4000 cycles. Figure 4 also shows that all the cells with coated electrodes tested to 4.1 and 4.2 V show very little sign of failure at all. Presumably, they will last for many thousands of cycles. It is important to recognize that testing to higher potential (i.e. 4.3 V) allows for the differentiation between the best electrolyte systems. During the long-term 1C/1C cycling, a discharge rate map of C/20, C/2, 1C, 2C and 3C (the charging rate was fixed at 1C) was performed every 100 cycles. Figure 5 shows the corresponding rate maps for the cells shown in Figure 4. The five capacity curves from high to low on each panel correspond to C/20, C/2, 1C, 2C and 3C, respectively. Figure 5 shows that the 3C discharge capacities of uncoated NMC532 cells tested to 4.3 V dropped sharply and exhibited rollover before 1000 cycles. The discharge capacities of coated NMC532 cells with 2% VC + 1% DTD, 2% FEC + 1% DTD and 1%LFO did not...
Figure 4. Long-term cycling of coated NMC532/AG (type I) and uncoated NMC532/AG (type II) pouch cells containing 2% VC + 1% DTD, 2% FEC + 1% DTD or 1% LFO at 20°C. (a1-a3) Discharge capacity versus cycle number; (b1-b3) normalized capacity versus cycle number; (c1-c3) ΔV versus cycle number. Left panels: cycling between 3.0 and 4.1 V; middle panels: cycling between 3.0 and 4.2 V; right panels: cycling between 3.0 and 4.3 V; Cells were cycled with a constant current corresponding to 1C and CCCV to C/20.

fade dramatically at 4.1 V and 4.2 V. The cell with 2% FEC + 1% DTD showed more capacity fade than the cell with 2% VC + 1% DTD at 3C and 4.3 V while the cell with 1% LFO still showed stable 3C capacity after about 4000 cycles. This is consistent with their 1C/1C cycling behaviors shown in Figure 4. The coated cell with 2% FEC + 1% DTD started to show “concave down” capacity fade, characteristic of rollover around cycle 1000 at 3C, while concave down fade did not begin till near cycle 2000 at 1C. Thus, the 3C capacity can be used as a predictor of rollover failure at 1C. This can be further evidenced by the more obvious capacity rollover of the cell with 2% VC + 1% DTD around cycle 2500 at 3C compared to the 1C data.

Figure 5 shows some interesting behavior that may interest readers. For the coated cells in Figure 5, the 1C discharge capacity for cells at 4.1 and 4.2 V is virtually flat, exhibiting almost no capacity loss for over 3000 cycles. However, capacity fade is observed in the C/20 cycles. How can this be? This occurs because the single crystal NMC532 used in these cells is not capable of extremely high rate discharge due to the relatively large primary particle size of the active material particles which leads to long Li-ion diffusion paths.9 The impact of this is demonstrated in Figure 6. Figure 6a shows a schematic of the positive electrode voltage (vs. Li/Li⁺), the negative electrode voltage (vs Li/Li⁺) and the full cell voltage all plotted versus capacity during an early C/20 cycle. The cell is fully discharged when the negative electrode is empty of lithium. The cell is negative electrode limited or anode limited in this situation. Figure 6b shows the same quantities, again for a C/20 cycle, plotted perhaps 2000 cycles later where Li inventory loss due to negative SEI growth has occurred. Notice that the negative electrode voltage capacity curve in Figure 6b has shifted to the right relative to the positive electrode curve compared to the situation in Figure 6a. The full cell has lost capacity because the negative electrode empties of lithium at a larger capacity compared to Figure 6a. Figure 6c shows the situation at the beginning of life for a 1C cycle of the same cell. In this case, the full cell is fully discharged when the surface of the positive electrode particles have been filled with lithium even though the cores of the particles are not yet filled (due to relatively slow solid state diffusion) and even though there is more lithium available in the negative electrode. The cell is now “cathode limited”. Figure 6d shows the situation perhaps 2000 cycles later, showing the same amount of Li inventory loss as Figure 6b. However, the 1C rate capacity of the cell is unaffected because the negative electrode still contains lithium atoms when the surface of the positive electrode particles has been filled with lithium. The cell is still cathode limited at the 1C rate even after 2000 cycles or so. Eventually, when enough Li inventory loss has occurred, the cell will become anode limited even at a 1C discharge rate and capacity fade will occur. It is worth pointing out, however, that capacity loss for cathode limited cells under load can still occur as the cell internal impedance increases.

Figure 7 shows the capacity, normalized capacity and ΔV vs. cycle number of uncoated and coated NMC532/AG cells tested (1C:1C CCCV, 20°C, with rate maps every 100 cycles) between 3.0 and 4.1 V or 4.3 V, with 2% VC + 1% DTD + 1% ES, 2% FEC + 1% DTD + 1% ES and 1% LFO + 1% ES in the top, middle and bottom panels, respectively. Figure 7 shows that all uncoated cells with 1% ES showed worse cycling performance than those without ES in Figure 4. A similar negative impact from 1% ES was observed for coated cells with 2% FEC + 1% DTD and 1% LFO. However, adding 1% ES did not obviously affect coated cells containing 2% VC + 1% DTD (Detailed graphs comparing all results for cells with 2% VC + 1% DTD and 2% VC + 1% DTD + 1% ES on the same graph show virtually no difference - these graphs are not shown here). Interestingly,
Figure 5. Capacity versus cycle number of the coated and uncoated NMC532/AG (type I and II) pouch cells in Figure 4 with a charge rate at C/2 and discharge rates at C/20, C/2, 1C, 2C and 3C, which were performed every 100 1C/1C cycles as shown in Figure 4. (a1-a3): cells with 2% VC + 1% DTD; (b1-b3): cells with 2% FEC + 1% DTD; (c1-c3): cells with 1% LFO. Left panels: cycling between 3.0 and 4.1 V; middle panels: cycling between 3.0 and 4.2 V; right panels: cycling between 3.0 and 4.3 V.

ΔV of coated cells containing 2% FEC + 1% DTD + 1% ES and 1% LFO + 1% ES remained relatively stable although they did display capacity loss, indicating that the rapid capacity fade does not derive from the impedance growth in all cases. The cell with 2% FEC + 1% DTD + 1% ES did produce a significant amount of gas which may have contributed to stack pressure loss and hence failure even in the testing fixtures used here. Coated cells with 1% LFO + 1% ES show rapid linear capacity fade even during the early cycles independent of the upper cutoff voltage (4.1 V to 4.3 V). In these cells ΔV remains relatively stable so we believe the major cause of capacity loss is Li inventory loss, not impedance growth.

Figure 6. Schematic diagrams illustrating the impact of negative electrode shift due to loss of Li inventory (SEI growth) on cells operating at low rate (left column) and at high rate (right column) where the positive electrode material has relatively slow diffusion kinetics. The cells are “anode limited” at low rate and lose capacity during low rate cycles. The cells are “cathode limited” at high rate and do not lose capacity when evaluated at high rate, even though they lose capacity when evaluated at low rate.

ΔV from the impedance growth in all cases. The cell with 2% FEC + 1% DTD + 1% ES did produce a significant amount of gas which may have contributed to stack pressure loss and hence failure even in the testing fixtures used here. Coated cells with 1% LFO + 1% ES show rapid linear capacity fade even during the early cycles independent of the upper cutoff voltage (4.1 V to 4.3 V). In these cells ΔV remains relatively stable so we believe the major cause of capacity loss is Li inventory loss, not impedance growth.

Figure 8 shows the capacity, normalized capacity and ΔV vs. cycle number for coated NMC532/AG (type I) and coated NMC532/NG (type III) cells containing 2% VC + 1% DTD in the top, middle and bottom panels, respectively. The cycling data were collected with upper cutoff voltages of 4.1 V and 4.3 V. Figure 8 shows that coated NMC532/NG cells containing VC + DTD show much worse cycling performance and much larger ΔV growth than coated NMC532/AG cells. Glazier et al. found that NMC532/NG pouch cells performed worse than NMC532/AG cells when they were charged and discharged at C/3.10 Natural graphite shows a lower probability of random stacking (P_r, also known as turbostratic misalignment) than artificial graphite (0.06 vs. 0.13) and NMC532/NG cells show more parasitic reactions with electrolyte than NMC532/AG due to larger irreversible expansion of NG compared to AG.19

Figures 8a, 8b and 8c show that the effects of resting at TOC and BOD, LiPF_6 concentration (1.2 M vs. 1.5 M) and additive amount (2% VC + 1% DTD vs. 1% VC + 1% DTD) on NMC532/AG cells were almost negligible at 4.1 V. Figures 8d, 8e and 8f show that no rest (i.e. shorter time in the highly lithiated and delithiated states), increasing LiPF_6 concentration from 1.2 M to 1.5 M or including more advanced additives (i.e. 2% VC + 1% DTD) can improve the cycling performance of NMC532/AG cells at 4.3 V, in part, due to better control of impedance growth (ΔV).
Figure 7. Long-term cycling of coated NMC532/AG (type I) and uncoated NMC532/AG (type II) pouch cells containing 2% VC + 1% DTD + 1% ES, 2% FEC + 1% DTD + 1% ES or 1% LFO + 1% ES at 20°C. (a, d) Discharge capacity versus cycle number; (b, e) Normalized capacity versus cycle number; (c, f) ΔV versus cycle number. Left panels: cycling between 3.0 and 4.1 V; right panels: cycling between 3.0 and 4.3 V; Cells were cycled with a constant current corresponding to 1C and CCCV to C/20.

Figure 8. Long-term cycling of coated NMC532/AG (type I) and coated NMC532/NG (type III) pouch cells containing 2% VC + 1% DTD or 1% VC + 1% DTD with or without rest at TOC and BOD and with 1.2 M or 1.5 M LiPF<sub>6</sub> at 20°C. (a, d) Discharge capacity versus cycle number; (b, e) Normalized capacity versus cycle number; (c, f) ΔV versus cycle number. Left panels: cycling between 3.0 and 4.1 V; right panels: cycling between 3.0 and 4.3 V; Cells were cycled with a constant current corresponding to 1C and CCCV to C/20.

Figure 9 shows the capacity, normalized capacity, and ΔV vs. cycle number of coated NMC532/AG cells with different NMC loadings (21.1 mg/cm<sup>2</sup> (type I) vs. 14.4 mg/cm<sup>2</sup> (type IV) in the top, middle and bottom panels, respectively. Cells contained 2% VC + 1% DTD, 2% FEC + 1% DTD, 1% LFO or 1% LFO + 2% FEC as additives. At 4.1 V and 4.2 V, all cells show similar cycling performance without apparent capacity fade or increases in ΔV. At 4.3 V, the normal loading cells with 2% VC + 1% DTD or 2% FEC + 1% DTD show obviously higher impedance growth rates than the low loading cells during the early cycles (<1000). No obvious ΔV difference, before 3000 cycles, was observed between the normal loading and low loading cells with 1% LFO or 1% LFO + 2% FEC, indicating that cells with 1% LFO or 1% LFO + 2% FEC outperformed cells with 2% VC + 1% DTD or 2% FEC + 1% DTD.

Figure 10 shows the corresponding rate maps for the cells in Figure 9. The five capacity curves from high to low in each panel correspond to C/20, C/2, 1C, 2C and 3C, respectively. All the cells show that the 3C rate capability is well-maintained at 4.1 V and 4.3 V. At 4.3 V, certain cells were stopped cycling after sufficient cycles at 20°C, certain cells were stopped cycling and disassembled in an Ar-filled glove box. The separators in these cells were all in good condition and had their original color. The cells had visible electrolyte remaining in the extremities of the pouch, in the separator and in the electrodes. The cells were not “dry”. Figure 12 shows the optical images of exposed negative electrodes of selected cells that were charged to 4.2 V. Figures 12a to 12c show the negative electrodes of coated NMC532/AG cells (type I) that were cycled at least 1000 times between 3–4.3 V with or without rest. The cell containing 2% VC + 1% DTD and tested with rest periods at top of charge and bottom of discharge shows small amounts plated lithium in certain spots on the negative electrode (see Figure 12a) while the cell containing 1% VC + 1% DTD tested without rest periods did not show any Li plating after 1500 cycles (see Figure 12b). Figure 12c shows a few lithium spots on the cell with 2% VC + 1% DTD + 1% ES tested without rest periods after 1500 cycles. None of the cells in Figures 12a, 12b or 12c displayed rollover failure (see Figures 7 and 8) and all retained more than 98% of their original capacity at 1C. We believe the small Li spots may be indicative of small regions where wetting was initially poor or where a gas bubble became trapped in the bottom panels, respectively. Adding 20% MA as a co-solvent to EC:EMC:DMC (25:5:70 vol. %) significantly enhances the rate capability of NMC532/AG cells but shortens their lifetime, due to the increased rates of parasitic reactions at the positive electrode side. Figure 11 shows that 20% MA worsened the lifetime of the NMC532/AG cells with 1% LFO at 1C/1C with an obvious rollover behavior after 500 cycles and dramatic impedance growth rate in Figure 11C. Therefore, the more conductive electrolyte containing 20% MA did not benefit the 1C/1C cycling of cells but, instead, accelerated the rollover failure of NMC532/AG cells. After sufficient cycles at 20°C, certain cells were stopped cycling and disassembled in an Ar-filled glove box. The separators in these cells were all in good condition and had their original color. The cells had visible electrolyte remaining in the extremities of the pouch, in the separator and in the electrodes. The cells were not “dry”. Figure 12 shows the optical images of exposed negative electrodes of selected cells that were charged to 4.2 V. Figures 12a to 12c show the negative electrodes of coated NMC532/AG cells (type I) that were cycled at least 1000 times between 3–4.3 V with or without rest. The cell containing 2% VC + 1% DTD and tested with rest periods at top of charge and bottom of discharge shows small amounts plated lithium in certain spots on the negative electrode (see Figure 12a) while the cell containing 1% VC + 1% DTD tested without rest periods did not show any Li plating after 1500 cycles (see Figure 12b). Figure 12c shows a few lithium spots on the cell with 2% VC + 1% DTD + 1% ES tested without rest periods after 1500 cycles. None of the cells in Figures 12a, 12b or 12c displayed rollover failure (see Figures 7 and 8) and all retained more than 98% of their original capacity at 1C. We believe the small Li spots may be indicative of small regions where wetting was initially poor or where a gas bubble became trapped in the bottom panels, respectively.
jelly roll. Figures 12d to 12h show the negative electrodes of uncoated NMC532/AG cells (type II) containing 2% VC + 1% DTD, 2% FEC + 1% DTD, 1% LFO or 1% LFO + 2% FEC at 20°C. (a1-a3) Discharge capacity versus cycle number; (b1-b3) Normalized capacity versus cycle number; (c1-c3) ΔV versus cycle number. Left panels: cycling between 3.0 and 4.1 V; middle panels: cycling between 3.0 and 4.2 V; right panels: cycling between 3.0 and 4.3 V. Cells were cycled with a constant current corresponding to 1C and CCCV to C/20.

Figure 9. Long-term cycling of coated NMC532/AG pouch cells with normal NMC loading (type I) and low NMC loading (type IV) containing 2% VC + 1% DTD, 2% FEC + 1% DTD, 1% LFO, or 1% LFO + 2% FEC at 20°C. Figures 13a and 13b show a coated NMC532/AG cell (type I) containing 2% VC + 1% DTD and the uncoated NMC532/AG cell containing 2% VC + 1% DTD + 1% ES, which showed serious capacity rollover in Figure 4 and Figure 7, respectively. The EIS results reveal that growing impedance on the positive side may be the cause for, or is at least a symptom of, capacity rollover.

A simple model was developed in order to explore how impedance growth can lead to the type of rollover failure observed in the majority of these experiments. As observed in general, Figure 15 shows the evolution of voltage versus discharge capacity curves with cycle number for coated NMC532/AG or NG pouch cells at 20°C. Figures 15a and 15b show a coated NMC532/AG cell (type I) containing 2% FEC + 1% DTD at 1C/3C and 1C/1C cycling, respectively. Figures 15c and 15d show an uncoated NMC532/AG cell (type II) containing 2% VC + 1% DTD at 1C/3C and 1C/1C cycling, respectively. Figure 15 shows that all the voltage-capacity curves obviously shifted downward during 2300 cycles for the cell with 2% FEC + 1% DTD (Figures 15a and 15b) or 500 cycles for the cell with 2% VC + 1% DTD (Figures 15c and 15d) and should shift further with increasing cycle number. As a result, the cell discharge capacity decreased gradually at constant upper and lower cutoff voltages. This behavior is believed to be caused by the impedance increase of cells.

Figure 16a shows a simplistic model for a Li-ion cell with an ideal cell having a voltage-capacity relation given by \( V_s(Q) \) and a DC internal resistance given by \( r \). The terminal voltage, \( V(Q) \), of such a cell...
Figure 10. Capacity versus cycle number of coated NMC532/AG pouch cells with normal NMC loading (type I) and low NMC loading (type IV) pouch cells in Figure 9 with a charge rate at C/2 and discharge rates at C/20, C/2, 1C, 2C and 3C, which were performed every 100 C/1C cycles as shown in Figure 9. (a1-a3): cells with 2% VC + 1% DTD; (b1-b3): cells with 2% FEC + 1% DTD; (c1-c3): cells with 1% LFO; (d1-d3) cells with 1% LFO + 2% FEC. Left panels: cycling between 3.0 and 4.1 V; middle panels: cycling between 3.0 and 4.2 V; right panels: cycling between 3.0 and 4.3 V.

Figure 11. Long term cycling of coated NMC532/AG pouch cells (type I) with 1% LFO and 1% LFO + 20% MA at 20°C. (a) Discharge capacity versus cycle number; (b) Normalized capacity versus cycle number; (c) ΔV versus cycle number. Cells were cycled between 3.0 and 4.3 V with a constant current corresponding to 1C and CCCV to C/20.

under load will be:

\[ V(Q) = V_o(Q) \pm I r, \]  

[2] where I is the magnitude of the current and the “+” sign is used during charging and the “−” sign is used during discharging. Figure 16b shows a set of “mock” voltage-capacity curves during discharge for a NMC532/graphite Li-ion cell under a constant discharge current but with sequentially increasing internal resistance. If a constant lower cutoff potential of 3.0 V is used during cycling, one can easily observe that the lower cutoff is reached at smaller capacity as the internal resistance grows. Figure 16c shows capacity versus cycle number curves for the model described above where the internal resistance was chosen to increase linearly with cycle number, much like is observed for \( \Delta V \) (notice that \( \Delta V \approx 2Ir \) in the model above) versus cycle number in Figures 4c, 7f, 8f, 9c. The capacity versus cycle number curves in Figure 16c have very similar shape to those observed experimentally with concave down behavior showing that rollover failure as observed here can be simply explained by impedance growth. The parameters used for Figure 16c were selected to approximately match the data for cells with 2% FEC + 1% DTD as shown in Figure 5b3. The 3C data and model show the earliest rollover, followed by 2C and finally by 1C. Obviously such a model is overly simplistic, but some of this author group have learned, much like Richard Feynman, that simple models to guide one’s thinking are often best.

Figure 17 shows a summary of UHPC results for coated NMC532/AG pouch cells (type I) containing 2% VC + 1% DTD, 1% VC + 1% DTD, 2% VC + 1% DTD + 1% ES, 2% FEC + 1% DTD, 1% LFO, 1% LFO + 2% FEC and 1% LFO + 20% MA at upper cutoff voltages of 4.1 V, 4.2 V and 4.3 V, respectively. Figures 17a, 17b and 17c show the coulombic inefficiency per hour (CIE, i.e. 1 - coulombic efficiency (CE)), the fractional capacity fade per hour and the fractional charge end point capacity slippage per hour, respect-
Figure 12. Optical images of negative electrodes of coated NMC523/AG (type I) and uncoated NMC523/AG (type II) pouch cells after sufficient cycles at 20°C. All cells were disassembled at 4.2 V. (a) coated NMC523/AG_2% VC + 1% DTD → 4.3 V, rest → 1000 cycles (represents the coated NMC523/AG cell containing 2% VC + 1% DTD which was cycled for 1000 times between 3.0 and 4.3 V with resting at TOC and BOD); (b) coated NMC523/AG_1% VC + 1% DTD → 4.3 V, 1500 cycles; (c) coated NMC523/AG_2% VC + 1% DTD + 1% ES → 4.3 V, 1500 cycles; (d) uncoated NMC523/AG_2% VC + 1% DTD → 4.1 V, 600 cycles; (e) uncoated NMC523/AG_2% VC + 1% DTD → 4.2 V, 600 cycles; (f) uncoated NMC523/AG_2% VC + 1% DTD → 4.3 V, 600 cycles; (g) uncoated NMC523/AG_2% VC + 1% DTD → 4.1 V, rest → 700 cycles; (h) uncoated NMC523/AG_2% VC + 1% DTD → 4.3 V, rest → 600 cycles.

Figure 13. Summary of $R_{ct}$ values before cycling (i.e., after formation) and after cycling for NMC523/graphite pouch cells containing different additive blends with different upper cutoff voltages. (a) coated NMC523/AG (type I), (b) uncoated NMC523/AG (type II) and (c) coated NMC523/NG (type III). “1VC + 1DTD → 4.2 V” represents the cell containing 1% VC + 1% DTD with an upper cutoff voltage of 4.2 V. (cells that have undergone rollover are highlighted in red or blue). The numbers in parenthesis correspond to the cycle numbers when EIS was measured.
Figure 14. Nyquist plots (10°C) of symmetric coin cells prepared from disassembled NMC532/graphite pouch cells after long-term cycling between 3.0 and 4.3 V at 1C charge and 1C discharge. (a1-a3) coated NMC532/NG cell (type III) with 2% VC + 1% DTD after 700 cycles; (b1-b3) coated NMC532/AG cell (type I) with 1% LFO and 20% MA after 1060 cycles; (c1-c3) coated NMC532/AG cell (type I) with 2% VC and 1% DTD after 3160 cycles; (d1-d3) uncoated NMC532/AG cell (type II) with 2% VC + 1% DTD + 1% ES after 570 cycles. Top panels: positive/negative symmetric cells; middle panels: positive/positive symmetric cells; bottom panels: the negative/negative symmetric cells. The pouch cells were disassembled at 3.8 V. Note the different scales between Figures a,b,c and Figure d.

Figure 15. Potential versus discharge capacity of NMC532/graphite cells after different cycle numbers at 20°C. (a) coated NMC532/AG cell (type I) containing 2% FEC + 1% DTD at 3C discharge; (b) coated NMC532/AG cell (type I) cell containing 2% FEC + 1% DTD at 1C discharge; (c) uncoated NMC532/AG cell (type II) containing 2% VC + 1% DTD at 3C discharge; (d) uncoated NMC532/AG cell (type II) containing 2% VC + 1% DTD at 1C discharge.
A model description of the relation between impedance growth and cell rollover failure. (a) a simplistic model for the serial connection of $V_0(1)$ and a DC internal resistance (given by $r$) in an ideal cell; (b) a set of “mock” voltage-capacity curves during discharge for a NMC532/graphite Li-ion cell; (c) capacity versus cycle numbers of a NMC532/graphite Li-ion cell with linearly increased internal resistance.

Figure 16. A model description of the relation between impedance growth and cell rollover failure. (a) a simplistic model for the serial connection of $V_0(Q)$ and a DC internal resistance (given by $r$) in an ideal cell; (b) a set of “mock” voltage-capacity curves during discharge for a NMC532/graphite Li-ion cell; (c) capacity versus cycle numbers of a NMC532/graphite Li-ion cell with linearly increased internal resistance.

tively. Figure 17a shows that cells with 1.2 M LiPF$_6$ have similar CIE (within error) to cells with 1.5 M LiPF$_6$ for 2% VC + 1% DTD. Cells containing 2% VC + 1% DTD show lower CIE than cells containing 2% FEC + 1% DTD and 1% LFO. Adding 20% MA significantly increased the CIE for cells with 1%LFO + 20% MA compared to those with 1% LFO. Figures 17b and 17c show that the higher the upper cutoff voltage for each specific additive composition, a higher charge end point slippage and a lower capacity fade were observed. High charge end point slippage means more oxidation reactions at the positive electrode. Figure 17 shows that all the cells that have undergone capacity rollover as highlighted in red were charged between 3 V and 4.3 V. Hence, the oxidation products on the positive side dramatically contributed to the rollover failure of cells. This also agreed with the significantly increased impedance at the positive side of the failed cells in Figure 14.

Figures 5 and 10 show that the loss of 3C rate capability is a signature of impending rollover failure during 1C:1C CCCV cycling. Positive electrode impedance increase appears to be the cause of the impedance increase. Therefore it makes sense to try to correlate a metric associated with the rate of electrolyte oxidation to the number of cycles until rollover. UHPC data collected and displayed in Figure 17 can be correlated with the cycling data displayed in Figures 5 and 10. Figure 18 shows a graph of the number of 1C cycles until the 3C rate map capacity drops below 90% of its initial value plotted versus the fractional charge end point capacity slippage per hour (Figure 17c) for cells that displayed rollover. All data in Figure 18 are for type I cells. Although there is limited data in Figure 18, there are two points that can be made. First: Cells containing VC + DTD or FEC + DTD (black points in Figure 18) show a reasonable correlation between loss of 3C capacity and increased charge end point capacity slippage. Second: The cells containing LFO (red points in Figure 18) retain 3C capacity much longer than the cells with VC + DTD or FEC + DTD even if their charge end point capacity slippage is larger, contrary to our expectation. One possible reason for this may be that the oxidation reaction products in the presence of LFO do not lead to internal impedance growth at same rates as the other additive systems. This is certainly borne out in the $ΔV$ vs. cycle number data for cells with 1% LFO and cells with 1% LFO + 2% FEC. Zhao et al. have found that 1.0 wt% LiPO$_2$F$_2$ formed a thin and more uniform SEI layer at the positive Li[$\text{Ni}_{0.5}\text{Mn}_{0.25}\text{Co}_{0.25}$]O$_2$ surface, which could improve the transport of Li ions through the positive electrode-electrolyte interface during long-term cycling of cells. It may also be that there are reversible shuttle-type reactions in cells containing LFO that lead to high charge end point capacity slippage and minimal cell damage.

**Conclusions**

Li[$\text{Ni}_{0.5}\text{Mn}_{0.25}\text{Co}_{0.25}$]O$_2$/graphite pouch cells were cycled at 20°C with both charge and discharge rates at 1C to study their propensity to rollover failure. Probing the discharge capacity at C/20, C/2, 1C, 2C and 3C after every 100 cycles at 1C is very useful for an advance indication of rollover failure. A simple model of DC resistance growth in cells was used to explain the qualitative features of the capacity versus cycle number curves for discharges at 1C, 2C and 3C. Rollover due to impedance growth occurs first at 3C, then at 2C and finally at 1C.

A series of measurements based on a variety of cell chemistries and cell designs show that cells are more prone to rollover failure if they are charged to higher potential. Based on the UHPC results, cells with higher charging potential show higher charge end point capacity slippage associated with higher rates of electrolyte oxidation at the positive electrode side.

For cells charged to the same upper cutoff voltage (i.e. 4.1 V, 4.2 V or 4.3 V), those showing higher rates of electrolyte oxidation at the positive electrode, due to poor additives like 2% VC + 1% DTD + 1% ES compared to 1% LFO, or uncoated positive electrodes compared to coated positive electrodes, are normally more prone to rollover failure. This was confirmed by the EIS spectra of symmetric cells that lead to high charge end point capacity slippage and minimal cell damage.

Lowering the electrode loadings or using artificial graphite instead of natural graphite delayed the occurrence of rollover in the experiments made here. Increasing LiPF$_6$ concentration, for example from 1.2 M to 1.5 M, was also beneficial to improve the cycling performance of cells with certain chemistries, but for reasons that are not fully understood. Further studies about the effects of variable LiPF$_6$ concentrations on rollover failure are still ongoing.

Finally, it has been demonstrated that single crystal NMC532/artificial graphite cells containing electrolytes with the additive combination of 2% FEC + 1% LFO can undergo at least 4000 1C CCCV cycles between 3.0 and 4.3 V (100% DOD) with minimal capacity loss. If the upper cutoff potential is reduced to 4.1 or 4.2 V, many more thousands of cycles are anticipated before failure based on the experiments reported here. In our opinion, such cells can find
Fractional charge endpoint slippage

Coulombic Inefficiency (CIE)

Fractional capacity fade

Figure 17. Summary of UHPC cycling data for coated NMC532/AG pouch cells (type I) containing different additive blends with different upper cutoff voltages. (a) Coulombic inefficiency (CIE); (b) Fractional capacity fade; (c) Fractional charge end point slippage. “2% VC+1% DTD_4.1V” represents the cell containing 2% VC + 1% DTD with an upper cutoff voltage of 4.1 V. (cells that have undergone rollover are highlighted in dotted red).

Figure 18. Number of 1C cycles between 3.0 and 4.3 V at 20°C until the 3C rate map capacity drops below 90% of its initial capacity plotted versus the fractional charge end point capacity slippage measured at 40°C using UHPC methods (3.0 V to 4.3 V at C/20). The UHPC data was extracted from Figure 17c, for the cells that exhibited rollover (the red highlighted bars in Figure 17c). The capacity retention data was extracted from Figures 5 and 10 as well as data not shown. Data for cells that contain LiPO2F2 (LFO) is shown in red.

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