Exploring Electrochemistry and Interface Characteristics of Lithium-Ion Cells with Li$_1.2$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ Positive and Li$_4$Ti$_5$O$_{12}$ Negative Electrodes

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Lithium-ion cells containing Li$_1.2$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$–based positive and Li$_4$Ti$_5$O$_{12}$–based negative electrodes were electrochemically cycled in the 0.75–2.55 V and 0.75–3.15 V voltage windows. The maximum voltage of the Li$_1.2$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ in the 0.75–2.55 V range is ~4.1 V vs. Li/Li$^+$, well below the oxide’s “activation” plateau; in contrast, in the 0.75–3.15 V range the oxide potential at top of charge is ~4.7 V vs. Li/Li$^+$, beyond the activation plateau. Our results show that the discharge energy density decreases after 500 cycles from 154.2 to 147.8 mW h/g (~10.2% reduction), and from 484.9 to 435.3 mW h/g (~10.2% reduction), in the 0.75–2.55 V and the 0.75–3.15 V ranges, respectively. Almost all of this energy density decrease, in both cycling ranges, can be attributed to voltage fade in the Li$_1.2$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ because cell capacity loss during cycling is small. An investigation of harvested electrolytes from cycled cells showed a noticeable, yet very small (ppb levels), increase in Mn, Ni and Co contents. In contrast, the content of these elements show a significant increase at the negative, indicating a preference for deposition at this electrode over accumulations in the electrolyte. In addition, XPS data showed significant amounts of organic and inorganic species at the negative electrode, which increased on cycling; this finding is consistent with previously reported data for Li$_4$Ti$_5$O$_{12}$ electrodes. Surface films, containing products of electrolyte degradation, were also observed on the positive electrode. Although transition metal element dissolution occurs at this electrode, the loss of Mn, Ni and Co is not sufficient to significantly alter the oxide’s composition and/or its capacity.

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Cell life is a critical performance factor for Li-ion batteries. A longer cell life lowers the lifetime operational costs associated with battery acquisition, replacement, and disposal. The life of commercial Li-ion cells is often limited by the graphite contained in the negative electrode. Li intercalation into graphite occurs at voltages below the stability window of conventional carbonate-based solvents leading to electrode-reduction reactions and build up of the solid electrolyte interphase (SEI) layer. These reactions irreversibly trap mobile Li reducing the cell capacity and often create obstacles to Li-ion motion thereby increasing the overall cell resistance.

An alternative to graphitic anodes are negative electrodes based on the spinel compound Li$_4$Ti$_5$O$_{12}$ (also referred to as “LTO” in this manuscript). LTO reversibly transforms to Li$_4$Ti$_5$O$_{12}$, a rock salt-type compound during the lithiation-delithiation process. The transformation occurs at ~1.55 V vs. Li/Li$^+$, well within the stability window of conventional carbonate-based electrolytes, and high enough to prevent Li-plating and allow use of lithium current collectors. LTO-based electrodes show excellent reversibility, good rate capability, enhanced thermal stability, minimal strain, and capacities up to ~170 mAh/g. Cells with LTO electrodes coupled to LiCoO$_2$, LiNi$_{0.5}$Co$_{0.5}$O$_2$, LiMn$_2$O$_4$, LiNi$_{0.2}$Co$_{0.2}$Mn$_{0.6}$O$_2$, and LiFePO$_4$ have demonstrated improved cycling stability over their graphite-based counterparts. However, the reduced cell voltages due to the use of a higher voltage anode results in lower cell energy densities.

In this work we detail the electrochemical characteristics of lithium-ion cells containing Li$_1.2$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ (aka 0.5Li$_2$MnO$_3$•0.5LiNi$_{0.375}$Mn$_{0.375}$Co$_{0.25}$O$_2$) based positive and Li$_4$Ti$_5$O$_{12}$ based negative electrodes. The Li$_1.2$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ (also referred to as “oxide” in this manuscript) compound is part of the lithium- and manganese- rich family of layered oxides that display capacities exceeding 250 mAh/g. To achieve these high capacities, the oxide is typically cycled beyond the activation plateau at ~4.45V vs. Li/Li$^+$, which is associated with the removal of lithium and oxygen from, and irreversible changes in, the oxide structure.

Here, we describe cell cycling behavior in 2 different voltage ranges ~0.75–2.55 V (oxide potential: 2.3–4.1 V vs. Li/Li$^+$), which is below the activation plateau, and 0.75–3.15 V (oxide potential: 2.3–4.7 V vs. Li/Li$^+$), which is well beyond the activation plateau. Changes in cell capacity, voltage, and energy over 500 cycles are reported in this article. After electrochemical cycling, the full cells were disassembled and both electrodes and electrolytes were harvested for further characterization by various wet chemical analysis techniques, X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). In this article, we show accumulation of Mn, Ni, and Co on the LTO-negative electrodes, but not in the electrolyte. We also note the presence of surface films on the positive electrode, and growth of electrode surface films on the LTO-negative, which is typically considered a non-SEI-forming electrode.

Experimental

All electrodes in this study are from the Cell Analysis, Modeling, and Prototyping (CAMP) facility at Argonne; details are shown in Table I. The positive and negative electrodes contain Li$_1.2$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ and Li$_4$Ti$_5$O$_{12}$, respectively as the active constituents. Both electrodes also contain carbonaceous additives to enhance electronic conduction and PVDf binder to ensure coating-cohesion and adhesion to the current collector. Electrochemical evaluation was conducted at 30 °C in planar stainless steel test cells containing 32 cm$^2$ area single-side coated positive and negative electrodes; all electrodes were dried overnight in a vacuum oven at 110 °C prior to cell assembly. Each cell also contained a Celgard 2325 (PP/PE/PP) separator and EC:EMC (3:7 w/w) + 1.2 M LiPF$_6$ electrolyte (also referred to as “Gen 2 electrolyte” in this manuscript). The cells were assembled and tested in an inert-atmosphere glove box to minimize the impact of moisture and oxygen.

Galvanostatic cycling was conducted either with a 15 mA/g (0.1 mA/cm$^2$) or a 105 mA/g (0.7 mA/cm$^2$) current; here, “g” refers to grams of oxide in the positive electrode. The initial three cycles after cell assembly were carried out with the lower current (15 mA/g), and subsequent (cell aging) cycles were carried out with the higher current (105 mA/g). Every 100 aging cycles, three reference...
performance charge-discharge cycles were performed, employing a current of 15 mA/g. These reference performance cycles provide a better measure of cell capacity due to the lower ohmic polarization associated with the lower current.

After aging, the cells were discharged to 0.75 V and held at this voltage for 24 h before cell disassembly in an argon-atmosphere glove box. Electrochemical characterization of the harvested positive or negative electrodes was conducted in 2032-type coin cells (1.6 cm² electrodes) containing fresh Celgard 2325 separator, Gen2 electrolyte, and a Li metal counter electrode; a schematic showing cells prepared from the harvested electrodes is presented in Figure 1. All cells were evaluated in a constant temperature oven held at 30°C. The positive electrode cells were cycled between 2.0 and 4.7 V vs. Li, and the negative electrode (LTO) cells were cycled between 2.05 and 1.05 V vs. Li; the results were compared with data from pristine positive or negative electrode cells. All cells contain Celgard 2325 separator and the Gen2 electrolyte.

Electrochemical characterization of the full cells.—Figure 2 contains the capacity-voltage profiles (a, b) and differential capacity profiles (c, d) of the initial three cycles. In the 0.75–2.55 V range the first cycle discharge capacity is 67 mAh/g (Figure 2a) and the columbic efficiency (CE) is 94%. The discharge capacity and CE increase to 68 mAh/g and 99.3%, respectively, for the third cycle. The differential capacity plots (Figure 2c) show peaks at ~2.43 V and ~2.40 V during delithiation and lithiation, respectively for all three cycles. In the 0.75–3.15 V cycling range the first cycle discharge capacity is 232 mAh/g (Figure 2b) and the columbic efficiency (CE) is 85%. The higher discharge capacity results from “electrochemical activation” of the Li₁₂Ni₀.15Mn₀.55Co₀.1O₂, which is seen as a plateau at ~2.93 V (corresponding to ~4.48 V vs. Li). The 85% CE is mainly a consequence of slow lithium-ion mobility into the oxide at high lithium contents, which reduces the apparent discharge capacity. Both discharge capacity and CE increase during subsequent cycles, rising to 235 mAh/g and >99.9%, respectively, for the third cycle. Significant differences are seen between the first and subsequent cycles in differential capacity plots in this voltage range (Figure 2d), which reflect structural changes induced in the oxide during activation.

Figure 3 shows discharge capacity as a function of cycle number for cells cycled in the 0.75–2.55 V and 0.75–3.15 V ranges; data obtained both with a 15 mA/g (low) and a 105 mA/g (high) current are shown. In the 0.75–2.55 V range, at the low current, the discharge capacity increases slightly during the first 100 cycles, from 67 to 70 mAh/g, then decreases (see Table II). After 500 cycles, the capacity value (67 mAh/g) is similar to that of the starting cycle, so that cell capacity fade relative to the initial cycle is effectively zero. At the higher current, the discharge capacity decreases gradually from 57 mAh/g to 48 mAh/g after 500 cycles. In the 0.75–3.15 V range, at the low current, the discharge capacity increases from 232 mAh/g initially to 245 mAh/g (Table II) after the first 100 cycles, then decreases to 228 mAh/g after 500 cycles. At the higher current, however, the...
discharge capacity continues to increase from 173 mAh/g initially to 185 mAh/g after 500 cycles. A closer examination shows that the increase in cell capacity follows the intervening low current cycles, i.e., additional capacity is accessed during the slower cycles, which appear to “heal” the oxide and increase lithium accessibility at the higher rates. During the 100 high current cycles, however, cell capacity decreases gradually during the initial period up to 300 cycles, then shows minimal changes during the latter 200 cycles.

The capacity increase during the low current cycling is also seen in Figure 4, which shows capacity-voltage (a, b) and hysteresis profiles (c, d) of the reference performance cycles in both voltage ranges. In both Figures 4a and 4b, the charge and discharge capacities after 100 and 200 high-current cycles are greater than the initial capacities. Voltage fade is also evident in the 0.75–3.15 V data (Figure 4b) during both charge and discharge cycles. The voltage drop is most prominent during the first 100 cycles, then decreases gradually (see Table II). For example, the average charge voltage decreases from 2.755 V initially to 2.291 V after the first 100 cycles, then to 2.183 V after 500 cycles, i.e., the total voltage drop is 572 mV over 500 cycles. The average discharge voltage decreases from 2.090 V initially to 1.968 V after the first 100 cycles, then to 1.909 V after 500 cycles, i.e. the total voltage drop is 181 mV over 500 cycles. Note, however, that the voltage changes are not uniform over the cycling range as seen clearly in Figure 4d.

Figure 4d shows the voltage hysteresis loop for the reference performance cycles performed after 100 and 500 cell aging cycles in the 0.75–3.15 V range. The data contained in Figure 4d is a subset of the data in Figure 4b, albeit plotted in a different way, and is also shown in Table II as the difference between the average cell voltage during charge and discharge cycles. This difference decreases from 664 mV initially to 274 mV after 500 cycles. Note again that the hysteresis is not uniform over the cycling window, especially after 500 cycles.
Table II. Performance of full cells cycled in the 0.75–2.55 V and 0.75–3.15 V ranges.

| No. of Fast Cycles | Capacity mAh/g | C Fade % | Energy mWh/g | E Fade % | Avg Volt Ch, V | Avg Volt Dch, V | Voltage Diff, V |
|--------------------|----------------|----------|---------------|----------|---------------|---------------|----------------|
| 1                  | 67             | 0.0      | 154           | 0.0      | 2.359         | 2.301         | 0.057          |
| 100                | 70             | −4.5     | 158           | −2.4     | 2.347         | 2.255         | 0.092          |
| 200                | 69.5           | −3.7     | 155           | −0.6     | 2.343         | 2.232         | 0.111          |
| 300                | 69             | −3.0     | 154           | 0.4      | 2.341         | 2.226         | 0.115          |
| 400                | 68             | −1.5     | 150           | 3.0      | 2.339         | 2.200         | 0.139          |
| 500                | 67             | 0.0      | 148           | 4.1      | 2.338         | 2.206         | 0.132          |

Cycling Window: 0.75–2.55 V; Cycling Current = 15 mA/g

| No. of Fast Cycles | Capacity mAh/g | C Fade % | Energy mWh/g | E Fade % | Avg Volt Ch, V | Avg Volt Dch, V | Voltage Diff, V |
|--------------------|----------------|----------|---------------|----------|---------------|---------------|----------------|
| 1                  | 232            | 0.0      | 485           | 0.0      | 2.755         | 2.090         | 0.664          |
| 100                | 245            | −5.6     | 482           | 0.6      | 2.291         | 1.968         | 0.323          |
| 200                | 241            | −3.9     | 468           | 3.6      | 2.242         | 1.940         | 0.302          |
| 300                | 236            | −1.7     | 454           | 6.3      | 2.214         | 1.926         | 0.288          |
| 400                | 232            | 0.0      | 444           | 8.4      | 2.194         | 1.914         | 0.280          |
| 500                | 228            | 1.7      | 435           | 10.2     | 2.183         | 1.909         | 0.274          |

Cycling Window: 0.75–3.15 V; Cycling Current = 15 mA/g

Capacity, capacity fade, energy, energy fade values are for the discharge cycles.
g refers to mass of oxide in the positive electrode.
Average Voltage = Energy/Capacity; values for both charge and discharge cycles are shown.
Voltage Diff = Difference in average voltage between charge (Ch) and discharge (Dch) cycles.

Figure 4. Capacity-voltage profiles (a, b) and voltage-hysteresis profiles (c, d) of full cells cycled in the 0.75–2.55 V and 0.75–3.15 V ranges. The data were obtained with a 15 mA/g current at 30°C; g refers to grams of oxide in the positive electrode. The data obtained are after initial cycles, and after 100, 200, 300, 400 and 500 high-current (105 mA/g) cycles.
The differential capacity (dQ/dV) profiles (see Figure 5) for the charge total drop in discharge voltage is higher (95 mV) as the cell voltage to 2.338 V after 500 cycles, dropping 20 mV over 500 cycles. The reduction in charge voltage is larger than the reduction in discharge voltage.

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Interestingly, voltage fade and voltage hysteresis are also observed for cells cycled in the 0.75–2.55 V range, but they are much smaller. Here, the average charge voltage decreases from 2.359 V initially to 2.338 V after 500 cycles, dropping 20 mV over 500 cycles. The total drop in discharge voltage is higher (95 mV) as the cell voltage decreases from 2.301 V initially to 2.206 V after 500 cycles. This difference is reflected in the voltage hysteresis displayed by the cell which increases from 57 mV initially to 132 mV after 500 cycles.

The electrochemical changes during cycling are also revealed in the differential capacity (dQ/dV) profiles (see Figure 5) for the charge and discharge cycles. The changes are relatively subtle in the 0.75–2.55 V cycling range, which shows main peaks at 2.42 V and 2.38 V during the charge and discharge cycles, respectively. The intensity of these peaks decreases gradually on cycling, but their positions do not change. This intensity decrease is accompanied by subtle intensity increases in the 0.75–1.75 V shown in the Figure 5a inset.

In contrast the dQ/dV changes are significant on cycling in the 0.75–3.15 V range (see Figure 5b). Relatively broad charge peaks at 1.93 V and 2.38 V, and discharge peaks at 2.18 V and 1.7 V are observed after the initial cycles. The intensity of these peaks decreases on cycling accompanied by intensity increases below the 1.7 V peak during discharge, i.e., the plots show capacity transfer from the higher to lower voltages resulting in voltage fade. Additionally, the lower voltage peaks move with cycling; after 500 cycles, a major charge peak is seen at 1.6 V and a discharge peak 1.43 V. The emergence of low voltage shoulders on these peaks (marked by arrows in Figure 5b) suggests the presence of other broader, less distinct peaks masked by the main peaks.

These changes in cell capacity and voltage profile with cycling translate into a varying energy density. Table II shows that the initial discharge energy density in the 0.75–3.15 V cycling range is 485 mWh/g more than three times the 154 mWh/g available in the 0.75–2.55 V range. This value, though, is much smaller than the 930 mWh/g that is delivered by the same Li$_{1.1}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$-positive when cycled over a comparable range (2.2–4.6 V) in a cell with a graphite-negative electrode. However, after 200 cycles in the 0.75–3.15 V cycling range, the discharge energy of the LTO-negative electrode cells is reduced to 345 mWh/g; an energy loss of only 10.2%. For cells cycled in the 0.75–2.55 V range, the discharge energy decreases to 148 mWh/g after 500 cycles; this energy loss of 4.1% is even lower. In contrast, the discharge energy of graphite-negative electrode cells (with the Gen2 electrolyte) fades much faster, decreasing more than 50% after 500 cycles in the 2.2–4.6 V voltage window (comparable to the 0.75–3.15 V range). Therefore, Li$_{1.1}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ cells with LTO-bearing negative electrodes become more attractive than cells with graphite-negative electrodes for applications where long-term cycling is required.

**Electrochemical characterization of harvested electrodes.**—Electrochemical data were obtained on harvested electrodes to determine the effect of extended cycling on electrode performance. Figure 6 shows representative capacity-voltage and differential-capacity profiles of harvested positive electrodes cycled in cells with a lithium counter electrode. Figure 6a shows that charge and discharge capacities for a fresh positive electrode cycled in the 0.75–2.55 V range are 72.4 and 71.3 mAh/g, respectively. The values for the aged electrode are 72.4 and 71.3 mAh/g for the charge and discharge cycles, respectively. In addition, the charge and discharge profiles for the aged electrode are lower than that of the fresh electrode, which indicates voltage fade. The capacity shifts to lower voltages, which is characteristic of voltage fade, is seen in Figure 6a which shows slightly lower intensities for the ~3.95 V vs. Li/Li$^+$ peak and higher intensities in the 2.5–3.5 V vs. Li/Li$^+$ region during both charge and discharge cycles.

In Figure 6b, voltage fade is clearly evident in the harvested positive electrode cycled in the 0.75–3.15 V range. The charge and discharge capacities for a fresh positive electrode cycled in this range are 273 and 272 mAh/g, respectively; the corresponding values for the aged electrode are 284 and 272 mAh/g, respectively. Both charge and discharge voltages profiles are distinctly lower for the aged electrode. This voltage depression is better understood by examining the differential capacity plots of Figure 6d. Here, the main peaks for the fresh sample are at 3.53 and 3.84 V vs. Li/Li$^+$ on charge, and at 3.74 and 3.25 V vs. Li/Li$^+$ on discharge. The aged sample shows significant reduction in the intensity of the higher-V peaks, which also move to lower voltages. The lower-V peaks also grow and shift, developing well resolved components at 2.94, 3.01, and 3.17 V vs. Li/Li$^+$ for the charge cycle, and at 2.82 and 2.97 V vs. Li/Li$^+$ for the discharge cycle. This evolution is consistent with significant capacity shifts to new, lower voltage lithium environments in the aged oxide that were not present in the pristine oxide, which results in voltage fade.

The harvested positive electrode, from the 0.75–3.15 V, 500-cycle cell, was examined in a Li-metal counter electrode cell using a specific protocol intended to track and quantify voltage fade in various layered oxide materials. Comparison of data from the harvested electrode cell with data from a fresh electrode cell, cycled in the 2.4–7 V vs. Li/Li$^+$ voltage window, is shown in Figure 7. The oxide-specific energy densities of pristine electrodes are 1100 and 990 mWh/g during charge and discharge cycles, respectively (Figure 7a). After 10 cycles, the values decrease to 1060 and 970 mWh/g, a reduction of 40 and 20 mWh/g during the charge and discharge cycles, respectively. In contrast, energy densities of the harvested electrodes are 965 and 905 mWh/g during charge and discharge cycles, respectively. These...
values are slightly higher after 10 cycles, suggesting that, after approximately 500-aging cycles, additional cycling does not degrade electrode energy densities. Furthermore, these discharge energy density values are still significantly higher than those for LiNi0.8Co0.15Al0.05O2 (800 mWh/g) and Li1.05(Ni1/3Mn1/3Co1/3)0.95O2 (700 mWh/g) cycled under similar conditions.15

Similarly, the average voltages of fresh electrodes are 3.934 and 3.624 V during charge and discharge cycles, respectively (Figure 7b). After 10 cycles, the values decrease to 3.814 and 3.553 V, a reduction of 120 mV and 71 mV during charge and discharge, respectively. In contrast, average voltages of the harvested electrode are 3.661 and 3.419 V during charge and discharge cycles, respectively. After 10 cycles, the values are 3.638 and 3.408 V, a reduction of 23 mV and 31 mV during charge and discharge, respectively. The significantly smaller changes in average voltage and the minimal energy density changes suggest that the aged-oxide has attained a quasi-equilibrium crystal structure that is more resistant to change on further cycling.

The capacities of harvested LTO negatives electrode, from the 500-aging cycles, additional cycling does not deteriorate electrode energy densities. Furthermore, these discharge energy density values are still significantly higher than those for LiNi0.8Co0.15Al0.05O2 (800 mWh/g) and Li1.05(Ni1/3Mn1/3Co1/3)0.95O2 (700 mWh/g) cycled under similar conditions.15

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The capacities of harvested LTO negatives electrode, from the 500-cycle sample, were also determined; these data are compared with fresh electrode data in Figure 8. The lithiation and delithiation capacities of 500-cycle LTO electrodes were similar to those collected on freshly prepared cells. Furthermore, the voltage hysteresis is also lower for the 500-cycle electrodes indicating that the performance of these LTO-based electrodes does not deteriorate on aging. The slightly higher capacities seen for the harvested electrodes suggest that progressively more LTO-particles become accessible to the electrolyte with cycling.

Summary of the electrochemical characterization data.— The data presented above show that changes to the LTO-negative electrode during cycling are small. Therefore, most performance changes observed in the full cell data can be attributed to the Li1.2Ni0.15Mn0.55Co0.1O2–based positive electrode.

A salient feature of the full cell data is the initial rise in cell capacity observed both in 0.75–2.55 V and 0.75–3.15 V cycling ranges. This capacity increase indicates that additional sites in the oxide crystal structure become accessible to the Li+ during cycling. In a recent article, we explained the capacity gain and voltage fade of Li1.2Ni0.15Mn0.55Co0.1O2 electrodes cycled below the activation plateau by invoking the development of local spinel environments in the oxide structure.16 A similar rationale is applicable for the capacity gain observed in the full cell data. For example, during full cell cycling between 0.75–2.55 V the oxide cycles between ∼2.3 and 4.1 V vs. Li/Li+, well below the oxide activation plateau. In this case, the gradual conversion of the oxides’ layered LiMO2 (M = Ni, Mn, Co) environments to spinel environments with lower Li+ site energies explains both the capacity increase and voltage reduction observed in the data (see Figs. 4a, 4c, 6a, 6c). During full cell cycling between 0.75–3.15 V the oxide cycles between ∼2.3 and 4.7 V vs. Li/Li+, beyond the voltage required to activate the oxides’ layered Li2MnO3.

Figure 6. Capacity-voltage (a, b) and differential-capacity (c, d) profiles of positive electrodes harvested from full cells (vs. LTO) cycled in the 0.75–2.55 V and 0.75–3.15 V range, after initial cycles and after 500 cycles. The data shown were obtained with a 15 mA/g current at 30 °C; g refers to grams of oxide in the positive electrode. The inset of (c) is a magnified view of the 2.0–4.0 V range showing peaks for the 500-cycle sample.
environments that also gradually transform to spinel environments making still more sites available for Li\(^+\) cycling.

After the rise over the first 200 cycles, cell capacities start a gradual decline (Figs. 3 and 4). This capacity vs. cycle number trend results from an interplay of processes that include the following: (i) capacity gain, from additional sites available to Li\(^+\) because of oxide-structure transformations, as explained above; and (ii) capacity loss, from Li\(^+\) trapping in surface films on the LTO negative electrode, as shown later. Because the oxide attains a quasi-equilibrium crystal structure that is more resistant to transformation on extended cycling, the latter (Li\(^+\) trapping) process becomes more dominant causing a gradual decline in cell capacity.

Other conspicuous features of the electrochemistry data include the voltage hysteresis observed in the cycling profiles (Figs. 4 and 6), and the increasing discharge capacity during high-current cycling in the 0.75–3.15 V range (Fig. 4). The voltage hysteresis is attributed to the energy required for reversible migration of transition metal ions between different sites in the oxide structure, depending on local Li concentration.\(^{15,16}\) The increasing discharge capacity during high current cycling apparently results from the observed Li\(^+\) inventory shifts to lower voltages because of the layered-spinel transformation. This structural change increases the oxides’ impedance at higher voltages, while reducing it at lower voltages,\(^{15}\) gradually improving oxide performance at the higher currents.

**Transition metal analysis of electrolyte and electrode coating samples.**—As stated previously, ICP-MS data (see Table IIIa) were obtained on samples of the fresh and harvested electrolyte and negative electrode coatings. Only trace amounts of Mn, Ni and Co were present in the fresh electrolyte sample, as expected. The concentrations of these elements in the electrolyte increase on cycling, yet remain small, possibly reflecting saturation in the electrolyte. The highest concentrations, observed for Mn, increased from 0.007 (fresh electrolyte) to 0.064 \(\mu g/gm\) for the 0.75–2.55 V, 500-cycle sample, and to 0.165 \(\mu g/gm\) for the 0.75–3.15 V, 500-cycle sample. That is, the Mn content in the electrolyte increases by \(\sim 9\) times after 500 cycles in the 0.75–2.55 V range, and \(\sim 23\) times after 500 cycles in the 0.75–3.15 V range. Similar trends are also observed for Co and Ni. However, the corresponding negative electrode samples show much higher transition metal contents (Table III). For example, the 0.75–3.15 V, 500-cycle electrode sample shows a Mn content of 264 \(\mu g/gm\), which is 1600 times more than that in the electrolyte; the Ni content in the electrode sample is 84 \(\mu g/gm\), \(\sim 715\) times that in the corresponding electrolyte. These data indicate that Mn, Ni and Co prefer to deposit on the negative electrode, rather than accumulate in the electrolyte, during cell cycling.

All of the transition metals deposited at the negative electrode originate at the positive electrode. In a previous article we examined transport of Mn\(^{2+}\) ions, from the positive to negative electrode, through the formation of complexes in which the cation is chelated by carboxylate groups that result from degradation of the carbonate solvents.\(^{19}\) To examine the effect of such transition metal migration on the oxide composition we conducted Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES) on fresh and harvested positive electrodes. Molar ratios for each element, calculated from mass fraction data obtained from the analysis are presented in Table IIIb. These ratios reflect changes in the lithium content of the electrode relative to the transition metal oxide matrix and changes in the composition of the oxide itself. When presented in this format, the data clearly show that the lithium content varies, while the transition metal composition of the various samples is the same within tight tolerances, readily attributable to measurement uncertainty. These data lead us to conclude that cycling, and the resulting transition metal dissolution, induces negligible changes to the oxide composition. This conclusion is in accordance with the negligible capacity fade determined for the harvested positive electrodes.

**SIMS data on fresh and harvested negative electrodes.**—Figure 9 shows SIMS sputter depth profiles for titanium, manganese, nickel, and cobalt from a fresh negative electrode and from electrodes harvested from discharged cells cycled in the 0.75–2.55 V and 0.75–3.15 V voltage ranges. The profiles of the fresh (as-prepared) negative...
Table III. Chemical analysis of electrolytes and electrode coatings.

\( \text{Concentration in sample, } \mu g/g \)

| Sample       | Cycling | Mn   | Co   | Ni   |
|--------------|---------|------|------|------|
| Electrolyte  |         |      |      |      |
| Fresh        | None    | 0.007| 0.001| 0.007|
| 500 cycles   | 0.75–2.55 V | 0.064| 0.004| 0.040|
| 500 cycles   | 0.75–3.15 V | 0.165| 0.016| 0.117|
| Negative Electrode | None    | 12   | 2    | 14   |
| 500 cycles   | 0.75–2.55 V | 69   | 6    | 30   |
| 500 cycles   | 0.75–3.15 V | 264  | 16   | 84   |

b. Molar Ratios of Individual Elements to the Sum of Transition Elements, obtained by ICP-OES analysis of positive electrode samples.

| Sample       | Cycling | Li/(Mn+Ni+Co) | Co/(Mn+Ni+Co) | Ni/(Mn+Ni+Co) | Mn/(Mn+Ni+Co) |
|--------------|---------|---------------|---------------|---------------|---------------|
| Positive Electrode |         |               |               |               |               |
| Fresh        | None    | 1.593         | 0.123         | 0.187         | 0.690         |
| 500 cycles   | 0.75–2.55 V | 1.517 | 0.122 | 0.187 | 0.691 |
| 500 cycles   | 0.75–3.15 V | 1.443 | 0.123 | 0.189 | 0.688 |

The most striking observation from Figure 9 is that the fresh, 1-cycle samples, and the 0.75–2.55 V 500-cycle sample show similar Mn, Ni and Co count rates, whereas the values for the 0.75–3.15 V 500-cycle sample are significantly higher. For the latter sample, the Ni and Co count rates are high initially, decrease with sputtering, and then level off at a relatively high value after a sputtering time of ~200s. The Mn count rates also show the initial decrease, and the leveling off after 200s; however, the count rates begin to increase again after 1000s, which suggests a relatively higher Mn content deeper in the electrode. In general, the sputtering times required for the transition metal count rates to level off are significantly lower than the times measured for graphite negative electrodes, under identical measurement conditions. That is, the SEI formed on LTO-negative electrodes is significantly thinner than on graphite-based electrodes, which is also in agreement with XPS data on these electrodes as discussed below.

XPS examination of fresh and harvested negative electrodes.—Figure 10 displays the O1s, Ti2p, F1s and C1s spectra from a fresh negative electrode and from electrodes harvested from discharged cells cycled in the 0.75–2.55 V and 0.75–3.15 V voltage ranges; the element concentrations estimated from the XPS spectra are listed in Table IV. The changes observed in the data clearly indicate the presence of electrode surface films that arise from cycling. This finding is somewhat surprising because solvent reduction processes associated with this electrolyte are typically assumed to occur at voltages <0.8 V vs. Li/Li\(^+\). However, surface films on LTO-negative electrodes have been observed previously.

The O1s spectrum (Fig. 10a) of the fresh negative electrode shows a peak at 530.2 eV that arises from O\(^2−\) anions in the Li\(_4\)Ti\(_5\)O\(_{12}\) crystal structure. Two corresponding peaks are observed in the Ti2p spectrum (Fig. 10c) because of spin-orbit coupling; these peaks are at 458.8 eV and 464.7 eV (Ti 2p\(_{3/2}\)) and at 464.7 eV (Ti 2p\(_{1/2}\)). The O1s spectrum also shows a broad peak centered at ~531.2 eV, which is assigned to a carbonaceous surface species that is associated with peaks centered at 285.1 eV and 288.5 eV in the C1s spectrum (Fig. 10g). Note that the C1s spectra of the fresh negative electrode also contains contributions from the PVdF [-((CH\(_2\))\(_n\)CF\(_2\))\(_2\)] binder (286.2 eV, 290.8 eV) and the C45 carbons added to improve electronic conductivity. The F1s spectrum of the fresh electrode (Fig. 10e) shows a dominant peak centered around 687.8 eV that arises from C-F bonds in the PVdF binder; a weak, broad peak centered at 685.1 eV is attributed to LiF. This LiF
probably results from a partial reaction of the carbonaceous surface species with hydrofluoric acid generated by a dehydrofluorination reaction in the PVdF binder.13

Significant changes are seen in the 1-cycle samples spectra. The 530.2 eV peak in the O1s spectra, and the Ti 2p3/2 and Ti 2p1/2 peaks in the Ti2p spectra, show reduced intensities, which indicates that the oxide is partially buried under a surface species formed during the cycling; the intensity reduction is greater for the sample cycled in the 0.75–3.15 V range. The F1s spectra show a small reduction in the PdF (P-F) peak intensity, but a significant increase in the 685.1 eV peak intensities, which result from a higher LiF content.

A further increase in LiF intensity, and a corresponding decrease in PdF intensity, is observed in the F1s spectrum (Fig. 10f) of the 500-cycle sample cycled in the 0.75–3.15 V range; the PdF intensity decrease is also observed in the C1s spectrum (Fig. 10h). The 500-cycle samples also show further intensity reductions in the 458.8 eV and 464.7 eV peaks (Ti 2p spectra), and in the 530.2 eV peak (O1s spectra), indicating further coverage of the Li4Ti5O12. A corresponding intensity increase, seen in the 531–534 eV range (Figs. 10a and 10b), indicates increasing oxygen content in the electrode surface films.

In addition to the above data, we obtained P2p spectra and spectra in the 40 to 85 eV range; these data are shown in Figure 11. As expected, the fresh electrode showed no intensity in the P2p region. On cycling, however, the P2p spectra (Figs. 11c, 11d) show a small intensity increase around 137.5 eV that is assigned to P-O functional groups, and a larger intensity increase around 134.5 eV that is attributed assigned to P-O functional groups; these intensity increases are a consequence of LiPF6 salt degradation. In the 40 to 85 eV range (Figs. 11a, 11b), the fresh electrode spectra show peaks centered at 62.5 eV (Ti3s) and 55.1 eV (Li1s), which arise from Li4Ti5O12. On cycling, the intensity of these peaks decrease; this intensity reduction is especially significant for the 0.75–3.15 V, 500-cycle sample. However, significant intensity increases are observed around 56.2 eV (Li1s), which indicates a buildup of lithiated compounds at the electrode surface. Peaks associated with Mn3p (≅49 eV), and Ni3p (≅68 eV) were also observed in some samples. The Co3p (≅61 eV) peaks could not be definitively identified because of overlap with the Ti3s peak intensity and its relatively low content in the surface films. The presence of transition metal elements on the negative electrode surface are consistent with the information obtained by the ICP-MS chemical analysis.

In summary, the negative electrode surface films increase on cycling and are more prominent for the sample cycled in the 0.75–3.15 V than in the 0.75–2.55 V range. These surface films apparently result from electrolyte solvent and salt decomposition. The significantly reduced intensities for the oxide, binder and C45 carbon peaks suggest an effective film thickness around 5 nm, which is roughly the

Table IV. Element concentrations (at.%) calculated from XPS spectra of fresh positive and negative electrodes, and from electrode samples harvested from cells cycled in the 0.75–2.55 V and 0.75–3.15 V ranges.

| Sample          | F  | Mn  | O   | Ti  | C   | P   | Li  |
|-----------------|----|-----|-----|-----|-----|-----|-----|
| Positive Electrode |    |     |     |     |     |     |     |
| Fresh           | 19.6 | 2.7 | 14.1 | 0.0 | 52.8 | 0.0 | 10.8 |
| 0.75–2.55 V, 1 cycle | 22.8 | 2.2 | 12.4 | 0.0 | 45.3 | 2.3 | 14.9 |
| 0.75–3.15 V, 1 cycle | 24.2 | 2.1 | 13.3 | 0.0 | 43.2 | 1.6 | 15.6 |
| 0.75–2.55 V, 500 cycles | 23.8 | 1.9 | 13.5 | 0.0 | 44.5 | 3.3 | 13.1 |
| 0.75–3.15 V, 500 cycles | 21.9 | 1.6 | 15.0 | 0.0 | 41.6 | 3.8 | 16.1 |
| Negative Electrode |    |     |     |     |     |     |     |
| Fresh           | 19.0 | 0.0 | 16.2 | 5.3 | 51.5 | 0.0 | 8.0 |
| 0.75–2.55 V, 1 cycle | 24.2 | 0.0 | 9.8 | 3.3 | 38.6 | 0.8 | 23.3 |
| 0.75–3.15 V, 1 cycle | 23.8 | 0.0 | 9.4 | 2.3 | 36.3 | 0.9 | 27.3 |
| 0.75–2.55 V, 500 cycles | 21.7 | 0.5 | 10.8 | 2.7 | 35.1 | 2.3 | 26.9 |
| 0.75–3.15 V, 500 cycles | 23.8 | 0.5 | 10.8 | 1.1 | 25.4 | 2.4 | 36.1 |
The XPS examination of fresh and harvested positive electrodes.—Figure 12 displays the O1s, C1s, F1s, and P2p spectra from a fresh positive electrode that arise from cycling; these observations are consistent with other reports of electrolyte degradation products in positive electrodes.17 The 500-cycle samples data show additional intensity increases centered around 687.8 eV, which is assigned to LiF. A peak centered near 686.5 eV, is assigned to P-O functional groups in the PVdF binder. The1-cycle samples data (Figs. 12c and 12d) show that the C-C peak is unchanged, which is because of the high specific surface area of the C45 carbons and its extensive redeposit on the electrode during cycling;25 further studies are needed to examine these hypotheses.

In summary, the XPS data indicate distinct surface films on the positive electrode. These observations are similar to those reported previously on positive electrodes from Li1.3Ni0.1Mn0.5Co0.2O2 graphite cells.26 The presence of oxide, C45 carbon and binder peaks in the O1s, C1s and F1s spectra, of even the 500-cycle sample data, indicates that these films are less than 5 nm thick on average, thin enough for photoelectrons to escape the high energy electrons that are observed for the 500-cycle samples; however, the higher intensity of peaks associated with C-O and P-O functionalities suggests an over-layer on this component. However, the 685.1 eV peak intensities either remain the same (Fig. 12e) or decreases (Fig. 12f), which indicates that either the LiF content does not increase, and/or is covered by other species, during the aging cycles.

Conclusions

Cells containing Li1.3Ni0.1Mn0.5Co0.2O2-based positive electrodes and Li4Ti5O12-based negative electrodes were electrochemically cycled in two voltage ranges, one above (0.75–3.15 V) and one below (0.75–2.55 V) the oxide activation plateau. The conclusions of our electrochemical and physicochemical diagnostic tests on these cells include the following:

1. As expected, cells cycled above the oxide activation voltage (> 4.5 V vs. Li/Li+) yielded much higher capacities (> 235 mAh/g) than cells cycled below this voltage (> 68 mAh/g).
2. Capacity fade is small, even for cells cycled in the 0.75–3.15 V cycling range.
3. Voltage fade is the dominant contributor to energy fade, especially for cells cycled in the 0.75–3.15 V range; a small reduction in average voltage is also observed for cells cycled in the 0.75–2.55 V range.
4. The root cause of both voltage fade and the initial increase in cell capacity is the transfer of capacity (Li inventory) form high to low voltages, driven by the emergence of new low-voltage Li environments in the oxide structure.
5. For the 0.75–3.15 V cycling, the capacity-voltage hysteresis decreased on cycling but persisted even after 500 cycles in the 0.75–3.15V range. The reduction in hysteresis is non-uniform over the cycling window.
6. The capacity-voltage hysteresis decreased on cycling but persisted even after 500 cycles in the 0.75–3.15 V range. The reduction in hysteresis is non-uniform over the cycling window.
7. Transition metal (Mn, Ni, Co) accumulation at the negative electrode is much higher than in the electrolyte, indicating a preference for deposition on the LTO-electrode over accumulation in the electrolyte.
8. Electrode surface films are observed on both positive and negative electrodes. These films contain organic and inorganic species, which are mainly the products of electrolyte solvent and salt degradation. The surface film presence on the ~1.55 V vs. Li/Li+ LTO-electrode is a surprising (though previously reported) result. Studies are underway to determine the mechanisms that lead to these films, and the information will be presented in future articles.

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