



Effects of Atomic Layer Deposition of Al₂O₃ on the Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ Cathode for Lithium-Ion Batteries

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The lithium-excess layered oxide Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ has been surface modified with Al₂O₃ films grown with atomic layer deposition (ALD) and examined as cathodes for lithium-ion batteries. Al₂O₃ was grown on powders prior to electrode fabrication, directly on the electrode, and directly on the electrode followed by a heat-treatment at 300°C in air. Compared to the bare electrode, an Al₂O₃ film on an as-formed electrode improved the cycle performance significantly. Furthermore, the heat treatment of the ALD-coated electrodes resulted in significant increase in capacity, due to the transformation of the as-deposited Al₂O₃ to a better Li⁺-conductive material. X-ray photoelectron spectroscopy (XPS) results indicate that the heat-treatment leads to an inter-diffusion of atoms between the Al₂O₃ coating and the Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ core.

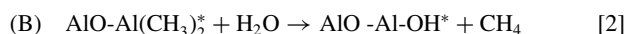
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Lithium-ion batteries (LIBs) are considered to be a possible energy storage device for hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), and electric vehicles (EV). For these applications, highly durable, safe, and high-energy LIBs are needed.¹ The Li-excess Li[Li_xM_{1-x}]O₂ (M = Mn, Ni, and Co) cathodes have a layered structure, which is considered as either a solid solution^{2,3} or a nanocomposite⁴⁻⁶ of Li₂MnO₃ and LiMO₂. In terms of energy density, the lithium-excess layered oxides are appealing because they are less expensive and offer much higher capacities (~250 mA h g⁻¹) than layered LiCoO₂ (~140 mA h g⁻¹). The high capacity of these oxides is known to originate from an activation process during the first charge above 4.5 V (vs. Li/Li⁺).^{7,8} During the activation process, oxygen is irreversibly lost from the lattice, and the oxidation state of the transition metal ions is lowered at the end of the first discharge compared to that in the initial material. The activation process is evidenced by *in situ* X-ray diffraction⁷ and differential electrochemical mass spectrometry⁸ studies performed at the end of first discharge.

However, the high operating potential (>4.5 V) of these lithium-excess layered oxides poses serious problems for the long-term stability of these cathodes due to their unfavourable reactions with the electrolyte. One way to mitigate the reaction between these cathodes and electrolytes is to modify the surface of these cathodes.⁹⁻¹¹ In most previous studies, wet-chemical methods such as sol-gel have been employed to coat the cathodes surface with other metal oxides^{9,11} and phosphates.¹⁰ These surface coatings have been found to improve the cycle performance and safety characteristics of these oxide cathodes. More importantly, our group has shown that the surface coating reduces the irreversible capacity loss (ICL) in the first cycle.^{12,13}

Recently, Jung *et al.* demonstrated that LiCoO₂^{14,15} and natural graphite¹⁶ coated with ultrathin conformal Al₂O₃ coatings by atomic layer deposition (ALD) exhibit significantly enhanced cycle life. The reaction sequences of an ALD process to deposit one atomic layer of Al₂O₃ utilizing trimethylaluminum (TMA) and H₂O as precursors are shown below:¹⁴⁻¹⁸



where the asterisk (*) denotes a surface species. By repeating these sequences, the thickness of ALD coatings can be precisely controlled in the atomic regime. ALD also provides the possibility to grow a film on an as-formed electrode. By growing the film directly on the as-formed electrode, the electrical pathways between active materials, conductive additives, and current collectors are maintained.¹⁶ While growing films directly on the as-formed electrode does not hinder the flow of electrons, it still hinders Li⁺ conduction as the Li⁺ ions must pass through the film. In this regard, development of a better Li⁺-ion conductive ALD film may not only maximize the rate performance but also enable to examine thicker coatings (>1 nm), leading to even better performance.

We present here the ALD coating of Al₂O₃ films on the lithium-excess layered oxide Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ powder and electrode. The effect of the Al₂O₃ film thickness as well as heat treatment after the ALD coating on the electrochemical performance is presented.

Experimental

The lithium-excess layered oxide Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ powders were prepared by a coprecipitation method.^{12,13} A transition metal acetate solution was first prepared by dissolving a total of 6 g of required amounts of acetates of Mn, Ni, and Co in 500 mL of deionized water (12 mM). This solution was then added dropwise to a 500 mL solution of 0.7 M KOH solution. The coprecipitated powders were then filtrated and washed with deionized water, followed by drying in air at 100°C in an oven overnight. The coprecipitated transition metal hydroxides were then ground with LiOH to achieve a Li/M mole ratio of 3/2, where M = Mn + Ni + Co. The mixture was then fired at 900°C in air for 24 h.

Al₂O₃ ALD films were grown both on the Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ powder prior to electrode assembly and directly on the as-formed electrode. The precursors utilized for Al₂O₃ ALD were trimethylaluminum (TMA) purchased from Aldrich and H₂O obtained from Fisher Scientific. ALD on the Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ powders was performed with a rotary ALD reactor.¹⁴ The Al₂O₃ ALD reaction sequence was: (i) TMA dose to 1.0 Torr, (ii) TMA reaction time, (iii) evacuation of the reaction products and excess TMA, (iv) N₂ dose to 20.0 Torr, (v) N₂ static time, (vi) evacuation of N₂ and any entrained gases, (vii) H₂O dose to 1.0 Torr, (viii) H₂O reaction time, (ix) evacuation of reaction products and excess H₂O, (x) dose N₂, (xi) N₂ static time, and (xii) evacuation of N₂ and any entrained gases. This sequence constitutes one cycle of Al₂O₃ ALD. The Al₂O₃ ALD was conducted at 180°C.

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The bare and Al₂O₃ ALD coated Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ particles were examined by transmission electron microscopy (TEM) with a FEI Tecnai F20 UT microscope operated at 200 kV. The atomic signals on the surface of Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ were measured by nano-probe energy dispersive X-ray spectroscopy (EDS).

X-ray photoelectron spectroscopic (XPS) measurements were performed on a PHI 5600 X-ray photoelectron spectrometer with a monochromatic Al K_α source (1486.6 eV). The base pressure in the XPS during analysis was 3×10^{-10} Torr. During the data acquisition, the constant analyzer energy mode was employed at pass energies between 29.35 and 93.9 eV and at a step size between 0.25 and 0.50 eV. Using the Al 2s, Mn 2p, Ni 2p, and Co 2p peaks, the Al/M (M = Mn, Ni, Co) atomic ratio was obtained.

A two-electrode 2032-type coin cell was employed to assess the electrochemical performance of the samples. The composite electrodes were prepared by mixing Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂, Super P, and polytetrafluoroethylene (PTFE) in a wt. ratio of, respectively, 75 : 20 : 5 in an agate mortar and pestle using isopropyl alcohol as a dispersant. The paste was rolled into thin sheets on a piece of Al Exmet. The as-prepared electrode was then pressed, followed by drying under vacuum at 120°C overnight. The heat treatment of the electrodes was performed at 300°C for 3 h in air. The coin cells were assembled with Li foil (Alfa Aesar) as the counter and reference electrodes, 1.0 M LiPF₆ dissolved in a 1:1 (by volume) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) electrolyte, and Celgard polypropylene separator. The galvanostatic charge-discharge cycling was carried out between 2.0 and 4.8 V (vs. Li/Li⁺) at 0.1C rate (25 mA g⁻¹) at room temperature.

Results and Discussion

The Al₂O₃ films were grown on both the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ powders and on the as-assembled Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ electrodes. Al₂O₃ films were grown with 2, 6, and 20 cycles of ALD. TEM images of the bare and Al₂O₃-coated (2, 6, and 20 ALD cycles) Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ particles are displayed in Figure 1. Small circular cross sections, labeled as p1-p8 in Fig. 1, were examined by EDS. For the Al₂O₃ ALD coated particles (Figs. 1b-1d), Al peaks are clearly identified on the surfaces (p3, p5, p7) but not on the bulk (p4, p6, p8). The peak intensity ratios of Mn/Al in the EDS signals (Mn K_α: 5.90 eV, Al

Table I. Atomic fraction on the surface of the bare and Al₂O₃ coated Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ particles obtained by XPS analyses.

ALD cycle number	Atomic fraction (%)				M/Al atomic ratio (M = Mn + Ni + Co)
	Al	Mn	Ni	Co	
2	70	18	5	7	2.32
6	64	22	9	6	1.74
20	36	23	11	5	0.92

K_α: 1.49 eV) in Fig. 1 are 6.7, 5.5, and 2.1, respectively, for the 2, 6, and 20 ALD cycles. The M/Al (M = Mn + Ni + Co) atomic ratios for the Al₂O₃ ALD coated particles were also collected with XPS as displayed in Table I. Lower M/Al atomic ratios for the samples with higher ALD cycle numbers indicates the thicker coating, which corroborates the Al₂O₃ growth on Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ by the ALD reactions.

Figure 2 shows the first and second charge-discharge voltage profiles of the bare and Al₂O₃-coated (6 ALD cycles on electrode) Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂. For the first charge of bare electrode (Fig. 2a), two regions are noticeable. There is a sloping region between 3.9 and 4.4 V and a subsequent long plateau region at ~4.5 V. The latter is attributed to an irreversible loss of oxygen from the lattice.⁸ The overall shape of the voltage profiles for the Al₂O₃-coated sample is similar to that of the bare electrode. This indicates that the Al₂O₃ film does not alter the main reaction mechanism. Comparing the bare electrode (Fig. 2a) to the Al₂O₃ ALD coated electrode (Fig. 2b) shows that there is a large overpotential on the Al₂O₃ ALD coated electrode during the first charge. The slow rate characteristics of the ALD coated electrode is due to the kinetic hindrance of Li⁺ ions through the Al₂O₃ coatings,¹⁶ which results in a lower capacity compared to that of the bare electrode.

Fig. 3 compares the first discharge capacities as a function of the number of cycles of Al₂O₃ ALD. For the ALD on powders, there is a gradual decrease in the capacity (open triangle) as the number of ALD cycles increases. This observation might be considered inconsistent with the previous reports in which a significantly decreased capacity was observed with only 10 cycles of Al₂O₃ ALD on LiCoO₂

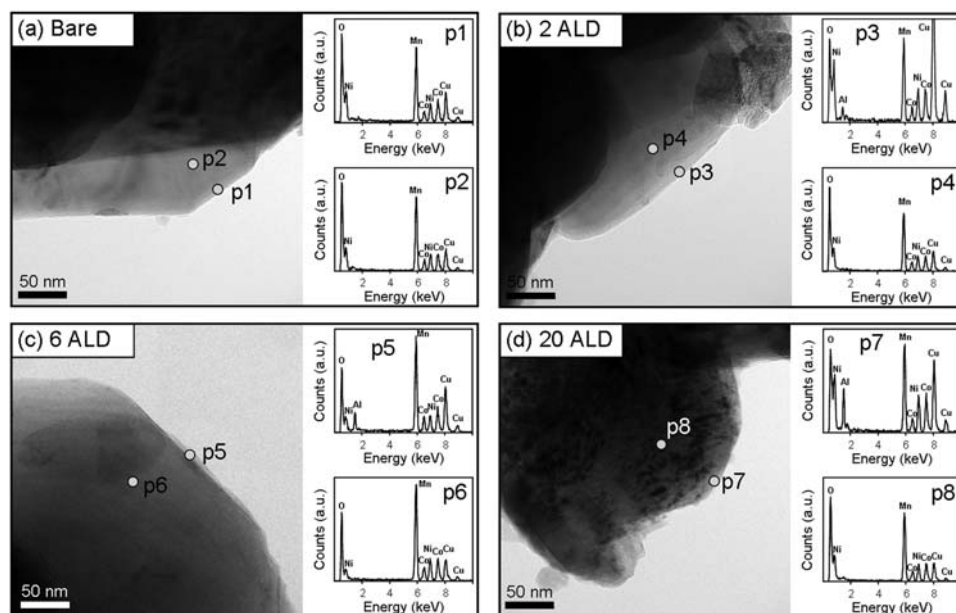


Figure 1. TEM images of bare and Al₂O₃ ALD coated Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ particles: (a) bare, (b) 2 ALD cycles, (c) 6 ALD cycles, and (d) 20 ALD cycles samples. The EDS signals of the areas labeled as p1-p8 are shown on the right.

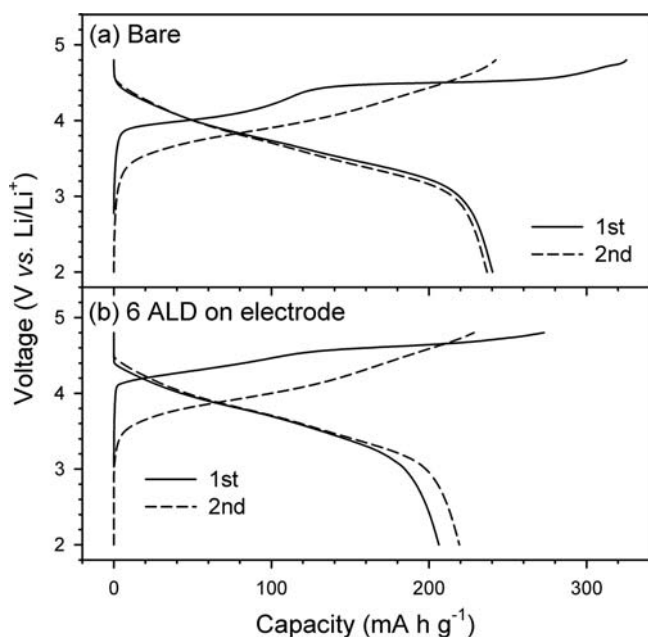


Figure 2. First two charge-discharge profiles of the $\text{Li}[\text{Li}_{0.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ electrode (a) before and (b) after 6 ALD cycles on the electrode.

powders.¹⁴ The origin of this inconsistency can be understood by considering the differences in the electrode fabrication process. In this work, a small amount (~ 25 mg) of the mixture of active material, Super P, and PTFE were thoroughly ground and mixed with an agate mortar and pestle. During this process, the Al_2O_3 film could have been removed. This would result in a lower surface coverage by the Al_2O_3 . If the ALD is performed directly on the as-formed electrodes, then the protective coating may not be damaged. Coating the electrode also has the advantage of preserving the inter-particle contacts (among layered oxide, Super P, and Al Exmet). In contrast, both electron and Li^+ -ion transport through the Al_2O_3 film could contribute to the decreased rate performance in the electrode made by ALD on powders.¹⁶ The ALD on the electrode displays a decrease in capacity (closed circle) with increasing number of ALD cycles. This electrochemical result strongly supports the conformal Al_2O_3 ALD on the lithium-excess $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$.

Fig. 4a displays the cycle performance of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ coated by direct ALD on the electrode. As seen in Table II, all the samples with Al_2O_3 ALD directly on the electrode shows improved cyclability compared to the bare

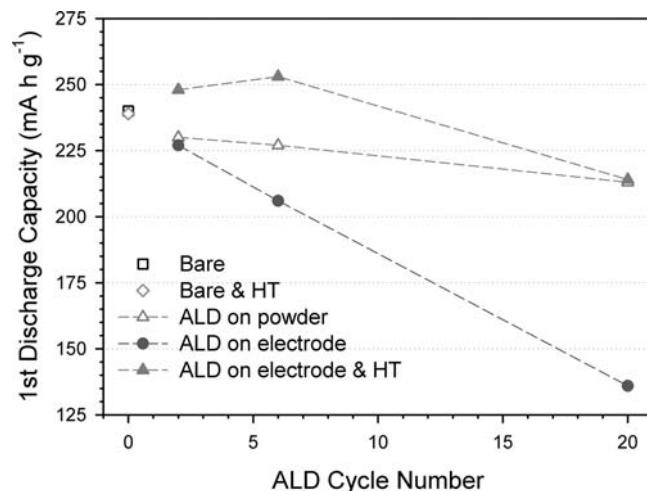


Figure 3. First discharge capacities of bare and Al_2O_3 ALD coated $\text{Li}[\text{Li}_{0.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ electrodes. The effects of the ALD type (ALD on powder and on electrode) and heat treatment after the ALD on electrode are illustrated as a function of ALD cycle numbers. HT refers to heat treated.

sample. The protective coating can mitigate undesirable surface reactions, which could be responsible for the gradual capacity decay with repeated charge-discharge cycles. The increase in the capacity observed during the initial charge-discharge cycles could be due to better electrochemical utilization of the electrode. Considering that the lithium-excess layered oxide may experience significant atomic/ionic diffusion and in turn dimensional changes related to the irreversible loss of oxygen from the lattice,⁸ new surfaces are likely exposed during initial charge-discharge cycles. The thicker Al_2O_3 films result in a better charge-discharge cycle retention than the thinner ones. The sample with 6 cycles of Al_2O_3 ALD shows a capacity of 205 mA h g^{-1} at 55 charge-discharge cycles while the sample by 2 cycles of Al_2O_3 ALD has a capacity of 186 mA h g^{-1} . This indicates that thicker coatings might be needed to obtain the best charge-discharge cycle performance. However, 20 cycles of Al_2O_3 ALD appear to be too thick resulting in reduced Li^+ -ion kinetics through the film. This is evidenced by the low capacity as seen in Fig. 4a and Table II. Further optimization of the Al_2O_3 film thickness is needed to achieve suitable Li^+ -ion conductivity with the most surface protection.

In order to enhance the Li^+ -ion conductivity through the protective film, the concentration of Li^+ ions in the protective film material should be increased.¹⁹ For the metal-oxide coated LiMO_2 system, it has been proposed that heat-treatment could induce an inter-diffusion

Table II. Electrochemical characteristics of bare and Al_2O_3 ALD coated $\text{Li}[\text{Li}_{0.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ electrodes.

ALD			Capacity at first charge-discharge cycle / mA h g^{-1}		ICL at first charge-discharge cycle / mA h g^{-1}	Capacity at 30th charge-discharge cycle / mA h g^{-1}
Type	Cycle number	Heat-treatment	Charge	Discharge		
Bare sample	–	No	325	240	85	192
	–	Yes	320	239	81	204
ALD on the electrode	2	No	298	227	71	217
	6	No	273	206	67	220
	20	No	207	136	71	172
	2	Yes	327	248	79	231
	6	Yes	337	253	84	242
	20	Yes	277	214	63	217
ALD on the powder	2	No	308	230	78	207
	6	No	308	227	81	202
	20	No	292	213	79	201

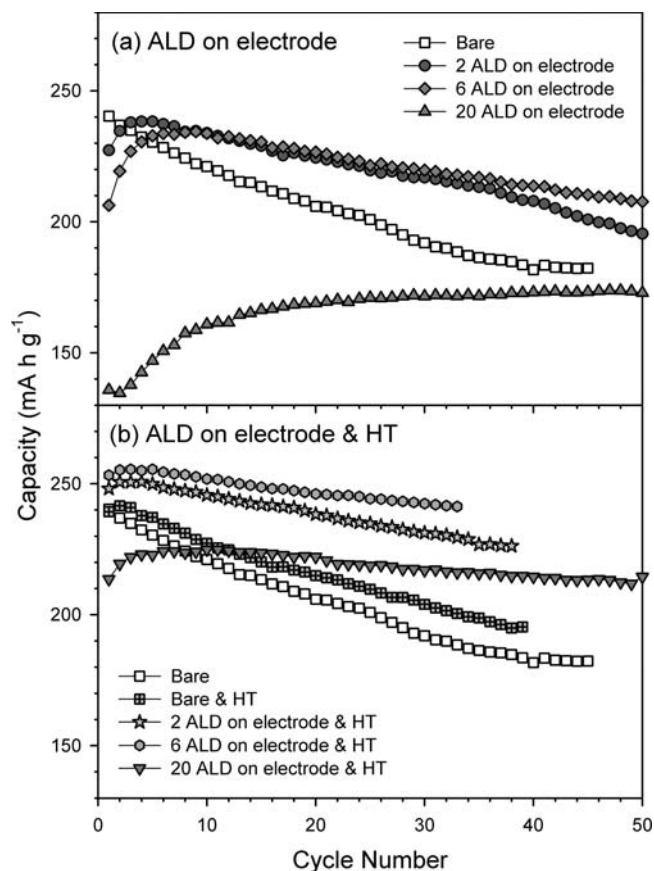


Figure 4. Cycle performance of Al_2O_3 ALD $\text{Li}[\text{Li}_{0.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ electrodes prepared (a) by ALD on the electrode and (b) by ALD on the electrode followed by heat treatment. Results from the bare and heat-treated bare electrodes are also shown for a comparison. HT refers to heat treated.

between atoms from the coating and the core active materials to form Li-Al-M-O solid solutions.^{20,21} In order to produce a Li-Al-M-O solid solutions, electrodes that had been directly coated with Al_2O_3 ALD were further heat-treated at 300°C in air for 3 h. This temperature was close to the maximum temperature at which the PTFE-based composite electrode may not be altered (m.p. of PTFE = $\sim 327^\circ\text{C}$). The M/Al (M = Mn, Ni, Co) atomic ratios in the electrodes with 6 cycles of Al_2O_3 ALD before and after the heat treatment were obtained from the XPS data. Fig. 5 depicts these ratios. In all cases, the M/Al atomic ratio increases after the heat treatment, indicating the inter-diffusion between Al and M occurs during the heat treatment. This result implies that Li^+ and M^{n+} ions could also be incorporated into the Al_2O_3 layer to form better Li^+ conductive phases such as layered $\text{Li}_{1-x}\text{Al}_{1-y}\text{M}_y\text{O}_2$.

As seen in Fig. 3, the electrodes that underwent heat treatment exhibit dramatically increased capacities (closed triangle) compared to the as-prepared electrode. As a control sample, a bare electrode was also subjected to heat treatment, and this sample has almost the same capacity (open diamond) as the bare electrode without heat treatment (open rectangle). The sample with 20 cycles of Al_2O_3 ALD directly on the electrode and subjected to heat treatment shows a specific capacity of 214 mA h g^{-1} on the first discharge. The same electrode without heat treatment shows a capacity of 136 mA h g^{-1} . In addition, the sample with 6 cycles of Al_2O_3 ALD directly on the electrode and subjected to heat treatment shows a higher capacity of 253 mA h g^{-1} than the bare electrode (239 mA h g^{-1}). The ‘artificial’ solid electrolyte interphase (SEI) layers constructed by ALD followed by heat treatment might show better Li^+ -ion kinetics than a SEI layer formed by the electrolyte decomposition reaction on the bare elec-

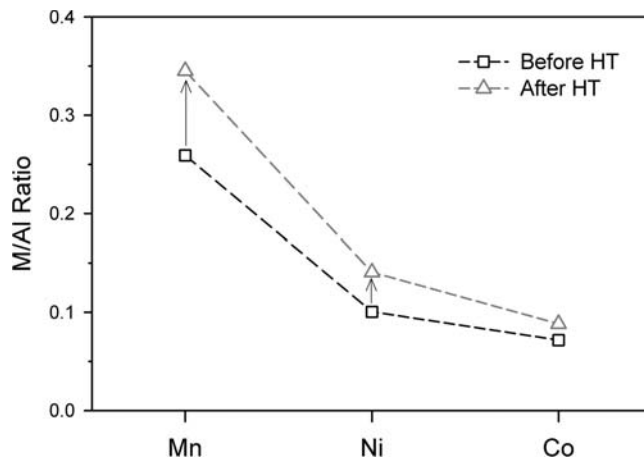


Figure 5. M/Al (M = Mn, Ni, Co) atomic ratios before and after the heat treatment of the Al_2O_3 -coated $\text{Li}[\text{Li}_{0.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ electrodes prepared by ALD on the electrode. The M/Al atomic ratios were calculated from the XPS data. HT refers to heat treated.

trode surface during charge-discharge cycles. As seen in the Table II, the ALD does not significantly reduce the irreversible capacity loss, in contrast to that observed with wet-chemical coating. This could be attributed to the different nature of the ALD film compared to that produced by wet-chemical techniques. The coated electrodes with heat treatment still exhibits significantly improved cyclability after the charge-discharge cycles compared to the bare electrodes (Fig. 4b). We believe that the durability of the ALD films directly on the electrode could be improved with thicker films that exhibit higher Li^+ -ion conductivity.

Conclusion

The surface modification of the lithium-excess layered oxide $\text{Li}[\text{Li}_{0.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ has been performed by ALD and further heat treatment. While the coatings by ALD on powder were damaged during the manual electrode-making process, the direct ALD on as-formed electrodes turned out to be a viable way to achieve conformal protective coatings. Direct ALD on the electrodes significantly improved cycle performance compared to the bare electrodes. It was demonstrated that while retaining the benefits of protective film, the limitation of Li^+ -ion kinetics through the coating could be enhanced by heat treatment of the ALD-coated electrode.

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