Improved Electrochemical Performance of LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{2} Electrodes Coated by Atomic-Layer-Deposited Ta_{2}O_{5}

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Surface coating of LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{2} (NMC532) is an effective approach to improve the capacity retain and energy density through increasing cutoff operation voltage. In this work, NMC532 electrodes are directly coated with Ta_{2}O_{5} via atomic layer deposition (ALD). The 5 cycles ALD-Ta_{2}O_{5} coated electrodes has the significantly enhanced capacity cycleability. The high-quality amorphous ALD-Ta_{2}O_{5} layer retards the interfacial reaction between NMC532 and electrolyte, and prevents the dissolution of the active materials, improving the phase stability of the NMC532 materials.

Keywords: Atomic Layer Deposition, Surface Coating, Ta_{2}O_{5}, Cathode Materials, Lithium Ion Battery.

LiNi_{x}Co_{1-x}Mn_{1-y}O_{2} (NMC; 0 < x, y < 1) with layered-structure has proved to be an alternative cathode materials in the rechargeable lithium-ion battery (LIB), which is successfully combines the superiorities of LiCoO_{2}, LiNiO_{2}, and LiMnO_{2}. NMC materials have drawn the attention from the scientific community and industry, because of low cost, high capacity stability, and enhanced cycling performance; they have been one of the most suitable active materials for LIBs in electric vehicles (EVs). The higher operation voltage will introduces the higher capacity and larger energy density. However, the high operation voltage will result in severe structural degradation because of an irreversible phase transition. Meanwhile, interfacial reactions between the active materials and the electrolyte will be accelerated at a high oxidation state. Consequently, cycling performance dramatically degraded during the long-term cycling process. While the structural and/or interfacial stability at the electrode/electrolyte interface must be enhanced for achieving the long-term cyclic stability and the strict safety standards.

Two important strategies, surface coatings and element substitute, are often utilized to improve the poor cyclic stability and reduced rate capability due to the increased operation voltage. Substituting for metal ions and/or oxygen for either element such as Al, Zn, Mg, Ti and Fe or anions such as F, in order to enhance the structural stability while reducing cation mixing. Stable surface coatings have been regarded as the most effective method to improving the NMC electrochemical performance, preventing the reactions at the electrolyte/electrode interface. This coating technique has been regarded as a promising approach for enhancing LIB capacity retain during long-term cyclic process.

Coatings on the active material powders or directly on the as-prepared electrodes have been utilized to improve the electrochemical performances. Recently, coating directly onto the as-prepared electrodes is popular because of this approach protects the electronic transport pathways during the coating process (Fig. 1). The films deposited via atomic layer deposition (ALD) have the excellent advantage of high-quality, dense, conformal and thickness controllable, which is suitable for the surface modification of the porous as-prepared electrodes.

In this work, the oxide material Ta_{2}O_{5} is directly coated on commercial LiNi_{0.5}Mn_{0.3}Co_{0.2}O_{2} (NMC532) electrodes via ALD technique. The electrochemical performance of electrodes with and without ALD-Ta_{2}O_{5} was investigated under the higher potential voltage (about 4.5 V). The optimized conformal coating is very effective in improving the electrochemical performance. The 5 cycles ALD-Ta_{2}O_{5} electrodes...
coated electrodes has the significantly enhanced capacity cycleability. The high-quality amorphous ALD-Ta₂O₅ layer retards the interfacial reaction between NMC532 and electrolyte, prevents the dissolution of the active materials, and enhances phase stability of the NMC532 materials.

The NMC532 work electrodes were prepared by doctor-blade method onto an Al foil current collector. The work electrodes mixture of NMC532 materials, acetylene black, and poly(vinylidene difluoride) (8:1:1 ratio by weight). The as-prepared electrodes were first dried in air for 1 h at 353 K and then transferred into the vacuum oven for 10 h at 383 K.

Ta₂O₅ films was directly deposited onto the as-prepared electrodes in our homemade ALD at 200 °C using Pentat(ethoxide) Tantalum [Ta(OEt)₅] and ultrapure grade H₂O as precursors. All precursors were dosed into the chamber by the n gas. Each dose was purged by nitrogen gas for 10 s. The NMC532 electrodes coated with 0, 2, 5, and 10 cycles ALD-Ta₂O₅ were denoted as NMC-x (x = 0, 2, 5, 10). The experimental details can be seen in supplemental materials.

Due to the advantage of high-conformal, ALD coating can be carried out both on powder materials and as-prepared electrodes. The process of coating ALD Ta₂O₅ directly on the as-prepared NMC532 electrode was shown in Fig. 1. The ALD Ta₂O₅ film was deposited layer-by-layer because of the sequential and self-saturation surface reactions.

Fig. 2 shows the X-ray diffractograms of the as-prepared NMC532 electrodes and ALD-Ta₂O₅ coated NMC532 electrodes. No traces of the related secondary phases or of extra diffraction peaks could be indexed as a hexagonal structure with space group of R-3m, which agreed with those of Ohzuku. The splits of the (006)/(102) and (108)/(110) peaks can be seen in all samples, which indicate the formation of layered structure. The intensity ratio of I(003)/I(104) is 1.74 and 1.76 for NMC-0 and NMC-5 electrodes, respectively. The obtained ratios are larger than 1.2, indicating that a well-ordered layered structure and less cation mixing is preserved even after ALD-Ta₂O₅ coating. Evidently, no Ta₂O₅ phase was detected in the XRD spectrum, indicating the amorphous ALD Ta₂O₅ coating has lowest impact on the NMC532 structure.

X-ray photoelectron spectroscopy is very sensitive for detecting the surface chemical nature. The as-prepared and ALD-Ta₂O₅ coated NMC532 electrodes was analyzed with XPS to confirm the Ta₂O₅ coating layer directly deposited on the surface of NMC532 cathodes. The core-level XPS spectrum of Ta 4f was shown in Fig. 3(a). The curves can be fitted by two peaks with binding energies of 28.2 eV (4f₇/₂, the red line) and 26.3 eV (4f₅/₂, the blue line), which indicates the surface coating layer on the NMC532 electrodes can be confirmed as Ta₂O₅. However, No signs for the Ta 4f is not detected on the as-prepared electrode.

The morphology of NMC532 electrodes was shown in Fig. 3(b) and 3(c). The as-prepared electrode presents the smooth surface without any impurity in Fig. 3(b). In contrast, a uniform and dense conformal ALD Ta₂O₅-coated layer (about of 4 nm) is clearly observed on the surface of NMC532-5 electrode in Fig. 3(c), where each ALD cycle growth rate for Ta₂O₅ is approximately 0.8 Å in thickness. The amorphous ALD Ta₂O₅ coating cannot change the NMC532 structure, which is consistent with the above discussed XRD results (Fig. 2). Typically, the thickness of materials coated by wet-chemical method is usually several nanometers can improve the performance stability. However, the thicker coating layer will hinder the diffusion of the lithium ion and lead to polarization. The conformal and
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density nature of ALD Ta2O5 was able to protect the surface of NMC532 materials with less chemical polarization.

The initial charge-discharge curves of the NMC-0 and ALD Ta2O5 coated NCM-5 electrodes at 0.1 C (1 C = 170 mAh g⁻¹) between 3.0 and 4.5 V (vs. Li/Li⁺) can be found in Fig. 4. All of the curves display a typical electrochemical behavior with stable and smooth voltage plateau in the initial charge/discharge process. There is no evidently difference in the initial charge/discharge curves, indicating that the ALD Ta2O5 coating layer to the intrinsic electrochemical performance of the NMC532 materials.34,35 The initial charge and discharge capacities for the NMC-0 electrodes are 222.0 mAh g⁻¹ and 181.9 mAh g⁻¹, with the coulombic efficiency of 81.9%. For the ALD Ta2O5 coated NCM-5 electrodes, the discharge capacity and initial coulombic efficiency are 200.1 mAh g⁻¹ and 87.8%, respectively. Evidently, the initial discharge capacity and coulombic efficiency of the as-prepared electrodes can be enhanced after optimized ALD Ta2O5 coating layer. Because of the electrochemical inactivity of the ALD Ta2O5 layer, surface coating would not play positive role on the discharge capacity. However, the ALD Ta2O5 layer will become activity due to Li intercalated, and the lithium ions can easily transport through the coating layer.36,37 The results are further confirmed by the later electrochemical impedance spectroscopy (EIS) measurement.

Fig. 5 shows the cyclic performances of different NMC532 electrodes (before and after ALD Ta2O5 coatings) at 1 C in potential range of 3.0-4.5 V (versus Li/Li⁺). As shown, the as-prepared electrode shows obvious capacity fade, which decrease from 173.9 mAh g⁻¹ at first cycle to 136.3 mAh g⁻¹ at 50th cycle. The calculated capacity retention is only 78.3% after 50 charge/discharge cycles. However, the capacity retentions for the Ta2O5-coated electrodes are 86.5% (NMC-2), 90.9% (NMC-5), and 82.3% (NMC-10), respectively. The cyclic stability of the NMC532 electrodes can be enhanced with ALD Ta2O5 coating. Obviously, the 5 cycles ALD Ta2O5-coated NMC532 (NMC-5) archives the highest cyclic stability and the maximum capacity of 161.7 mAh g⁻¹ after 50 charge/discharge cycles. It can be seen that the cyclic performances of NMC532 cathodes can be significantly improved with optimized cycles of Ta2O5 coating. The improvement is mainly ascribed to the ALD Ta2O5 coating, which retards the interfacial reaction between the active materials and the electrolyte and reduces the dissolution of active materials into the electrolyte.38,39 However, 10 ALD cycles (over thick layer) of Ta2O5 coating hinder the diffusion of the lithium ion and reduce polarization, which is harmful to the capacity and cyclic stability.

Fig. 6 shows the rate performances of the as-prepared and ALD Ta2O5-coated NMC532 electrodes at different C-rates under 3.0 - 4.5 V. The electrodes are firstly charged to high voltage (4.5 V) at 0.2 C before the rate performance test. Then, the electrodes are discharged at different C-rates (0.2, 1, 2 and 5 C), respectively. As the current density increase, the discharge capacity of all NMC532 electrodes
with and without ALD Ta$_2$O$_5$ coating decreases owe to polarization.$^{40}$ The Ta$_2$O$_5$-coated NMC532 electrode exhibits a better rate capability than the as-prepared one, especially at high C-rates. Moreover, the NMC532 with ALD Ta$_2$O$_5$-coated shows a better cycling performance. The ALD Ta$_2$O$_5$ layer increased to 10 cycles, the rate capability changes worse. The above results reveal that only optimized cycles of coated Ta$_2$O$_5$ can enhance the rate capability of the NMC532 electrode, which is consistent to the above cycle performances.

Fig. 6. Cycle performance of as-prepared and ALD-Ta$_2$O$_5$-coated NMC532 electrodes at 1 C under 3.0-4.5 V (1 C = 170 mAh/g).

The electrochemical impedance spectroscopy (EIS) is carried out to further study the possible reason of enhanced electrochemical performance of the ALD Ta$_2$O$_5$-coated NMC532 electrodes, which is tested after 20th and 50th cycles at 1 C under potential range of 3.0 - 4.5 V. Fig. 7 shows the EIS spectra for the NMC532 electrodes with and without ALD Ta$_2$O$_5$ coating. The obtained Nyquist plots can be expressed by two parts: a half semicircle at high frequency region and a sloping line at low frequency region. The equivalent circuit model is given (Inset of Fig. 7), in which $R_{sol}$ corresponds to the ohmic resistance of the electrolyte, $R_a$ represents the charge-transfer resistance, CPE represents the electrode/electrolyte double layer capacitance, and $Z_W$ refers to the Warburg impedance.$^{39,41-43}$ The fitted $R_{sol}$ and $R_a$ values for the as-prepared and NMC532-5 electrodes after 20th and 50th charge/discharge cycles are listed (Table 1). Obviously, the $R_{sol}$ between as-prepared and NMC532-5 electrodes has a little difference, which indicated that the coated ALD Ta$_2$O$_5$ layer is stable and not dissolved into the electrolyte to change the conductivity.$^{39,42}$ However, the charge transfer resistance $R_a$ changes quite evident during cycling. The $R_a$ for NMC-0 cell is 41.53 $\Omega$ at the 20th cycle and reached to 57.87 $\Omega$ at the 50th cycle, while the $R_a$ for NMC-5 cell only increases from 26.76 to 39.58 $\Omega$. Obviously, the $R_a$ for NMC-5 is much smaller than that of NMC-0, which is attributed to the ALD coated layer Ta$_2$O$_5$ can retard the interfacial reaction between the NMC532 and electrolyte, reducing the interface resistance.$^{39,41-44}$ Fig. S1 and Table S1, and the impact of ALD Ta$_2$O$_5$ coating layer on the electrochemical properties was discussed (supplemental materials). In addition, the coated ALD Ta$_2$O$_5$ layer can inhibit the dissolution of the NMC532 during long cycling performance.$^{39}$ Therefore, the improvement of the electrochemical properties for NMC532 should be attributed to the ALD Ta$_2$O$_5$ coating.

Table 1. Values of the fitted parameters for as-prepared and ALD-Ta$_2$O$_5$-coated NMC532 cells after 20th and 50th cycles.

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>$R_{sol}$ ($\Omega$)</th>
<th>$R_a$ ($\Omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20$^{th}$ cycle</td>
<td>50$^{th}$ cycle</td>
</tr>
<tr>
<td>NMC-0</td>
<td>6.53</td>
<td>41.53</td>
</tr>
<tr>
<td>NMC-5</td>
<td>6.67</td>
<td>26.76</td>
</tr>
</tbody>
</table>

NMC532 electrodes are directly coated with Ta$_2$O$_5$ via ALD. 5 cycles ALD Ta$_2$O$_5$ (about 4 nm) coated on the surface of NMC532 can significantly improve electrochemical performance during charge/discharge process, especially at higher cutoff voltage (4.5 V). The interfacial reaction can be retarded by ALD Ta$_2$O$_5$ coating layer between the NMC532 and the electrolyte, while the ALD Ta$_2$O$_5$ coating layer can also prevent the dissolution of the active materials, improving the phase stability of the NMC532 electrodes.

Fig. 7. Nyquist plots of as-prepared and ALD-Ta$_2$O$_5$-coated NMC532 electrodes (NMC-5); Inset: The equivalent circuit model.
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