Enhanced Cycling Stability of Cation Disordered Rock-Salt Li$_{1.2}$Ti$_{0.4}$Mn$_{0.4}$O$_2$ Material by Surface Modification With Al$_2$O$_3$

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Cation disordered rock-salt lithium-excess oxides are promising candidate cathode materials for next-generation electric vehicles due to their extra high capacities. However, one major issue for these materials is the distinct decline of discharge capacities during charge/discharge cycles. In this study, Al$_2$O$_3$ layers were coated on cation disordered Li$_{1.2}$Ti$_{0.4}$Mn$_{0.4}$O$_2$ (LTMO) using atomic layer deposition (ALD) method to optimize its electrochemical performance. The discharge capacity after 15 cycles increased from 228.1 to 266.7 mAh g$^{-1}$ for LTMO after coated with Al$_2$O$_3$ for 24 ALD cycles, and the corresponding capacity retention enhanced from 79.7 to 90.9%. The improved cycling stability of the coated sample was ascribed to the alleviation of oxygen release and the inhibition on the undesirable side reactions. Our work has provided a new possible solution to address some of the capacity fading issues related to the cation disordered rock-salt cathode materials.

Keywords: lithium-ion batteries, cathode, cation disorder, rock-salt, Li-excess

INTRODUCTION

Cathode materials with high energy densities are crucial for next generation of lithium-ion batteries, especially when used in hybrid and electric vehicles (Zu and Li, 2011; Goodenough and Park, 2013; Rui et al., 2015; Wang et al., 2017; Lv et al., 2018; Tan et al., 2018; Zhang et al., 2019). For this reason, Layer-structured Li-excess materials, which could deliver capacities as high as 300 mAh g$^{-1}$, have been researched for more than 10 years (Lu et al., 2002; Wang et al., 2013; Yu et al., 2014; Hu et al., 2018). But these materials undergo irreversible O loss in the first cycle, which may cause structure densification and voltage degradation in subsequent cycles (Xu et al., 2011). Recently, cation disordered rock-salt Li-excess materials, sharing similar chemical compositions with layered Li-excess materials, have also attracted lots of attentions because of their high capacities (Yabuuchi et al., 2011, 2015, 2016a,b; Lee et al., 2014, 2015, 2017, 2018; Twu et al., 2015; Freire et al., 2016, 2017; Cambaz et al., 2018; Kitchaev et al., 2018; Zhao et al., 2019). Besides, it is reported that the O redox may undergo irreversible reactions in the first cycle in this material (Wang et al., 2015), which provides the possibility to achieve reversible changes during the lengthy electrochemical cycles. However, many of these materials have problems in their cycling performances. Wang et al. prepared a cation disordered Li$_{1.23}$Ni$_{0.155}$Ru$_{0.615}$O$_2$ material, and the capacity drops from 295.3 to 250 mAh g$^{-1}$ only after 5 charge-discharge cycles (Wang et al., 2017). Okada's group prepared another cation disordered Li$_{1.2}$Mn$_{0.4}$Ti$_{0.4}$O$_2$ material, but its capacity drops from 226 to about 200 mAh g$^{-1}$ just after 6 cycles (Kitajou et al., 2016).
Similar problems happened to layered Li-excess materials, and some literatures have reported that atomic layer deposition (ALD) method may be an effective method to alleviate the problem. ALD is a powerful technique to precisely render a uniform and conformal layer at Å level on arbitrary substrate surfaces due to its pulsing and controllable reaction. Belharouak’s team coated Li1.2Ni0.13Mn0.54Co0.13O2 porous powder with ultrathin Al2O3 film using ALD technique, and the coated material shows higher first cycle coulombic efficiency and improved cycling performance (Zhang et al., 2013). Xiao et al. reported that the AlPO4 coating layer by ALD can effectively protect the Li1.2Mn0.54Co0.13Ni0.13O2 against the attack from the electrolyte, and can significantly improve its initial coulombic efficiency and thermal stability (Xiao et al., 2017a). Meanwhile, Oxide-based coatings at the surface of different cathode materials via ALD method have been demonstrated to be very conformal and uniform as reported in the literatures (Zhao and Wang, 2012; Zhao et al., 2012; Zhao and Wang, 2013a,b), thus they can effectively prevent from the electrolyte attack for enhanced cycling stability of the coated cathode.

In this study, we coated a cation disordered rock-salt Li1.2Ti0.4Mn0.4O2 material with different thicknesses of Al2O3 layers by ALD technique and studied their effects on the cycling stabilities. Li1.2Ti0.4Mn0.4O2 is a typical cation disordered rock-salt material but with poor cycling performances (Kitajou et al., 2016; Yabuuchi et al., 2016a). In our previous study, we found that the valence of Mn in disordered materials may be lower than 3+ after the first cycle (Wang et al., 2015), and this low valence may cause Mn dissolution into the electrolyte (Nicolaou et al., 2018). In this case, we infer that Al2O3 coating may be an effective method to increase the reversibility and cycling performances of this cation disordered material.

EXPERIMENTAL

Li1.2Ti0.4Mn0.4O2 was synthesized by the traditional solid-state reaction using the precursors of Li2CO3 (99%, Alfa Aesar), Mn2O3 (98%, Alfa Aesar), and TiO2 (99%, Sigma-Aldrich). Stoichiometric amounts of precursors were ball-milled for 4 h and then pressed into a pellet. The pellet was calcinated at 900°C for 4 h, and then move out and back into the cathode material (Kitajou et al., 2015). According to the XRD patterns, no signal of Al2O3 was detected, and the reason may be that the amount of coated Al2O3 is too small or the coated Al2O3 is amorphous. The morphologies of LTMO before and after Al2O3 coating are shown in Figures 1b,c. No obvious differences are observed, indicating the coated Al2O3 particle may be too small to be surveyed in SEM. Energy Dispersive Spectrometers of the two samples are shown in Figure 2a. The characteristic peak of Al element could clearly be observed in the LTMO/24Al2O3 sample, while didn’t show up in the LTMO sample. The LTMO/24Al2O3 sample was further examined by the elemental mapping experiments. and the results are shown in Figures 2b-f. Results show that Ti, Mn, O and Al elements distribute uniformly in the sample, which infer the Al2O3 layer exists uniformly in the sample.

In order to directly observe the coating Al2O3 layers on the surface of LTMO particles, we investigate bare LTMO and LTMO/24Al2O3 samples using high resolution transmission electron microscope (SEM, SU 8010) and powder X-ray diffractometer (XRD, Bruker D8 Advance), respectively. High Resolution Transmission Electron Microscope (HRTEM, TF 20) was used to record detailed crystalline structures of the samples. X-ray photoelectron spectroscopy (XPS, ESCALab 250Xi) with monochromatic Al K-α radiation was carried out to investigate the valences of the species in the samples.

To fabricate the cathode electrode, different Al2O3-coated LTMO samples were firstly ball-milled with Ketjen black at 150 rpm for 4 h, then manually mixed with polytetrafluoroethylene (PTFE) binder. The mixture was rolled into a thin film, in which the weight ratios of LTMO/nAl2O3, Ketjen black, and PTFE are 70: 20: 10. The surface mass density of each electrode film is about 4.4 mg cm−2. Cells were assembled according to our previous study (Wang et al., 2015). Typically, a two electrode swagelok cell was fabricated using the Al2O3-coated LTMO thin film and lithium foil as the working electrode and the counter electrode, respectively. Borosilicate glass fiber membrane (Whatman) was used as the separator, and 1 M solution of LiPF6 dissolved in ethylene carbonate/dimethyl carbonate (1:1 by volume) was used as the electrolyte. All cells were cycled on a LANHE CT2001A system (Wuhan LAND Electronics Co.) between 4.8 and 1.5 V with a current density of 10 mA g−1 at room temperature. The electrochemical impedance spectroscopy (EIS) data were recorded using a Gamry Reference 3,000 equipment. Cyclic voltammetry (CV) was measured on a CHI760E electrochemical workstation with the scanning rate of 0.5 mV s−1 and the potential range of 4.8–1.5 V.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns of the samples are shown in Figure 1a, and all the results correspond well to the disordered rock-salt structure. According to previous studies, cations are randomly placed on the 4b position (1/2, 1/2, 1/2), and the O atom is placed on the 4a position (0, 0, 0) (Wang et al., 2015). In cation disordered rock-salt materials, Li excess could build the 0-TM channels, through which Li ions could move out and back into the cathode material (Lee et al., 2015). According to the XRD patterns, no signal of Al2O3 is detected, and the reason may be that the amount of coated Al2O3 is too small or the coated Al2O3 is amorphous. The morphologies of LTMO before and after Al2O3 coating are shown in Figure 2a. The characteristic peak of Al element could clearly be observed in the LTMO/24Al2O3 sample, while didn’t show up in the LTMO sample. The LTMO/24Al2O3 sample was further examined by the elemental mapping experiments. and the results are shown in Figures 2b-f. Results show that Ti, Mn, O and Al elements distribute uniformly in the sample, which infer the Al2O3 layer exists uniformly in the sample.

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electron microscopy (HR-TEM). Figure 3a is the HR-TEM image of bare LTMO particles, showing well-defined lattice fringes in the surface region as well as those in the bulk region. In contrast, an obvious coating film in the surface region is clearly observed for LTMO/24Al sample (Figure 3b). It is different from the inner areas, and we infer it may be the Al$_2$O$_3$ coating layer. The thickness of the coating layer is around 3–5 nm.

In order to confirm Al$_2$O$_3$ layer exists on the sample surfaces, XPS was used to probe the surface compositions of the LTMO and LTMO/24Al$_2$O$_3$. All spectra were calibrated with the C 1s peak at 284.6 eV. Figure 4A presents the elemental XPS spectra of LTMO and LTMO/24Al$_2$O$_3$ samples, showing both samples contain the characteristic peaks of Ti, Mn, O, and C. From the partial enlarged figure (inset of the Figure 4A), the elemental peak of Al is only observed in the LTMO/24Al$_2$O$_3$ spectrum. The core level binding energies of Ti are aligned at 457.9 eV (2p$_{3/2}$) and 463.6 eV (2p$_{1/2}$) (Figure 4B), which is in good agreement with Ti$^{4+}$ ions in other titanium-based compounds (Kim et al., 2017). The Mn 2p XPS spectra of LTMO and LTMO/24Al$_2$O$_3$ reveal peaks at 641.6 eV and 653.2 eV (Figure 4C), which are characteristic peaks of Mn$^{3+}$ 2p$_{3/2}$ and 2p$_{1/2}$ (Das et al., 2011, 2013). This result confirms the valences of Mn in both samples are 3+. The Al 2p$_{3/2}$ core level XPS spectrum displays a binding energy of 74.7 eV for the LTMO/24Al$_2$O$_3$ (Figure 4D), affirming that the chemical composition of the surface coating is Al$_2$O$_3$ for the LTMO/24Al$_2$O$_3$ sample.

The charge and discharge profiles of uncoated and coated LTMO samples for the first cycle are shown in Figure 5A, showing all the samples have the identical profiles except for the voltage platform and capacity. It is obviously seen that all the coated LTMO samples have higher first discharge plateau and coulombic efficiency, and we think this may be the effect of Al$_2$O$_3$ layer. Though the O reaction in LTMO may happen in the form of O redox, there might still be little amount of oxygen release in the first cycle. We infer the Al$_2$O$_3$ layer may alleviate this oxygen release and improve the O reaction reversibility, thus improve the discharge plateau and coulombic efficiency. The charge and discharge profiles for the 10th cycle are shown in Figure 5B, and the LTMO/24Al$_2$O$_3$ sample presents the largest discharge capacity. Figure 5C shows the cycling stability of the pristine and ALD coated samples. Bare LTMO shows an initial discharge capacity of 286.3 mAh g$^{-1}$ (818.6 Wh kg$^{-1}$) and the capacity drops rapidly to 228.1 mAh g$^{-1}$ (587.7 Wh kg$^{-1}$) after 15 cycles, which is only 79.7% for its initial discharge capacity. After coated with Al$_2$O$_3$ for 16 ALD cycles, an initial discharge of 289.1 mAh g$^{-1}$ (856.6 Wh kg$^{-1}$) is observed and the capacity retention reaches 85.2%. It is worth noting that the LTMO/24Al$_2$O$_3$ sample could deliver a capacity of 293.4 mAh g$^{-1}$ and energy density of 884.5 Wh kg$^{-1}$ in the first cycle. After 15 cycles, the capacity and energy density could still maintain 266.7 mAh g$^{-1}$ and 709.5 Wh kg$^{-1}$, respectively. And the capacity retention after 16 cycles is 90.9%, which is 11.2% higher than that of the pristine LTMO. Besides, the coulombic efficiencies also increased from 91.5 to 93.0% after the 24 cycles ALD coating. However, further increasing the ALD cycle numbers of coated Al$_2$O$_3$, the inferior performance for LTMO/40Al$_2$O$_3$ is obtained, and the capacity retention decreases to 84.6%. The reason should
be the thick insulated Al₂O₃ layer may inhibit the electric and ionic transportation (Jung et al., 2010). Based on above results, it can be concluded that proper thickness of Al₂O₃ layer can greatly improve the cycling stability of LTMO electrodes, while the over-thick Al₂O₃ layer leads to the reverse effect on the electrode.

**Figure 6** show the cyclic voltammetric (CV) curves of LTMO and LTMO/24Al₂O₃ samples in the first three cycles at a...
scanning rate of 0.5 mV s\(^{-1}\). For the LTMO electrode (shown in the Figure 6A), the anodic peaks located at about 3.95 V corresponds to the oxidation of Mn\(^{3+}\) to Mn\(^{4+}\) (Xiao et al., 2017b) during the initial charge process. Another anodic peaks at around 4.63 V may be attributed to the oxygen loss from the crystal structure and formation of O\(^{2-}\) or O\(_2\) from O\(^{2-}\), which is usually observed on the Mn-based Li-excess cathode materials (Ma et al., 2016). While this peak disappears in the subsequent cycles, showing the irreversibility of the oxidation of O\(^{2-}\) in the LTMO electrode. In the following cathodic process, the peak at around 2.89 V corresponds to the reduction of Mn\(^{4+}\) to Mn\(^{3+}\) (Kong et al., 2017). It can be clearly seen that this peak moves to lower voltage range in the following cycles, indicating the decreasing of the valence of Mn. As to LTMO/24Al\(_2\)O\(_3\) (shown in Figure 6B), two differences can be observed. First, the anodic peak at around 4.63 V still can be observed in the second and third cycles. Second, the cathodic peak located at around 3.17 V doesn’t move during the cycles. These results infer the oxygen loss from the crystal structure in LTMO/24Al\(_2\)O\(_3\) is milder than in LTMO. As a result, the Mn redox reaction in LTMO/24Al\(_2\)O\(_3\) happens between Mn\(^{4+}\) and Mn\(^{3+}\). While Mn in pristine LTMO reduces to lower than 3+ because of the O loss and related densification in the first cycle.

In order to investigate the intrinsic factor of the improvement in the electrochemical performance of the LTMO/24Al\(_2\)O\(_3\)
sample, electrochemical impedance spectra (EIS) were collected on the bare LTMO and the LTMO/24Al\textsubscript{2}O\textsubscript{3} after charging to 4.8 V and resting for 4 h at the different cycles, shown in Figures 7A,B, respectively. All the Nyquist plots comprised a depressed semicircle from high to middle frequencies and an inclined line at low frequency. The simulated equivalent circuit is presented as an inset. The $R_1$ represents the Ohmic resistance coming from the separator, electrolyte and other components. The semicircle shows the charge transfer reaction composed of a charge transfer resistor ($R_2$) and a constant phase element (CPE\textsubscript{1}), the inclined line stands for the Warburg diffusion impedance (ZW). The LTMO/24Al\textsubscript{2}O\textsubscript{3} electrode shows the smaller $R_2$ of 101.6 $\Omega$ before cycling and remains at 228.4 $\Omega$, 433.8 $\Omega$ and 851.3 $\Omega$ after 1st, 5, and 10th cycling, respectively. Nevertheless, the much larger $R_2$ values of the LTMO electrode are seen (i.e., 255.8 $\Omega$ before cycling and changed to 557.7 $\Omega$ after 1st cycling, even to 10,207 $\Omega$ for the 5th cycling, respectively), which infer complex side reactions may happen on the electrode surface and these reaction products may have blocked the ionic transfer process and result in worse cycling performance. Thus, it can be concluded that an appropriate thickness of Al\textsubscript{2}O\textsubscript{3} layer guarantees the stable charge transfer and structural integrity of the cathode electrodes, which led to good cycling performance.

CONCLUSION

ALD technique was successfully used to deposit ultrathin Al\textsubscript{2}O\textsubscript{3} coating layer onto the surface of the LTMO particles. Comparing with the uncoated LTMO, ALD process can reduce the polarization, restrain the undesirable side reactions, and suppress the increasing charge transfer resistance during cycling, which results in the significantly improved electrochemical performance of Al\textsubscript{2}O\textsubscript{3}-coated LTMO (LTMO/24Al\textsubscript{2}O\textsubscript{3}). The controllable ALD technology provides a promising guideline for the surface modification of disordered rock-salt cathode materials with high electrochemical performance.

AUTHOR CONTRIBUTIONS

RW conceived and designed the research. BaH carried out the experiments. YG and HW contributed to the discussion. RW wrote the manuscript with the help of BeH. All authors reviewed the manuscript.

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