Lithium-ion batteries are currently used in a wide range of applications: cell phones, power tools, vehicles and even grid energy storage.

While changes to the negative electrode, positive electrode and engineering components can improve the lifetime, safety and energy density of Li-ion cells, it has also been shown that modifying electrolyte composition is a cost-effective way to increase cycle and calendar lifetime of Li-ion cells. It has also been shown that modifying electrolyte composition is a cost-effective way to increase cycle and calendar lifetime of Li-ion cells. In addition, the positive and negative electrodes can undergo multiple analyses to determine their organic and inorganic components. In the experiments reported here, negative electrodes were analyzed via GC-MS and ICP-MS as discussed below. Electrolytes extracted from cells containing this original electrolyte were later analyzed via GC-MS and ICP-MS as discussed below. Electrolytes recovered from these cells were also analyzed via μ-XRF as discussed below.

**Experimental**

**Electrolyte.** The original electrolyte used in cells destined for cycling and electrolyte analysis were prepared with 1.1 m LiPF<sub>6</sub> salt (BASF, 99.94%, water content < 14 ppm) in 3:7 weight ratio (3:7 ethylene carbonate (EC): ethyl methyl carbonate (EMC) (BASF, USA, EC purity: 99.95%, EMC purity: 99.99%, water content < 10 ppm) solvent. Additives included 2% weight fluoroethylene carbonate (BASF, 99.94%, water content < 100 ppm) and 1% 1,3,2-dioxathiolane-2,2-dioxide (DTD) (Suzhou Yacoo Chemical Reagent Co., >98%). Electrolytes extracted from cells containing this original electrolyte were later analyzed via GC-MS and ICP-MS as discussed below. Electrolytes recovered from these cells were also analyzed via μ-XRF as discussed below.

**Cell specifications.** Sealed, dry (no electrolyte), machine-produced 402035-size (240 mAh) pouch cells were purchased from LiFun Technologies (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000). These positive electrodes in these cells used single crystal Li[Ni<sub>0.5</sub>Mn<sub>0.3</sub>Co<sub>0.2</sub>O<sub>2</sub> (NMC532) positive electrode material with 94% NMC532, 4% conducting diluents, and 2% polyvinylidene fluoride (PVDF) binder. The positive electrode loading was 21.3 mg/cm<sup>2</sup> and the density after compression was 3.5 g/cm<sup>3</sup>. The negative electrode consisted of 96% graphite, 2% carbon black, 2% sodium carbon methylcellulose (NaCMC)/styrene butadiene rubber (SBR) binder. The positive electrode loading was 21.3 mg/cm<sup>2</sup> and the density after compression was 3.5 g/cm<sup>3</sup>. The negative electrode was prepared by sputtering a thickness “wedge” of Mn (from 0 to 40 μg/cm<sup>2</sup>) on the surface of a fresh negative electrode and preparing a calibration curve of Mn concentrative XRF counts to Mn loading. Calibrations were not made for Ni and Co, but the sensitivity of the instrument to Ni and Co is like that for Mn.

The major outcomes from this work are that increased transesterification occurred as the upper cutoff potential increased and that the amount of transition metal dissolution from the positive electrodes of these cells was very minimal and unlikely to have impacted cell lifetime.

A set of LiNi<sub>0.5</sub>Mn<sub>0.3</sub>Co<sub>0.2</sub>O<sub>2</sub>/graphite lithium-ion cells underwent 750 charge-discharge cycles during about 8 months at 55 °C to upper cutoff potentials of 4.0, 4.1, 4.2, 4.3, and 4.4 V. The electrolyte in these cells was extracted using a centrifuge method and studied using gas chromatography/mass spectrometry to determine the changes to the solvents and by inductively coupled plasma-mass spectrometry to determine the changes to the salt content in the electrolyte. The negative electrodes from the cells were harvested and studied by micro-X-ray fluorescence to quantify the amount of transition metals which migrated from the positive electrode to the negative electrode during the testing. Emphasis is given to a detailed description of the quantitative methods used in the hope that others will adopt them in similar studies of different types of aged lithium-ion cells. The cells studied here initially had 1.1 molal LiPF<sub>6</sub> ethylene carbonate (EC): ethyl methyl carbonate (EMC) (3:7 by weight) electrolyte. The aged cells showed increasing amounts of dimethyl carbonate and diethyl carbonate created by transesterification as the upper cutoff potential increased. Only extremely small amounts of Mn, less than 0.1% of the total Mn in the positive electrode, were found on the negative electrode after this aggressive testing.
1.55 g/cm$^3$ after compression. Prior to filling, cells were cut open below the heat seal and placed in a (100 ± 1)$^\circ$C antechamber under vacuum for 14 hours to remove residual moisture before transferring to an argon-filled glove box.

**Cell filling.**—Once in the Ar-filled glove box, cells were filled with $\sim$1.0 g of prepared electrolyte and vacuum sealed at 170$^\circ$C under $\sim$90 kPa gauge pressure with a vacuum heat sealer (Model MSK-115A from MTI Corporation). Cells were weighed before and after sealing to ensure no significant solvent loss.

**Cell formation.**—Sealed cells were first held at 1.5 V for 24 hours to help ensure full wetting of the electrodes and then transferred to a (40.0 ± 0.1)$^\circ$C temperature-controlled box to undergo formation on a Maccor 4000 series charger at C/20 (11 mAh) to 3.5 V, held at 3.5 V for 1 hour and removed to degas SEI formation products in the same atmosphere and sealing conditions as above. Degassed cells then continued formation on the Maccor to their designated upper cutoff potential.

**Cell cycling.**—Cells were placed in a (55.0 ± 0.1)$^\circ$C temperature-controlled box for the duration of testing and cycled using a Newware (Shenzhen, China) charging system at C/3 (80 mAh) rate between 2.8 V and the designated upper cutoff voltage. Constant current – constant voltage (CCCV) mode was used to charge cells until the current was less than C/20 (11 mAh). After every 50 cycles, a C/20 (11 mAh) charge and discharge cycle was performed. The negative to positive capacity ratios for the cells cycled to 4.0, 4.1, 4.2, 4.3 and 4.4 V are 1.66, 1.50, 1.39, 1.30 and 1.22, respectively.

**Gas measurements.**—The volume of gas produced during formation and during cycling was measured using Archimedes principle.$^{21}$ Cells were hung below an analytical balance (Shimadzu, AUW00D) and suspended in room temperature de-ionized water (18.2 M$\Omega$-cm, Thermo Scientific Barnstead Nanopure Water Purification System). Because the mass of the sealed cells remains constant, the difference in weight of the cells before and after testing is measured and proportional to gas produced.

**Previous extraction method.**—An existing method for liquid-liquid electrolyte extraction is shown schematically in Figure 1a. The method includes removing a discharged (2.0 V) jelly roll from the pouch bag and adding to a polytetrafluoroethylene (PTFE) vial containing dichloromethane (CH$_2$Cl$_2$) solvent for electrolyte extraction. The PTFE vial is then machine shaken in two directions for a total of 30 minutes. Some of the extract is removed and filtered with a syringe filter containing a PTFE membrane with a 0.45 $\mu$m pore size into a second PTFE vial containing additional CH$_2$Cl$_2$ and deionized-water for LiPF$_6$ and HF extraction.$^{17}$ The new solution is then shaken for another 5 minutes, centrifuged for 20 minutes at 2200 RPM (800 g) to separate the organic and inorganic layers. The bottom, organic layer is then removed for gas chromatography-mass spectrometry (GC-MS) analysis. This method extracts approximately 95% of electrolyte in wound cell but renders the remainder of the cell unavailable for additional study.

**Modified extraction method using a centrifuge.**—Figure 1b shows a schematic of the centrifuge method. For this method, the pouch bag of discharged cell (2.0 V) was cleaned of any markings and scored on either end of the jelly roll. Previous centrifuge techniques have removed the separator to extract electrolyte,$^{13}$ however here, the entire cell was placed in a 15 mL polypropylene (PP) vial. The cap was fitted with a 9 mm PTFE/silicon seal to prevent solvent evaporation. The tube was then centrifuged at 2200 RPM (800 g) at 30$^\circ$C for 20 minutes. The sealed vials were weighed before and after centrifuging to ensure no significant solvent loss. Of the original 0.9 g of electrolyte added during cell filling, approximately 0.1g to 0.2 g of electrolyte was recovered from this process. The pure electrolyte

![Figure 1. a) Schematic of the previous liquid-liquid extraction method.$^{17}$ b) schematic of the modified extraction method which uses a centrifuge to extract electrolyte from cells.](image-url)
was then removed from the PP vial with a 1 mL syringe and diluted for GC-MS and inductively coupled plasma-mass spectrometry (ICP-MS) analyses. Electrodes were separated from the jelly roll and allowed to dry in a fume hood. A representative segment of the anode was then used for μ-XRF analysis.

The liquid-liquid extraction and centrifuge methods are compared in Figure 2. Here, cells with three different electrolyte systems were processed through both methods. Figure 2a shows 2% VC and 98% EMC, Figure 2b shows 20% EC, 50% EMC and 30% DEC, and Figure 2c shows 30% EC and 70% EMC. Results, reported in panels a, b and c, show no significant difference between samples prepared through liquid-liquid extraction or centrifuge extraction at 95% confidence intervals.

**Is the electrolyte centrifuged from a cell representative of the electrolyte within the core of the jelly roll?**—A possible concern is that the electrolyte centrifuged from a cell may be dominated by electrolyte from the periphery of the jelly roll and not from the core of the jelly roll. This is because there is normally a small excess of electrolyte added to cells. Experiments were designed to probe the time needed for the electrolyte to be homogeneous between the periphery and core of a jelly roll within a pouch cell. As will be shown, the charge-discharge cycle test times of the cells tested here (about 8 months) were much longer than the time needed for the electrolyte to homogenized between core and periphery. Thus, the centrifuge method extracts electrolyte representative of that in the core of the jelly roll.

The time needed for electrolyte to be homogeneous in the cell was explored to ensure the electrolyte removed was an accurate representation of the entire electrolyte, not just the electrolyte at the periphery of the jelly roll. A fresh, dry cell was filled with 0.8 mL of 1.1 m LiPF6 in EC:DEC (3:7), sealed and wet for 24 hours at 1.5 V to allow for electrolyte permeation into electrodes (Figure 3a). The cells were cut just below the heat seal in an Ar-filled glove box and filled with an additional 0.7 mL of DMC (Figure 3b). The cells were then sealed again and later opened for GC-MS and ICP-MS analysis at various times after the second filling (1 hour, 1 day, 8 days and 21 days). The organic mass ratios and Li concentration were compared to the expected homogeneous compositions to determine the time required for the jelly roll electrolyte system to become homogenous (Figures 3c and 3d). Results (Figure 4) showed that the expected homogeneous EC content was (90 ± 10) % recovered after 1 day (Figure 4a), the expected homogeneous DEC content was (90 ± 10) % recovered after one day (Figure 4b) and DMC was (107 ± 7) % recovered after 1 day (Figure 4c). The errors are determined by the deviation between electrolyte analysis from duplicate cells (n = 2) at a 95% confidence interval. The data shows no statistically significant difference between mass ratios of organic species measured after one day and the expected mass ratios. After 8 days, the mass ratios matched the expected ratios for a homogeneous electrolyte suggesting full mixing after 8 days.

ICP-MS analysis for Li concentration showed that after 8 days (90 ± 10) % of the expected lithium was recovered (Figure 4d). The data shows no statistically significant difference between measured and expected lithium concentration at 95% confidence intervals after 8 days. After 21 days the expected and measured lithium contents agreed exactly. Thus, whatever electrolyte extracted using a centrifuge from a cell tested for 21 days or more will be representative of the liquid electrolyte in the core of the jelly roll.

**GC-MS sample preparation.—**One drop of a pure electrolyte sample was diluted into 20 mL of a CH2Cl2 organic phase and ~0.1 mL aqueous phase to ensure complete extraction of salts. The samples were then shaken for a total of 30 minutes in two directions and centrifuged for 20 minutes at 15°C and 2200 RPM (800g) to ensure adequate extraction and separation of phases, respectively. The bottom, organic layer was then sampled using a transfer pipette for analysis. The aqueous layer is small enough that it does not cover the entire surface and the pipette is inserted to avoid the aqueous layer. To be sure that only the organic layer is used, only the bottom portion of pipetted liquid is delivered to the sample vial.

Care was taken to determine detection limits for various electrolyte degradation components expected in the electrolyte. One drop of a stock solution of known amounts EMC, DEC, DMC, DEC, DE-OHC (diethyl-2,5-dioxahexane carboxylate), DMOHC (dimethyl-2,5-dioxahexane carboxylate) and four other compounds was added to a known amount of CH2Cl2. This was injected to the GC-MS in exactly the same way as the electrolyte samples described in the paragraph above. Detection limits for EMC, DEC, DMC, DE-OHC and DMOHC were all between 30 ppm and 50 ppm by weight. That is, if there was more than 50 ppm of any of these solvents on the electrolyte, the instrument would detect it.

**GC-MS sample measurement.—**An Agilent 7890 gas chromatograph coupled to an Agilent 5977B single-quadrupole mass spectrometer was used for organic analysis. The inlet was equipped with a split/spitless injector and a 30 m BR-5MS column with an inner diameter of 0.25 mm and coating thickness of 1 μm. The carrier gas

![Figure 2](image-url) **Figure 2.** Comparing known electrolyte mixtures measured using liquid-liquid extraction and centrifuge extraction methods a) 2% VC and 98% EMC, B) 20% EC, 50% EMC and 30% DMC, c) 30% EC and 70% EMC.

![Figure 3](image-url) **Figure 3.** Schematic view of the pouch cell during the electrolyte mixing study. a) pouch bag wet with 1.1 m LiPF6 in EC:DEC (3:7 weight %). b) DMC added to the pouch cell. c) solutions begin mixing. d) time later when electrolyte achieves uniform composition.
was helium (99.999%) at a constant flow of 1.3 mL/min. Samples were injected into the inlet at 250 C and carried onto the column in an oven held at 35 C for 8 minutes followed by a ramp at 40 C/min until the oven temperature reached 290 C. The final oven temperature was held for 5 minutes to ensure all compounds were evolved from column. The transfer line to the MS detector was held at 250 C. The mass spectrometer, containing an electron impact ionization module, had a 200 C ion source and electrons had 70 eV energy. A minimum 5-point calibration curve with an r^2 value of > 0.998 was generated from standards prepared on analysis day with known concentrations. Each sample and standard were injected twice to ensure reproducibility. A full scan was performed on each injection. Data analysis used the primary mass/charge ratios to identify and quantify each peak at the appropriate retention time.

**ICP-MS sample preparation.**—Figure 5 shows a schematic of the ICP sample preparation process. About 0.10 g of pure electrolyte was weighed into PTFE vials containing ~20.0 g of aqueous 2% HNO3 and ~0.2 g of CH2Cl2 for organic separation. Vials were shaken for 20 minutes in one direction, 20 minutes in the perpendicular direction and centrifuged at 15 C and 2200 RPM (800 g acceleration) for 20 minutes to adequately extract the Li^+ into aqueous phase and separate the aqueous and organic layers. For the second dilution, approximately 0.11 g of the aqueous top layer was added to ~50.0 g of 2% HNO3 and shaken for 5 minutes. Target concentrations for the ICP-MS instrument were between 0 and 100 μg/L Li. Samples were then sealed in PP vials and stored in a refrigerator at 10 ± 2 C until analysis.

**ICP-MS sample measurement.**—On the day of sample analysis, lithium standards were diluted from 1000 mg/L stock solution with 2% HNO3, to produce a six-point calibration curve of 0 μg/L, 20 μg/L, 40 μg/L, 60 μg/L, 80 μg/L and 100 μg/L of Li with an r^2 value greater than 0.9999. A freshly prepared 1.1 m LiPF6 in EC:EMC (3:7) electrolyte with known concentration also underwent sample processing and ICP-MS analysis to ensure measured concentrations were accurate.

An iCAP Q ICP-MS (Thermo Fisher Scientific, MA, USA) paired with an ESI SC-4DXS auto sampler (Elemental Scientific, NE, USA) was used for sample analysis following the protocol developed by Smith et al. All samples were run in Kinetic Energy Discrimination (KED) mode, using high purity helium (99.999%) as the collision gas. Online internal standard addition was performed to correct for any instrumental drift if necessary using 50 μg/L scandium and an SC FAST Valve (Elemental Scientific, NE, USA). A quality control check standard was analyzed every 20 samples. Samples were measured with 0.01 s dwell time and 25 sweeps. A minimum of 3 main runs with a maximum relative standard deviation of 5.0% were taken for each sample.

**Robustness of ICP measurements.**—The ICP-MS method was tested periodically with electrolytes of known concentrations to ensure the robustness, reproducibility and stability of the method over time. This test included four ICP-MS samples prepared on day 1 from an electrolyte of known salt and solvent concentration. These samples were then stored in a 10 ± 2 C refrigerator in PP vials which were wrapped with Parafilm. On day 6, an additional four samples were prepared from a new electrolyte of known salt and solvent concentration prepared the same day. Both sets of samples were measured by ICP-MS on day 6 and on day 7. The average fraction of Li recovery for both electrolyte samples on both days are shown in Figure 6. Within a 95% confidence interval, there is no significant difference between the expected Li concentration and the measured concentration on either day of measurement and after seven days of sample storage. Each of the four samples also have good agreement (within 5%).

**Mn calibration for X-ray fluorescence analysis.**—A Mn calibration curve was prepared using a Corona Vacuum Coaters (Vancouver, BC, Canada) model V-3T sputtering system. This method, developed by Dahn et al., uses a mask opening over the target and a rotating substrate table to create gradients in the amount of deposited material on a substrate. The linear mask used in this work generates a linear mass per unit area increase versus position on the substrate (Figure 7a). Pre-weighed aluminum foil discs were used to measure the mass per unit area deposited versus position. (Figure 7b). Deposition increased from 0.0 μg cm^2 to about 30 μg cm^2 across the sputtering track. The scatter in the mass-position curve in Figure 7b is due to variations in the average amount of adhesive left on the back side of the foil discs. The average value was subtracted from the mass vs. position calibration.

During the same sputtering run, fresh graphite negative electrodes were mounted on the substrate table next to the aluminum foil weigh discs. The same “wedge” of Mn was deposited onto the graphite negative electrodes. Several of these Mn-coated electrodes were then used to record the Mn count per unit area versus position on the electrode (Figure 7c) to be compared with the mass per unit area versus position of the weigh discs (Figure 7b), thus allowing a calibration curve to be constructed.

**μ-XRF measurements.**—The Mn-coated fresh electrode was used to calibrate signal counts measured with a M4 Tornado Micro-X-Ray Fluorescence Instrument with a (Bruker, Madison, WI, USA). Figure 7c shows the Mn signal counts versus position on the electrode. The samples were placed in a vacuum sealed chamber directly on a motion stage. The sample analysis and imaging were carried out with

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**Figure 4.** GC-MS and ICP-MS results for the electrolyte mixing study. a) fraction of EC recovered compared to that expected based on homogeneous mixing (solid line), b) fraction of DEC recovered compared to expected (solid line), c) fraction of DMC recovered compared to expected (solid line), d) fraction of Li concentration recovered compared to expected concentration (solid line).
Figure 5. A schematic showing ICP sample preparation.

a Rh X-ray tube\textsuperscript{19} using 0–50 keV range and a tube current of 200 μA. Sample scanning was done at a rate of 4.00 mm/sec. using a 40 μm spot size. Complete elemental analysis was performed at each position. The Mn signal count for the samples was then fitted using calibration data from Figures 7b and 7c to determine the Mn mass per area on the electrodes. The average Mn loading over the sampled anode area was then calculated and is reported here. Error was calculated using a regression analysis of calibration curve at 95% confidence intervals. Ni and Co μ-XRF signals were also measured from the aged electrodes and were compared to the Mn μ-XRF signals.

A negative electrode from a dry pouch cell and from a freshly formed pouch cell were measured via μ-XRF to quantitatively show the magnitude of Mn deposition before electrolyte filling and after formation, before cycling. Figure 8a shows the Mn loading on the negative electrode of a dry cell (0.0 ± 0.0 μg/cm\textsuperscript{2}) and Figure 8b shows the Mn loading on the negative electrode of a freshly formed cell (0.52 ± 0.09 μg/cm\textsuperscript{2}). Figure 8 shows images of the Mn signal maps over the approximately 3 cm × 2 cm electrode studied. The negative electrode from a dry fresh pouch cell showed no Mn signal. Similar measurements on the copper foil current collector also showed no Mn signal.

Results and Discussion

Figure 9a shows the capacity vs. cycle count for the NMC532/graphite cells studied here. The cells were tested using CCCV cycling using currents corresponding to C/3 at 55°C. The upper cutoff potentials for the tested cells are given in the legend of Figure 9. As expected, the initial capacity increases with increased upper cutoff potential. Cells cycled at higher upper cutoff potentials (4.3 V and 4.4 V) had lost 30 mAh of capacity. All cells have lost on average (12.2 ± 0.2)% capacity after almost 750 cycles at 55°C. Figure 9b shows the difference in average charge and discharge voltage (ΔV) vs. cycle count. This polarization tracks impedance growth\textsuperscript{24} which increases as upper cutoff potential increases. Cells cycled at 4.4 V have faster impedance growth than cells cycled at 4.0 V.
Figure 7. a) Schematic sputtering loading vs position on the sputtering track. b) Mn loading ($\mu$g cm$^{-2}$) vs position on the sputtering track. c) $\mu$-XRF Mn signal count per cm$^2$ vs position on the fresh negative electrode exposed to the Mn sputtering procedure.

Figure 10 shows post cycling analysis for this matrix of cells. Figure 10a shows gas production after cycling plotted for the five different upper cutoff potentials. There is a general trend of increased gas production as the upper cutoff potential increases, however, one cell at 4.0 V exhibited gas production comparable to the 4.4 V cells, therefore no definitive trend can be reported. The scale of gas production for these pouch cells remains small (<0.4 mL) compared to the original volume of the cells (2.5 mL).

Figure 10b shows DMC and DEC solvent fractions compared to EMC plotted as the fraction of transesterification, defined here to be:

$$\frac{\text{Fraction DMC} + \text{Fraction DEC}}{\text{Fraction DMC} + \text{Fraction DEC} + \text{Fraction EMC}}$$

Figure 10b shows that transesterification increases as the upper cutoff potential increases from 0.0% transesterification at 4.0 V to $11.8 \pm 0.2\%$ at 4.4 V. DMC and DEC have been shown to be formed from the Li-alkoxide facilitated trans-esterification reaction for EMC.$^{10,17}$ In freshly formed cells the presence of these products indicates the existence of Li-alkoxides, likely formed from the reduction of EMC at an un-passivated anode.$^{8,10,17}$ Li-alkoxide formation and subsequent reaction with linear carbonate are shown in Equation 1 and Equation 2, respectively. The presence of transesterification products later in life was hypothesized to originate from the passivation of dissolved transition metals upon deposition at the negative electrode.$^{25}$

However, limited transition metals found at the negative electrode, as discussed below, suggests another mechanism is involved. Li-alkoxides can also facilitate reactions between linear carbonates and ethylene carbonate (EC). DEOHC (diethyl-2,5-dioxahexane carboxylate) and DMOHC (dimethyl-2,5-dioxahexane carboxylate) are dimerization products also expected in the presence of Li-alkoxides as shown by Equation 3.$^{8,10,17}$

DMOHC and DEOHC were not observed in any of the electrolyte samples to the detection limit of 50 ppm by weight. This suggests that Li-alkoxides were not present and another mechanism is responsible...
Figure 10. Post-testing analysis results for the cells described by Figures 9. a) gas produced (mL) vs upper cutoff potential. b) fraction of transesterification vs upper cutoff potential. c) EC: linear carbonate ratio vs upper cutoff potential. d) Li concentration (m) vs upper cutoff potential. e) Mn loading on the negative electrode (μg cm⁻²) vs upper cutoff potential.

Figure 11. Comparing the Ni (black) and Co (blue) μ-XRF signals to the Mn μ-XRF signal for the electrodes recovered from the cells described by Figures 9 and 10. The solid black and solid blue lines represent the expected ratios of all transition metals have equal probability for dissolution from NMC532.
lines in Figure 11 represent the expected ratios based on equal probabilities for dissolution of Ni, Mn and Co from NMC532. The relative sensitivity of the µ-XRF instrument was estimated by measuring the count rates per cm² from pure Ni, Co and Mn metal samples which were found to be in the ratio 1:0.96:0.81. These correction factors have not been applied to the data in Figure 11. The purpose of Figure 11 is to show that Ni and Co dissolve from the NMC532 positive electrode to approximately the expected extent and that Mn does not dissolve in far greater quantities. In a recent study published by Gilbert et al. 29 it was also observed that transition metals were deposited onto the anode at the expected mass ratios.

Figure 12 compares results for Mn deposition on the negative electrode from this study to those recently published by Gilbert et al. 29 Gilbert et al. reported the Mn content as weight fraction of the negative electrode so it was necessary to convert the data in Figure 10 into the same units. This required some thought, because the positive and negative electrode loadings used in ref. 29 were different than those used here. Gilbert et al. used a positive loading of 9.2 mg/cm² while a loading of 21.3 mg/cm² was used here. However, because the negative/electrode mass ratios in the cells ref. 29 and the cells studied here were about the same, the negative electrode loading scales with the positive electrode loading. Therefore, in the end, it was only necessary to divide the Mn mass loadings in Figure 10 by the negative electrode mass per unit area (12.8 mg/cm²) to get a meaningful comparison.

Gilbert et al. found that amount of Mn deposition at the negative electrode increased as the fraction of capacity loss increased. The NMC532/graphite coin cells in their study contained 1.1 M LiPF₆ in EC:EMC (3:7) and no additives. Their cells experienced 37% capacity loss after cycling between 3.0 and 4.4 V at 30 °C for about 900 hours (200 cycles at C-rate). By contrast, cells in this study experienced a maximum of 12.2% capacity loss after cycling for over 5000 hours at 55 °C (750 cycles at C/3 rate). Figure 12 suggests that the Mn loading found on cycled anodes in this study appears to fall within the Mn loading found on cycled anodes in this study to those recently published by Gilbert et al. 29 The legend in the Figure indicates the upper cutoff voltage and which study the data points correspond to. Cells in the Gilbert et al. study were tested at 30 °C for 900 hours. Cells in this study were tested at 55 °C for 5000 hours.

The data in Figure 12 for the cells in this study suggests that when transition metal dissolution is controlled through the selection of suitable additives and/or other strategies, transition metal dissolution and subsequent deposition on the negative electrode does not play a dominant role in the failure mechanism of NMC/graphite Li-ion cells. This is a very important point that readers need to appreciate.

Gilbert et al. 29 state in their conclusions: “... it is our belief that controlling TM dissolution from the oxide surfaces through various possible preventive measures can lead to the development of high voltage LIBs with extended operation time. Any method of reducing the stress and fracture of oxide particles that leads to enhanced TM dissolution should reduce both capacity fade and impedance rise. These methods could include changes in oxide synthesis conditions to strengthen primary particle boundaries, oxide coatings and electrolyte additives to minimize corrosion reactions at the oxide-electrolyte interfaces, etc."

The electrolyte mixture in this study likely provides more stable SEI layers on both the positive and negative electrode which prevents severe transition metal dissolution. Since transition metal dissolution has been shown to be driven by HF formation from PF₆⁻ 30 it could also be that the difference in the results from this study and the Gilbert study originates from relative amounts of formed PF₆ and HF. This is also consistent with the lack of dimerization products measured in the electrolyte in this study. 31 Additionally, Li et. al found that NMC532/graphite pouch cells with single crystal positive electrode materials, as used in this study, had longer cycling lifetime and better performance than cells with polycrystalline materials. 32 Figure 12 suggests that further reductions in transition metal dissolution and deposition at the negative electrode may have little impact on lifetime, however, more data points are needed, particularly at larger capacity losses, to make an adequate comparison and prediction.

Figure 9b showed that the difference in average charge and discharge voltage (ΔV) increased with cycle number more rapidly as the upper cutoff potential increased. Since ΔV is a measure of impedance growth in the cells it is interesting to see how it correlates to the amounts of degradation products found. The value of ΔV at the end of the testing in Figure 9b was used for comparison. Figure 13a shows that the fraction of transesterification products (DMC and DEC) increased as ΔV increased, suggesting that the amount of transesterification may be related the impedance growth. It would not be prudent to suggest causality without knowing the reaction mechanisms responsible for the transesterification. Similarly, Figures 13b suggests the Mn loading at the anode increases as ΔV increases but the data shows significant scatter. Again, it is not possible to suggest a causal relationship between Mn on the negative electrode and impedance growth, when the amount of Mn on the negative electrode is very small.
Qualitative methods for determining the solvents present, the Li⁺ ion concentration and the loading of transition metals transferred to the negative electrode in aged Li-ion cells were carefully described. These methods were applied to a set of single crystal NMC532/graphite cells with effective electrolyte additives that had been tested at 55 °C for about 8 months. The cells were charged and discharged between 2.8 V and various upper cutoff potentials ranging from 4.0 to 4.4 V using currents corresponding to C/3. The cells all attained about 750 cycles over a 9-month period with approximately 10% capacity loss. The results showed that increased upper cutoff potential increased the amount of the transesterification products DMC and DEC. The increased fraction of transesterification products in cells tested to higher potential correlated well to the increase in impedance growth rate (Figures 9b and 13a) in cells tested to higher potential. This suggests that the mechanism of impedance growth is associated with electrolyte oxidation at the positive electrode side and that transesterification is an indicator or a product of these reactions.

The amount of transition metals transferred from the positive to the negative electrode was less than 0.1% of all the transition metals in the positive electrode for all the cells tested. There may be an increase in the amount of transition metals transferred with upper cutoff potential, but scatter in the data makes it hard to discern if this trend is real. Cells tested at 4.1 V and at 4.3 V for 8 months and 55 °C showed only about twice as much Mn on the negative electrode as freshly formed cells (Figure 10e). It is therefore difficult for the authors to believe that twice as much Mn on the negative electrode as freshly formed cells is an indicator or a product of these reactions.

The results from this study were compared to those of a similar study by Gilbert et al.29 The amounts of Mn and other transition metals found on the negative electrode were an order of magnitude smaller than the Gilbert et al. study, even though cells studied here were tested over a 9-month period with approximately 10% capacity loss. The results showed that older cells with more extreme capacity loss.

Acknowledgments

The authors thank NSERC and Tesla Canada under the auspices for Industrial Research Chair Program for financial support. AE acknowledges NSERC for support under the USRA program.

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