Aluminum Borate Coating on High-Voltage Cathodes for Li-Ion Batteries

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Li-rich layered-layered nickel manganese cobalt oxides (LLNMC) of the type Li2MnO3-LiMO2 (M = Mn, Co, Ni) are promising cathode materials due to their higher specific capacities and discharge voltages compared to state of art materials. However, these materials have yet to exhibit adequate cycle life and power characteristics in practical cells, partly due to the instability of electrolytes at these high voltages. Thin coatings of inorganic materials such as Al2O3, AlPO4, and AlF3 have been shown to minimize these degradation processes, especially on high voltage cathodes. Here, we report the use of a new aluminum borate-based coating material on the LLNMC cathode at high active mass loadings. AlBO3-coated cathodes demonstrate a sevenfold increase in lifetime compared to uncoated material, as well as higher specific discharge energies vs. analogous AlPO4-coated materials. SEM and TEM confirm the thin coatings of amorphous material. Detailed electrochemical studies including Tafel polarization, FITT, and Electrochemical Impedance Spectroscopy (EIS) show that the AlBO3 coating improves the kinetics of electron transfer.

Experimental

Materials synthesis.— The LLNMC cathode powder used in these studies was synthesized at Argonne National Laboratory (Argonne, IL) using processes previously developed by UT Austin and NASA and appropriately modified by ANL. The material was used as received for the pristine sample. The composition of the material is Li1.2Ni0.54Mn0.13Co0.13O2 and the measured tap density was 1.97 g/cm3. The 2 wt% AlPO4- and AlBO3-coated materials were prepared using a modification of the previously published procedure, as described below.

For the 2 wt% AlPO4 coating, 20 g of cathode powder was suspended in 150 mL of diH2O, and a stoichiometric amount of aluminum nitrate nonahydrate (1.23 g, 3.2 mmol) was dissolved in the suspension. The phosphate solution was added drop-wise to the cathode solution at a rate of 1 drop/s with rapid stirring, and then allowed to stir at 100 ◦C for 4 h, then allowed to cool to room temperature. The solution was evaporated to dryness at 100 ◦C. The dried powder was crushed and annealed at 400 ◦C for 4 h, then allowed to cool to room temperature in the furnace. For the 2 wt% AlBO3 coating, 20 g cathode powder was suspended in 150 mL of diH2O, and a stoichiometric amount of aluminum nitrate nonahydrate (1.75 g, 4.7 mmol) was dissolved in the suspension. A solution of the anion precursor was prepared by separately dissolving ammonium phosphate (0.43 g, 3.2 mmol) in 50 mL diH2O. The phosphate solution was added drop-wise to the cathode solution at a rate of 1 drop/s with rapid stirring, and then allowed to stir at room temperature overnight. The solution was evaporated to dryness at 100 ◦C. The dried powder was crushed and annealed at 400 ◦C for 4 h, then allowed to cool to room temperature in the furnace. For the 2 wt% AlBO3 coating, 20 g cathode powder was suspended in 150 mL of diH2O, and a stoichiometric amount of aluminum nitrate nonahydrate (1.75 g, 4.7 mmol) was dissolved in the suspension. A solution of the anion precursor was prepared by separately dissolving ammonium phosphate (0.43 g, 3.2 mmol) in 50 mL diH2O. The phosphate solution was added drop-wise to the cathode solution at a rate of 1 drop/s with rapid stirring, and then allowed to stir at room temperature overnight. The solution was evaporated to dryness at 100 ◦C. The dried powder was crushed and annealed at 400 ◦C for 4 h, then allowed to cool to room temperature in the furnace.

Material characterization.— Phase characterizations were performed using X-Ray powder diffraction (Panalytical, PW3040-PRO, Cu Ka radiation between 5◦ and 90 ◦ 2θ, scan rate 0.02◦ 2θ/min) at an accelerating voltage of 45 kV and tube current of 20 mA. Surface morphologies were studied using a JEOL 1550VP Field Emission scanning electron microscope (SEM) equipped with an Oxford EDS detector. Additional morphological studies were conducted with a FEI Tecnai F30ST (300 kV) transmission electron microscope

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Improving our energy storage and transport capabilities remains a key challenge as we move toward a society based on renewable energy sources. A central problem in the development of next-generation lithium-ion batteries is to develop improved cathode materials with increased energy storage capacities. Li-rich layer-stacked cathode materials of the form Li2MnO3-LiMO2 (M = Li, N, Al, Co, Ni) have attracted considerable interest over the last decade due to their higher specific capacities and discharge voltages compared to state-of-the-art materials. However, these high capacity materials have yet to be adopted in commercial cells due to multiple technical barriers, including voltage and power fade during cycling, poor power characteristics, and modest cycle life at the high charging voltage (~4.5 V) necessary to achieve these capacities. A unique feature of these layered-layered NMC (Li-rich layer-stacked) cathode materials is that they release oxygen during the first charge step at 4.5 V, concomitant with oxidation of the Li2MnO3 component. Although this process enables the material to yield its high specific capacity, the resulting structural instability and degradation, oxygen-induced reactions, and loss of lithium to oxidation products cause an irreversible capacity loss of 50–100 mAh/g during the formation cycle. Additionally, although the high voltage needed to fully cycle this cathode increases the energy yield, it appears to be a contributing factor to the decrease in overall cell cycle life, possibly caused by the buildup of electrolyte-derived surface films.

One successful strategy for stabilizing high-voltage LLNMC cathodes against electrolyte decomposition processes involves coating the active material with a thin layer of inorganic material, such as Al2O3,11,12 AlPO4,13–15 AlF3,16–19 or FePO4.20 While some of these materials have yet to exhibit adequate cycle life and power characteristics in practical cells, partly due to the instability of electrolytes at these high voltages. Thin coatings of inorganic materials such as Al2O3, AlPO4, and AlF3 have been shown to minimize these degradation processes, especially on high voltage cathodes. Here, we report the use of a new aluminum borate-based coating material on the LLNMC cathode at high active mass loadings. AlBO3-coated cathodes demonstrate a sevenfold increase in lifetime compared to uncoated material, as well as higher specific discharge energies vs. analogous AlPO4-coated materials. SEM and TEM confirm the thin coatings of amorphous material. Detailed electrochemical studies including Tafel polarization, FITT, and Electrochemical Impedance Spectroscopy (EIS) show that the AlBO3 coating improves the kinetics of electron transfer.

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(TEM). Samples were dispersed on Cu/Au grids with iProH and allowed to dry. Selected samples were embedded in epoxy, microtomed to yield thin cross-sectional images, and dispersed onto grids as described above. Tap density measurements were performed with a Quantachrome Autotap instrument with 1000 taps per sample. The compositions of the cathode materials were determined using inductive coupled plasma (ICP), which was performed at the UC Davis Interdisciplinary Center for Plasma Mass Spectrometry.

Electrochemical studies.— One-sided electrodes were prepared by spreading cathode slurries on Al foil substrates using a doctor blade. The slurries consisted of 86 wt% cathode active material, 7 wt% poly(vinylidene difluoride) binder (PVDF, Sigma-Aldrich, MW$_{avg}$ = 534,000), and 7 wt% carbon black powder (Sigma-Aldrich) in N-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich). The electrode loading (14–16 mg/cm$^2$) is much higher than what is normally reported in the literature and was chosen to match the values used in prototype cells with high specific energies being built by our industrial partner (SAFT America) with the LLNMC cathode. In our experience, cells built with lower loading capacities exhibit longer lifetimes, but are less applicable to prototype and real-life cell development.

Cycle life and rate capacity studies were carried out in coin half cells, prepared by assembling the cathode, 20 μm Tonen separator, and 2 layers of a Li foil anode in Al clad CR2032 cases with stainless steel hardware and 100 μL of electrolyte (1.0 M LiPF$_6$ and 0.1 M lithium bis(oxoloxalate)borate dissolved in 20:70:10 vol% fluoroethylene carbonate : ethyl methylcarbonate : triphenylphosphate). This electrolyte was previously developed at JPL, has been shown to be compatible with the high voltage LLNMC cathode, and is less flammable for improved safety of Li-ion cells. Electrochemical studies, including DC Tafel polarization for electrode kinetics, Electrochemical Impedance Spectroscopy (EIS) for SEI characteristics, and Potentiostatic, Intermittent Titration Technique (PITT) for diffusional kinetics of Li$^+$ within the cathodes were carried out in three-electrode pock cells. These cells were assembled with a 40 cm$^2$ LLNMC cathode, a Li-wrapped Ni mesh anode, a Li reference electrode, and 3 mL of electrolyte. The Li reference electrode was made with a 1 x 1 cm Ni mesh substrate spot-welded to a Ni tab and wrapped with two layers of Li foil. The electrode was sealed in an envelope made of Tonen separator and placed between the cathode and anode, covering only a small portion of the anode/cathode. In all cases, the cells were initially charged to 4.6 V vs. Li$^+$/Li, undergoing a total of five formation cycles between 2.5 V and 4.6 V. Long term cycling was then carried out in a window of 2.5 to 4.5 V vs. Li$^+$/Li. All cycling was done at a rate of C/10 followed by a constant voltage step at the charge cutoff voltage for one hour, during which the current was observed to fall to 3–5% of the rated capacity. EIS, Tafel, and PITT measurements were made as a function of cycle number at 4.3 V (approximately 80% SOC) using a potentiostat/galvanostat/frequency response analyzer (Bio-logic VMP2). For the EIS measurements, the applied AC signal was 5 mV peak-to-peak over a frequency range of 200 kHz–10 mHz. Tafel polarization measurements were performed by applying a 0.5 mV/s potentiodynamic sweep from 4.3 V to 4.15 V vs. Li$^+$/Li to approximate steady-state conditions, and the resulting curves were corrected for mass transfer interference. PITT measurements were performed by applying 10 mV discharge pulses from 4.3 V to 4.25 V vs. Li$^+$/Li. Impedance spectra and PITT data were fitted using the Bio-Logic EC-Lab software. All charge-discharge cycling and capacity measurements were performed using an Arbin battery cycler.

Results and Discussion

Coating procedure and bulk analyses.— It is important to note that variations in synthetic conditions can have dramatic effects on the uniformity of inorganic surface coatings. One variation used earlier in our labs involved precipitating nanoparticles of the coating material, subsequently co-suspending them with cathode powder, then filtering and sintering at a relatively low temperature (400 °C, 4 hrs) to keep the coating amorphous. TEM observations of an AlPO$_4$-coated LLNMC material prepared via this suspension method showed uneven deposition of AlPO$_4$ “agglomerates”, resulting in areas of extremely thick (∼200 μm) coating interspersed with bare surface (Figure S1). This pattern suggested that adsorption of the AlPO$_4$ nanoparticles is kinetically controlled, and that an alternate synthesis procedure could provide a more controlled method of achieving uniform surface coatings. Thus, we opted for an in situ precipitation method: the active material was suspended in a solution of the cationic component followed by subsequent addition of the anionic component, using drop-wise addition and rapid stirring to control the precipitation of small coating particles on the active material. The suspension was dried and sintered at the same temperature of 400 °C to ensure that the coating remained amorphous. We found that it was important to maintain rapid stirring during mixing and drying in order to achieve the best electrochemical performance. TEM observations of the AlPO$_4$-coated LLNMC material prepared using this in situ method confirmed the superiority of this procedure in its ability to apply a thin, even layer of AlPO$_4$ to the surface of the cathode particles (Figure S2), consistent with reports of other materials synthesized in this manner. This procedure was used for both coated materials to keep their treatments as consistent as possible, even though the borate coating does not precipitate at the initial concentration.

The tap densities of the pristine, AlPO$_4$-coated, and AlBO$_3$-coated materials were 1.97 g/cm$^3$, 1.88 g/cm$^3$, and 1.51 g/cm$^3$, respectively. A range of 1.4–1.8 g/cm$^3$ has been commonly observed for these layered materials. ICP analyses of the pristine and coated materials are summarized in Table I. The measured compositions of the base cathode powder and the wt% of coating material were consistent and in good agreement with the expected values. ICP analysis of separately prepared and isolated “AlBO$_3$” showed that this material contains a 1:1 ratio of Al:B.

X-ray diffraction.— Figure 1 shows the X-Ray powder diffraction (XRD) patterns of the pristine, AlPO$_4$-coated, and AlBO$_3$-coated cathode powders prior to cycling; (d) pure “AlBO$_3$” prepared in the absence of cathode powder.

| Material | Composition | Coating wt% |
|----------|-------------|-------------|
| Pristine | Li$_{12}$Mn$_{0.53}$Ni$_{0.17}$Co$_{0.12}$O$_2$ | - |
| AlPO$_4$-coated | Li$_{12}$Mn$_{0.55}$Ni$_{0.15}$Co$_{0.10}$O$_2$•0.013(AlPO$_4$) | 1.9 |
| AlBO$_3$-coated | Li$_{12}$Mn$_{0.53}$Ni$_{0.17}$Co$_{0.12}$O$_2$•0.019(AlBO$_3$) | 1.9 |
| “AlBO$_3$” | Al$_{0.97}$BO$_3$ | - |

Figure 1. XRD data of (a) pristine, (b) AlPO$_4$-coated, and (c) AlBO$_3$-coated cathode powders.
LLNMC cathode materials as well as the isolated AlBO3 coating material. The XRD analyses of all three cathode materials were nearly identical and could easily be indexed to that expected for the Li2MnO3-LiMO2 (M = Mn, Co, Ni) class of materials, demonstrating that the coating materials and methodology do not alter the structure of the base cathode material. The absence of coating-based artifacts in the XRD patterns is consistent with the small (2 wt%) amount of coating material. The diffraction pattern of pure “AlBO3” prepared in the absence of cathode powder was generally broad and diffuse, consistent with production of an amorphous material at the sintering temperature of 400 °C.

**SEM studies of morphology and elemental composition.—** The morphologies of the powders were investigated by SEM and are shown in Figure 2. In all cases, the cathode particles are spherical but finely micro-structured. The primary particles are crystals 100–200 nm in diameter. These primary particles agglomerate into spherical secondary particles between 6–10 μm in diameter, with an average diameter of approximately 8 μm. Application of an AlPO4 or AlBO3 inorganic coating does not appear to significantly agglomerate, disintegrate, or otherwise change the size distribution of these secondary particles (Figures 2a, 2b, 2c). However, small particles and fibers (see arrows) were observed to have been randomly deposited on the surfaces of some AlPO4-coated (Figure 2e) and AlBO3-coated samples (Figure 2f). Their enrichment in elements comprising these coatings (Al and either P or B) were confirmed by EDS (Table II).

EDS mapping corrected for spectral overlap demonstrated even distribution of Al over the surfaces of the coated particles, even where a coating was not visually observed in the SEM image (Figure 3). This suggested that the coating might be conformal despite the mixed morphology observed in SEM. However, the resolution of SEM/EDS mapping is insufficient to directly image this layer. Thus, both materials were further studied by TEM.

**TEM studies of AlPO4- and AlBO3-coated material.—** HRTEM images taken at the circumference of AlPO4–coated and AlBO3–coated particles are shown in Figures 4a and 4b, respectively. Both coatings are clearly visible at this level of magnification. The lines in the bulk regions of the particles are due to the lattice ordering of transition metal layers, which is highly characteristic of this class of layered-layered cathode material.

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**Table II. Comparative amounts of elements detected by SEM-EDS on the overall surface of the particle vs. specific features (arrows) in AlPO4-coated (Figure 2e) and AlBO3-coated (Figure 2f) samples.**

| Analysis site | O   | AlPO4-coated | AlBO3-coated |
|---------------|-----|--------------|--------------|
| Overall       | 23.2| 44.7         | 36.8         |
| Arrow         | 50.9| 7.3          | -            |

**Figure 4.** (a) HRTEM (490kX) image of an AlPO4 coating layer on LLNMC, (b) HRTEM (790 kX) image of an AlBO3 coating layer on LLNMC.
The AlPO₄ coating layer in Figure 4a is about 3 nm thick and can be recognized by its dissimilar, granular appearance and non-layered internal structure. EDX of these regions detected Ni, Mn, Co, and O in the purported LLNMC region and Mn, Al, and P in the purported coating layer. No other elements were detected in the respective regions, indicating a clear difference in their compositions and a strong likelihood that Al/P-enrichment in the outer layer was due to the applied coating. The presence of Mn in this outer layer may indicate partial diffusion and/or trapping of Mn cations from the LLNMC in the coating layer during coating or sintering.

The AlBO₃ coating layer in Figure 4b has a similarly granular, amorphous structure and was also observed by EDX to be enriched in Al relative to the bulk. The thickness of the coating is slightly less uniform than in the AlPO₄-coated sample, ranging from 2 nm in some regions to >10 nm in others. It is unclear whether the more variable distribution of the AlBO₃ network arises during the solvent evaporation process or during sintering.

Given the microcrystalline surface morphology observed in SEM and the fact that the high capacity LLNMC material used in this study is relatively new, we took the opportunity to investigate its internal structure by taking microtome slices of AlPO₄-coated particles embedded in epoxy. The bright field TEM image in Figure S3 shows that these LLNMC materials are porous in a way that allows epoxy or electrolyte access to surfaces of the center of the particle, which are not as likely to be coated if the precipitation procedure is under kinetic control. Thus, although coverage on the outer surface of the particles appears to be fairly conformal, it appears that some uncoated cathode/electrolyte Li⁺ diffusion boundaries are still present at the interior surfaces of these particular LLNMC materials. This demonstrates that the structural interplay between the coating and base cathode material is an important aspect of these coating studies and that the results of one study should not be generalized to all materials, even if they have the same nominal composition.

**Electrochemical performance.—** Initial charge and discharge voltage profiles at C/10 for all three materials in Li half-cells are shown in Figure 5. The first cycle charge capacities of both coated materials (AlPO₄, 247 mAh/g; AlBO₃, 262 mAh/g) are lower than that of the pristine material (313 mAh/g). However, the pristine material exhibits the greatest irreversible capacity loss (61 mAh/g). Both inorganic coatings stabilize the capacity of the LLNMC cathode, but the AlBO₃-coated material exhibits the smallest irreversible capacity (7 mAh/g) of all three samples. The discharge performance of the AlBO₃-coated material is highly improved over that of the AlPO₄-coated material, which exhibits a much lower discharge capacity (195 mAh/g), as well as a steeper discharge slope (Table III).

Long-term cycling studies at C/10 with 5 initial activation cycles between 2.5–4.6 V also show substantial differences in cycle life and capacity (Figure 6). The AlBO₃-coated material shows the best cycle life, achieving and maintaining an initial discharge capacity above 240 mAh/g for about 50 cycles. After this, the material continues to exhibit a slow fade, achieving a total of 180 cycles above 200 mAh/g (80% capacity retention). The pristine, uncoated cathode material exhibits a similar initial capacity, but rapidly fails after only 25 cycles. The AlPO₄-coated material exhibits a comparatively lower initial capacity of about 210 mAh/g, which is maintained for 75 cycles until the material exhibits rapid capacity fade and cell failure. The AlBO₃-coated material thus exhibits the highest capacity and the best capacity retention in this study. Again, we note that these cycle lives reported here are for cells built to prototype loading specifications rather than the lower loadings that are more commonly reported in the literature.

Destructive physical analyses (DPA) were performed on cells with these three cathode materials at the end of their cycling tests. These analyses showed that cell failure was correlated with “cell drying”, in which the electrolyte appears to have completely degraded, leaving a thick, pasty, water-reactive solid on surface of the Li anode facing the cathode (Figure S4). This phenomenon was previously observed when we attempted to make prototype cells with LLNMC cathodes, and was correlated with subsequent formation of lithium dendrites.29 Interestingly, when the cathodes from these cells were harvested and placed into fresh cells, the cells resumed their normal cell cycling behavior at the capacity level observed prior to rapid fade and failure (Figure S5). This demonstrates that the cathode materials are not

| Table III. First cycle charge, discharge, and irreversible capacities of representative cells of LLNMC cathode materials at C/10 between 2.5–4.6 V. |
|------------------|-------------------------|-------------------------|-------------------------|
| Material         | Charge Capacity (mAh/g) | Discharge Capacity (mAh/g) | Irreversible Capacity (mAh/g) |
| Pristine         | 313                      | 252                      | 61                       |
| AlPO₄-coated     | 247                      | 195                      | 52                       |
| AlBO₃-coated     | 260                      | 253                      | 7                        |

![Figure 5](image5.png)  
**Figure 5.** First cycle charge and discharge curves (at C/10) of AlBO₃-coated, AlPO₄-coated, and pristine cathodes between 4.6–2.5 V in coin half-cells.

![Figure 6](image6.png)  
**Figure 6.** Cycle life and capacity stability of coin-format Li half cells with AlBO₃-coated, AlPO₄-coated, and pristine cathodes at C/10 between 4.6–2.5 V (first five cycles) and 4.5–2.5 V (long term).
Figure 7. Rate capacity of AlBO3-coated, AlPO4-coated, and pristine cathodes.

severely degraded in their performance during cycling, and that the loss of electrolyte and the interfacial degradation at the anode are responsible for the failure of these cells. The large increase in coin cell cycle life for the coated materials (70+ cycles for the coated materials vs. ~25 cycles for the pristine material) suggests that application of a surface coating appreciably slows this electrolyte decomposition failure mode.

The rate capacities of all three samples at room temperature (23 °C) were compared by subjecting cells to five C/20 formation cycles, then cycling at increasing rates between C/10 to 2 C before returning to C/10 (Figure 7). The AlPO4-coated material performs similarly to the pristine material at most rates. The AlBO3-coated material yields the highest capacities at all rates. The superior rate capability of the AlBO3-coated material is more strongly evident at high discharge rates; at 2C the AlBO3-coated material yields 55 mAh/g while the two others yield 20 mAh/g. The capacities of all three materials were fairly constant for all materials throughout cycling at increasing rates between C/10 to 2 C before returning to C/10, which suggests that cycling at high rates does not damage the LLNMC material.

Electrochemical Impedance Spectroscopy (EIS).—EIS studies were carried out in three-electrode pouch cells over 25 cycles to see if the coatings have an effect on the initial electrochemical characteristics or their rate of change over time (Figure 8). All studies were carried out at 4.3 V (approximately 80% SOC) at 25 °C. These measurements were made under potentiodynamic conditions at slow scan rates of 0.5 mV/s, approximating steady-state conditions. The specific exchange currents were extracted from limiting current-corrected Tafel plots (Figure S7) and are plotted vs. cycle number (Figure 10). The AlPO4-coated and pristine materials both maintain similar and constant values throughout the 25 cycles, in the range of 5-7 mΩg. This corresponds to an exchange current density of 0.07–0.1 mA/cm², which is consistent with the values from the EIS data. The AlBO3-coated material, in comparison, exhibits a higher exchange current of approximately 15 mΩg. While this value decreases over 25 cycles to 10 mΩg, it is still twice that of the other samples. The high specific exchange currents exhibited by the AlBO3-coated material suggests that this cathode composition provides an electrochemical environment that is comparatively more conducive to electron transfer reactions at room temperature, even as the materials age.

Diffusion Coefficients using Potentiostatic Intermittent Titration Technique (PITT).—The PITT technique was used to measure the diffusion constant of Li⁺ in all three materials to compare their initial values and evolutions over cycle life. All studies were carried out at 4.3 V (approximately 80% SOC) at 25 C and the potential was stepped in increments of 10 mV. A plot of ln(I) vs. t during these steps was found to be linear. It was thus possible to treat the data by solving Fick’s law for a semi-infinite system with a surface concentration perturbation, as outlined in Wen et al.:[30–32]

\[
I(t) = \frac{2Fa(C_C - C_S)}{L} \exp \left( \frac{\pi^2Dt}{4L^2} \right)
\]

where \(I(t)\) is current as a function of time, \(F\) is Faraday’s constant, \(a\) is the electrode surface area, \(C_C - C_S\) is the concentration change during the step, and \(L\) is the diffusion length, taken to be the particle radius (3 μm). The lithium diffusion coefficient \(D\) for each sample/cycle was then calculated using the long-time approximation \((t \gg L^2/D)\):

\[
D = \frac{d \ln(I)}{dt} \frac{L^2}{4\pi^2}
\]
Figure 8. EIS data for pristine, AlPO₄-coated, and AlBO₃-coated cathode materials in 3-electrode pouch cells after 2, 5, 15, and 25 cycles.

Figure 9. $R_{CT}$ (outline markers) and $R_{SEI}$ (solid markers) calculated from EIS data as a function of cycle number for pristine, AlPO₄-coated, and AlBO₃-coated cathode materials.

where $\frac{dln(I)}{dt}$ is the slope of ln I vs. t plot and $L$ is again the particle radius. The initial diffusion constants for all three materials were close, between $1.25-1.46 \times 10^{-10}$ cm²/s (Figure 11). These values rose slightly for the pristine material after formation. In comparison, the values measured for the AlBO₃-coated material remained fairly constant while those for the AlPO₄-coated material dropped slightly over 25 cycles. It should be noted that the diffusion coefficients measured here pertain to the combined effect of diffusion through the surface film and the bulk of the cathode, and it is difficult to separate these two processes.
Overall, it appears that an AlBO3 coating highly improves the cycling performance and stability of the LLNMC cathode. The irreversible capacities and cycle life of this new material are much increased over the pristine cathode as well as the AlPO4-coated cathode. The rate capability of the AlBO3-coated material is also slightly improved. This is consistent with EIS and Tafel measurements of all materials over multiple cycles, which show that the interfacial impedance is lower and the specific exchange currents are slightly higher for the AlBO3-coated material. The coatings appear to have a neutral (AlBO3-coated) to slightly negative (AlPO4-coated) effect on the Li+ mobility according to PITT diffusion coefficient measurements at room temperature. Cells with uncoated (pristine) LLNMC cathodes sustained premature failure in half-cells during cycling. The cause of this failure was identified as cell drying and not the degradation of the cathode’s structural or electrochemical properties; this “dry out” failure phenomenon may be unique to the LLNMC cathode.

Studies on other aluminum-based coatings suggest that it might be possible to further improve the performance of AlBO3 coated NMC cathodes by optimizing the amount of coating as well as the sintering temperature. This may be a fruitful topic for future study. The application and effect of this coating on other cathode types is another topic of interest, and studies are ongoing in our labs.

Conclusions

An aluminum borate (AlBO3)-based surface coating was applied to an LLNMC cathode material using a simple solution-based in situ precipitation procedure. SEM and TEM studies confirmed the success of this procedure in applying a thin coating layer to the outside surface of the LLNMC particles. However, cross-sectional TEM showed the existence of uncoated internal electrolyte/cathode interfaces in the LLNMC materials used in this study, demonstrating the unavoidable interplay between particle morphology, coating method, and coating efficacy. The AlBO3 coating treatment was found to improve the cycle life of high active mass loading cells from 25 to 180 cycles with a high discharge capacity of 240 mAh/g at C/10, making it a substantially improved alternative to the pristine and AlPO4-coated materials. The treatment was also found to have a smaller positive effect on the irreversible capacities and rate capacities of LLNMC. These performance improvements are attributed to a decrease in cathode surface electrolyte interface (SEI) resistance as well as an increase in electron transfer kinetics. Aluminum borate has thus emerged as a useful and effective surface coating for improving the cycling stability of high capacity Li-rich NMC cathodes at high voltages. This coating may also be advantageously used to increase the specific capacity of conventional cathode materials by improving their stability at high charge voltages.

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