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Minimized Metal Dissolution from High-Energy Nickel Cobalt Manganese Oxide Cathodes with Al₂O₃ Coating and Its Effects on Electrolyte Decomposition on Graphite Anodes

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High-energy nickel cobalt manganese oxides have been studied intensively as cathode materials for lithium-ion batteries. However, several hurdles need to be overcome to adopt these cathodes in commercial lithium-ion batteries. Herein, aluminum oxide (Al₂O₃) coating was applied to high-energy nickel cobalt manganese oxides (HE-NCM, Li_{1.33}Ni_{0.27}Co_{0.13}Mn_{0.60}O_{2+d}) by atomic layer deposition (ALD) and its effects on HE-NCM/graphite full cells were investigated. HE-NCM/graphite full cells have better cycling performance and efficiency when HE-NCM is coated with Al₂O₃. ICP-MS measurements show that the Al₂O₃ coating can effectively prevent transition metal dissolution from HE-NCM. XPS and FT-IR analysis suggests that the surface film on HE-NCM cathodes does not change significantly with the Al₂O₃ coating even after 50 cycles, however the surface film on graphite anodes shows a significant change. The resistance of graphite electrodes cycled with the uncoated HE-NCM is higher than that of graphite electrodes cycled with the Al₂O₃-coated HE-NCM due to the increased SEI thickness. The improved cycling performance of HE-NCM/graphite cells with Al₂O₃ coating can be attributed to the minimized resistance increase on graphite as well as the suppression of cathode active material loss.

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Because of their high capacity (>240 mAh g⁻¹), high-energy nickel cobalt manganese oxides (usually called, “Lithium-rich layered oxides”) are considered as promising cathode candidates for the next-generation lithium-ion batteries.^{1–3} However, several hurdles need to be overcome to adopt these cathodes into commercial lithium-ion batteries. The undesired transition metal dissolution from these cathodes is one of the key challenges, since it not only damages the structural stability of cathodes but also alters the composition of solid electrolyte interphase (SEI) on the surface of anodes.^{4–7} The previous report about the capacity recovery of NCM cathodes collected from full cells suggests the deterioration of anode is the main cause of full cell degradation.⁸

Although transition metal dissolution from various cathodes has been studied extensively,^{9–13} the effect of transition metal dissolution on the SEI layer of anode has not been well-established due to the large number of different materials investigated. Dissolved transition metal ions accumulate on the anode, where they induce additional side reactions of electrolyte, continuous SEI growth and further the loss of active lithium.^{6,14} It is reported that an electrolyte containing Mn ions generates a non-passivating SEI on the anode surface from the model experiments¹⁵ and also transition metal ions are electrochemically reduced on the surface of anode leading to metal deposition.¹⁶ The effect of transition metal ions on the composition and stability of the SEI on the anode has not been well addressed.

Surface coatings of cathode materials with various inert metal oxides including Al₂O₃ is one of the most common approach to suppress transition metal dissolution from cathodes.^{17–19} Al₂O₃ coating provides a stable protection layer on the cathode surface and prevents interfacial degradation of the cathode. It has been reported that an Al₂O₃ coating can minimize transition metal dissolution from cathodes.^{20,21}

In this work, an Al₂O₃ coating was applied on high-energy nickel cobalt manganese oxide (HE-NCM, Li_{1.33}Ni_{0.27}Co_{0.13}Mn_{0.60}O_{2+d}) cathodes by atomic layer deposition (ALD) and the effect on HE-NCM/graphite full cells were investigated. Changes in cycling performance of full cells due to the effect of transition metal dissolution on both electrodes are presented. To understand the effects of transition metal dissolution on the surface film of each electrode, both surface films were analyzed using X-ray photoelectron spectroscopy (XPS)

and infrared spectra with attenuated total reflectance (IR-ATR) upon cycling. A possible mechanism for degradation of HE-NCM/graphite full cells is discussed based on the findings.

Experimental

Coin cell preparation.—HE-NCM electrodes were prepared using a composition of 93 wt% HE-NCM (with/without Al₂O₃ coating), 3 wt% conductive carbon, and 4 wt% polyvinylidene difluoride (PVDF) binder. Each slurry was mechanically blended with N-methyl-2-pyrrolidone (NMP) solvent in a nitrogen-filled glove box and pasted onto aluminum foil. Both HE-NCM powders and graphite electrodes were supplied from a commercial supplier as battery grade.

2032-type coin cells containing HE-NCM positive electrodes (13.7 mm diameter), PP/PE/PP separators (19 mm diameter, Celgard 2325) and graphite negative electrodes (14 mm diameter) were assembled in an argon glove box (M-Braun) with oxygen and water contents < 1 ppm. Both HE-NCM and graphite electrodes were punched to a specific diameter, and dried at 110°C under vacuum overnight before cell assembly. The average active mass loading and areal capacity of HE-NCM electrodes are 7.3 mg cm⁻² and 1.83 mAh cm⁻², respectively. The n/p ratio is controlled within a range of 1.05 to 1.1 (capacity), using the 1st charge capacity of HE-NCM and graphite (330 and 372 mAh/g). 100 µL of 1.2 M LiPF₆ in EC:EMC is used as an electrolyte for each cell.

Electrochemical testing.—Galvanostatic cycling of HE-NCM/graphite cells was conducted using an Arbin BT2000 battery cycler in a constant temperature oven (25°C). The cycling procedure consists of three steps; (i) 10 mA/g within 2.0–4.8 V (1st cycle), (ii) 20 mA/g within 2.0–4.6 V (2nd–5th cycle), and (iii) 40 mA/g within 2.0–4.6 V (the prolonged cycle). Each current was calculated based on the active mass of HE-NCM electrode. A 6-hour rest period was also introduced at the beginning of each cycling protocol to confirm uniform wetting of all cell components.

Inductively coupled plasma mass spectrometry (ICP-MS).—An iCAP Q ICP-MS instrument (Thermo Scientific) with He KED interference reduction system was used for ICP-MS measurements. After cycling and allowing to equilibrate for 48 hours, the HE-NCM/graphite cells were disassembled in an argon glove box. Without the HE-NCM electrodes, all other cell parts were sealed in 15 mL centrifuge vials

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and centrifuged at 2200 RPM for 10 minutes to collect as much of the electrolyte as possible. After centrifuging, the cell parts were removed from the vial and the graphite electrodes were separately dissolved in 10 mL of 2% HNO_3 solution to extract metal ions from graphite. The extracted solution and collected electrolyte were combined again and filtered for the ICP-MS measurements. A three-point calibration was conducted in 2% HNO_3 before each sample set. The calibration range was from 50 to 500 ppm for Ni and Mn and 10 to 100 ppm for Co.

X-ray photoelectron spectroscopy (XPS).—A K-alpha spectrometer (Thermo Scientific) using Al K α radiation ($h\nu = 1486.6$ eV) under ultra-high vacuum ($< 1 \times 10^{-12}$ atm) was used for XPS measurements. The measuring spot size and pass energy were 400 μm in diameter and 60 eV for this instrument. After equilibration for 48 hours, the HE-NCM/graphite cells were disassembled in an argon glove box. Each electrode was washed with battery grade EMC, three times with 0.5 mL per wash, to remove the electrolyte residue, dried overnight under vacuum, and transferred in an air-free container to the XPS chamber. The PVdF (688 eV) and LiF peaks (685 eV) were used as reference peaks for HE-NCM and graphite to correct the binding energy scale for all spectra, respectively. Relative atomic concentrations were calculated from the integration of each XPS peak, upon consideration of respective atomic sensitivity factors. An argon flood gun was used as needed to avoid charge accumulation on samples.

Infrared spectra with attenuated total reflectance (IR-ATR).—A Bruker Tensor 27 equipped with an attenuated total reflection (ATR) system and LaDTG detector was used for IR measurements. After cycling and allowing equilibration for 48 hours, the HE-NCM/graphite cells were disassembled in an argon glove box. Each electrode was washed with battery grade EMC, dried overnight under vacuum, and transferred in a closed container to a nitrogen-filled glove box. The spectra were acquired with a resolution of 4 cm^{-1} and 256 scans in the nitrogen glove box. An atmospheric compensation and baseline correction were applied to all spectra.

Results and Discussion

The galvanostatic cycling performance of the HE-NCM/graphite full cells is provided in Fig. 1 with discharging capacity, normalized based on the active mass of HE-NCM. The Al_2O_3 coating on HE-NCM clearly improves the capacity retention of HE-NCM/graphite full cells. The HE-NCM/graphite cells containing the uncoated or Al_2O_3 -coated HE-NCM electrode show similar discharging capacity after the pre-cycling step (6th cycle, ~ 240 mAh/g), however the capacity of the cell containing uncoated HE-NCM decays faster upon prolonged cycling. This rapid decay is consistent with a loss of cyclable lithium ions during cycling when HE-NCM is not coated with Al_2O_3 . Since there is no excess lithium in the HE-NCM/graphite full cells, any lithium loss directly affects the cycling performance of the cells.

The ICP-MS results for quantification of metal dissolution provide insight into the source of cycling performance decay of HE-NCM/graphite cells (Fig. 2). The transition metal dissolution from the uncoated HE-NCM electrode is four times higher than the transition metal dissolution from the Al_2O_3 coated HE-NCM electrode. This suggests that the Al_2O_3 coating stabilizes the surface structure of HE-NCM and prevents transition metal dissolution from HE-NCM into electrolytes.^{17,22,23} It is reported that transition metal dissolution from the cathode has a detrimental effect on graphite anode and overall cell performance, yet the specific mechanism is not fully established.^{24,25}

To elaborate the effect of metal dissolution on the surface chemistry of full cells, the surface film on both HE-NCM and graphite electrodes was investigated using XPS analysis (Figs. 3–5). While the surface modification was applied to HE-NCM positive electrodes, the surface films developed on the uncoated and Al_2O_3 -coated HE-NCM are very similar even after 50 cycles (Fig. 3). Before cycling (pristine, gray lines), both electrodes have strong features of PVdF in the C 1s (291 eV, Figs. 3a and 3d) and F 1s spectra (688 eV, Figs. 3c and 3f).²⁶ In the O 1s spectra, the Al_2O_3 -coated HE-NCM has a dis-

Figure 1. (a) Discharge capacity vs. cycle number and voltage profiles obtained from HE-NCM/Graphite full cells containing (b) the uncoated and (c) Al_2O_3 -coated HE-NCM electrodes. The capacity was calculated based on the active mass of HE-NCM electrodes.

tinct shoulder around 531.8 eV (Fig. 3e), suggested to come from the Al_2O_3 coating, consistent with the presence of the corresponding peak in the Al 2p spectrum at 74 eV (Fig. 3h).^{26,27} After cycling, C-O (533.5 eV) and C=O (531.8 eV) peaks in the O 1s spectra grow on both electrodes,^{28–30} indicating the decomposition of carbonate solvents (Figs. 3b and 3e). These peaks are relatively greater intensity on the uncoated HE-NCM, implying more electrolyte decomposition

Figure 2. ICP-MS results obtained from HE-NCM/Graphite full cells containing the uncoated and Al_2O_3 -coated HE-NCM electrodes.

HE-NCM

Figure 3. XPS spectra obtained from the uncoated and Al_2O_3 -coated HE-NCM electrodes collected from HE-NCM/Graphite full cells.

Graphite

Figure 4. XPS spectra obtained from the graphite electrodes collected from HE-NCM/Graphite full cells.

Figure 5. Corresponding relative atomic concentrations from XPS spectra obtained from the HE-NCM electrodes and graphite electrodes. The total concentration of Ni, Mn and Co is presented as metal concentration.

has occurred on the electrode surface. A broad peak characteristic of $\text{Li}_x\text{PF}_y\text{O}_z$ (around 686–687 eV) and a small LiF peak (685 eV) are also observed on both electrodes after cycling (Figs. 3c and 3f).²⁶ Although these changes provide evidence for electrolyte decomposition on HE-

NCM positive electrodes, it is suggested the surface of HE-NCM is not completely passivated upon prolonged electrochemical cycling. Even after 50 cycles, the peaks characteristic of PVdF and bulk metal oxide (530 eV) can be observed from the HE-NCM surface.^{26,31} Further, the relative atomic concentrations calculated from the corresponding XPS spectra of HE-NCM (Fig. 5a), illustrate that the surface of HE-NCM electrode does not change significantly upon cycling.

Interestingly, the surface chemistry of graphite appears to be more altered by the Al_2O_3 coating on HE-NCM than the surface of the HE-NCM itself (Fig. 4 and Fig. 5b). The relative atomic concentration of graphite changes notably upon cycling (Fig. 5b). The relative concentration of fluorine increases significantly on the surface of graphite when cycled with the uncoated HE-NCM. However, the surface of graphite cycled with the Al_2O_3 -coated HE-NCM is relatively stable over the first 50 cycles. While the relative atomic concentrations show a large difference, the XPS spectra from two graphite electrodes contain similar peaks (Fig. 4). This denotes that the types of electrolyte decomposition products do not change, however, the relative ratio of the different decomposition products on the graphite surface are altered. Both graphite electrodes have C–O and C = O features (286.8 & 289 eV in the C 1s and 531.8 & 533.5 eV in O 1s spectra) as well as a LiF peak (685 eV in the F 1s).^{28–30} The F 1s spectrum for the graphite electrode cycled with the uncoated HE-NCM contains an intense peak characteristic of $\text{Li}_x\text{PF}_y\text{O}_z$ (686–687 eV),²⁶ which increases upon prolonged cycling. The P 2p spectra also shows broad peaks characteristic of $\text{Li}_x\text{PF}_y\text{O}_z$ (134–135 eV) and LiPF_6 (136–138 eV).^{32,33} Overall, more LiPF_6 salt decomposition occurs on the surface of graphite when cycled with the uncoated HE-NCM.

The IR-ATR spectra for both HE-NCM and graphite electrodes after 50 cycles are provided in Fig. 6. As with the XPS results described above, the IR spectra for the uncoated and Al_2O_3 -coated HE-NCM after 50 cycles are very similar (Fig. 6a). Most of the features in the spectra of both HE-NCM electrodes are attributed to PVdF binder (a 800–1300 cm^{-1} region, peaks at 1400 cm^{-1} and 1740 cm^{-1}),³⁴ supporting the XPS result for HE-NCM electrodes (Fig. 3). However, the IR spectra for the graphite electrodes cycled with the uncoated and Al_2O_3 -coated HE-NCM reveal some notable differences

Figure 6. IR-ATR spectra obtained from the (a) HE-NCM electrodes and (b) graphite electrodes after 50 cycles.

Figure 7. The Nyquist plots obtained from graphite/graphite symmetric cells, in which graphite electrodes were collected from two identical HE-NCM/Graphite full cells containing the uncoated and Al_2O_3 -coated HE-NCM electrodes.

(Fig. 6b). While both spectra contain peaks characteristic of lithium ethylene dicarbonate (LEDC, 1652, 1400, 1315, 1100, and 825 cm^{-1}) and Li_2CO_3 (1490, 1433 and 875 cm^{-1}),^{35–37} the graphite cycled with the uncoated HE-NCM contains additional features of oligo or poly carbonate (1750, 1300, and 1260 cm^{-1}).³⁸ The oligo carbonates are likely generated on the uncoated cathode surface from electrolyte oxidation and then cross over to the anode where they are reduced and deposited. Consistent with the XPS results (Fig. 4g), a strong peak is observed at 840 cm^{-1} on the graphite cycled with the uncoated HE-NCM which is characteristic of the P-F bond³⁹ suggesting the presence of $\text{Li}_x\text{PF}_y\text{O}_z$ and residual LiPF_6 . This further supports LiPF_6 salt decomposition is a major component of the SEI evolution on graphite when it is cycled with the uncoated HE-NCM.⁴⁰

With the above surface analysis results (XPS and IR), it can be concluded that metal dissolution from HE-NCM leads to the additional electrolyte decomposition on the surface of graphite. To further understand the effect on the degradation of graphite, the resistance of graphite was measured using the electrochemical impedance spectroscopy (EIS). In Fig. 7, Nyquist plots of graphite/graphite symmetric cells, in which graphite electrodes were collected from HE-NCM/graphite cells are provided. After the 1st cycle, the resistance of graphite electrodes is almost identical whether they were cycled with the uncoated or Al_2O_3 -coated HE-NCM electrodes. Upon the cycling, however, the resistance of graphite cycled with the uncoated HE-NCM has increased significantly while the one of graphite cycled with the Al_2O_3 -coated HE-NCM is stabilized. Therefore, it is reasonable to infer that metal dissolution from HE-NCM eventually increases the resistance of graphite and further causes the full cell degradation.

Conclusions

The influence of aluminum oxide (Al_2O_3) coating on to high-energy nickel cobalt manganese oxides (HE-NCM, $\text{Li}_{1.33}\text{Ni}_{0.27}\text{Co}_{0.13}\text{Mn}_{0.60}\text{O}_{2+d}$) has been investigated in HE-NCM/graphite full cells. Al_2O_3 coating on HE-NCM improves the cycle performance of HE-NCM/graphite full cells and effectively prevents the transition metal dissolution from HE-NCM into electrolytes. Ex-situ surface analysis on HE-NCM and graphite electrodes reveals that the surface chemistry of HE-NCM is not significantly altered with Al_2O_3 coating, however, the surface chemistry of graphite is affected significantly. When cycled with the Al_2O_3 -coated HE-NCM, the surface of graphite is stable over the first 50 cycles, while the surface of graphite cycled with the uncoated HE-NCM has strong features of LiPF_6 salt decomposition products and oligo or poly carbonates. The results suggest transition metal dissolution catalyzes additional electrolyte decomposition on the graphite surface. The additional electrolyte decomposition induces the resistance increase of graphite and further affects full cell performance. The improved cycling performance can be attributed to the prevention of transition metal dissolution from HE-NCM resulting in minimized resistance increase on the graphite anode.

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