Ultrathin Surface Coatings for Improved Electrochemical Performance of Lithium Ion Battery Electrodes at Elevated Temperature

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S Supporting Information

ABSTRACT: To enhance the cycling stability of LiMn_2O_4 especially at elevated temperature, we use the atomic layer deposition (ALD) method to deposit ultrathin and highly conformal ZnO coatings (as thin as 0.34–1.7 nm) onto LiMn_2O_4 cathodes with precise thickness-control at atomic scale. We prepare two types of ALD-modified electrodes: one is an electrode composed of ALD-coated LiMn_2O_4 particles and uncoated carbon/polyvinylidene fluoride (PVDF) network; the other is ALD-coated LiMn_2O_4 composite electrode. All ALD-modified LiMn_2O_4 electrodes demonstrate significantly enhanced cycling performances than bare electrodes at both 25 and 55 °C. In particular, the electrode coated with 6 ZnO ALD layers (1.02 nm thick) shows the best cycling performances among electrodes coated with ALD films of different thicknesses at both 25 and 55 °C, indicating cycling performances of coated electrodes can be easily optimized by accurately tuning coating thickness via varying ALD growth cycles. Furthermore, an electrode consisting of LiMn_2O_4 particles coated with 6 ZnO ALD layers and uncoated carbon/PVDF network shows even better electrochemical performances than an electrode coated with 6 ZnO ALD layers at both 25 and 55 °C. The enhanced electrochemical performances of ALD-coated cathodes are ascribed to the high-quality ALD coatings that are highly conformal, dense, complete, and thus effectively protect active material from Mn dissolution especially at elevated temperature.

INTRODUCTION

Lithium manganese oxide (LiMn_2O_4) has been considered as a promising cathode alternative to the commercial lithium cobalt oxide (LiCoO_2) for rechargeable lithium ion batteries (LIBs) due to its nontoxicity, low cost, and excellent rate capability for applications in portable electronic devices and plug-in electric vehicle.^{1,2} However, this electrode material suffers from the Mn dissolution, crystal structure transformation, and electrolyte decomposition during electrochemical cycling, especially at the elevated temperature. The poor capacity retention of LiMn_2O_4 cathode material limits its practical applications.^{3–6} Mn dissolution during electrochemical cycling is caused by the attack from the acidic hydrofluoric acid (HF) formed by the residual H_2O and hexafluorophosphate (LiPF_6) in the electrolyte. This irreversible decomposition of LiMn_2O_4 yields impurity phases of the rock salt phase (Li_2MnO_3) and tetragonal phase ($\text{Li}_2\text{Mn}_2\text{O}_4$), which is the key factor for the capacity fading.^{7,8} Phase transition of the spinel LiMn_2O_4 also occurs, and the crystal structure of LiMn_2O_4 changes from the cubic to tetragonal symmetry during long-term cycling. Such structural degradation resulted from the Jahn–Teller effect considerably increases the disorder of lithium ions.⁹ The strong oxidation ability of Mn^{4+} at the end of charge reaction will bring about the decomposition of electrolyte on the surface of the working electrode. The formed solid electrolyte interphase (SEI) can cause increased charge transition resistance and distinct electrochemical polarization on the electrode.² The

factors mentioned above will together result in poor capacity retention of LiMn_2O_4 .⁷

The surface modification technique has been reported as an effective approach to improve the cycling performance of LiMn_2O_4 by coating different conductive carbon materials, phosphates, amphoteric oxides, and composite oxides.^{3–5,10–14} In order to circumvent the key issue of Mn dissolution for LiMn_2O_4 , various oxides such as Al_2O_3 , ZnO , ZrO_2 , MgO , SiO_2 , TiO_2 , Cr_2O_3 , and SnO_2 have been employed as surface coatings to protect LiMn_2O_4 particles from the HF's attack in electrolyte.^{6–9,15–22} The oxide coating on LiMn_2O_4 scavenges trace hydrogen fluoride acids (HF) in LIBs, and thus slows down dissolution of manganese ions and degradation of organic electrolyte at cathode, resulting in better electrochemical performance of LiMn_2O_4 . Most surface modifications of lithium transition metal oxides reported in literature are carried out with wet chemical methods such as sol–gel processing or solution processing,^{5,23} such as soaking cathode materials into a nanoalumina sol.²⁴ Other methods include melting impregnation method and pulsed laser deposition.^{20,25} However, these methods are not well-controlled processes. The resulted coatings lack conformality, uniformity, and completeness. One is not capable of controlling or tuning the coating

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thickness and quantity by using these methods, which limits the repeatability, reliability, and optimization of these processes. Moreover, wet chemistry methods require a large amount of solvent and precursor and a postheat-treatment to obtain the desired coatings. In addition, nanostructured battery electrodes have received tremendous attention lately, owing to their high surface area and high capacities. However, coatings resulted from wet processing are usually 50–100 nm thick,²⁶ which is too thick to be coated onto nanostructured electrodes. Moreover, the conventional thick oxide coatings on the cathode materials would hinder Li ion diffusivity, resulting in both low energy and power density of the working electrodes.²⁷ Therefore, it is necessary to explore new surface coatings that are much thinner and have high conformality for next-generation battery technology.

In this study, we deposit ultrathin and highly conformal oxide coatings onto LiMn_2O_4 by using the atomic layer deposition (ALD) method with precise thickness control at atomic scale. ALD requires only a minimal amount of precursor and can be used to deposit ultrathin and highly conformal surface coatings.^{28,29} The basic advantage of ALD lies in the fact that the film growth is surface controlled, rather than source controlled as in many other deposition methods such as chemical vapor deposition (CVD). This is achieved by using sequential exposures, separating the (usually binary) reaction between the precursor compounds into two half-reactions. During each half-reaction, only one monolayer of the reactant chemisorbs (or is chemically bound) on the surface. Further layers that are only physisorbed are removed by an inert gas purge before the other reactant is introduced. As a result, the process proceeds stepwise in self-limiting surface reactions, separated by purge steps. Hence, films grown using ALD are typically uniform, dense, homogeneous, pinhole-free, and extremely conformal to the underlying substrate. Moreover, ALD has excellent step coverage ($\sim 100\%$) and refilling ability on particles and porous structures.^{27,29–31}

To date, there are only a few reports about surface modifications of lithium ion battery electrodes via ALD coatings and most of them focused on LiCoO_2 .^{32–39} To the best of our knowledge, there is no report about the effect of ALD coatings on electrochemical properties of LiMn_2O_4 so far, except a communication paper we published recently.⁶ In the present work, we fabricate ZnO ALD modified LiMn_2O_4 cathodes to enhance cycling performances of cathodes at both room temperature (25 °C) and elevated temperature (55 °C). The ZnO ALD coatings are either deposited onto individual LiMn_2O_4 particles or onto an entire LiMn_2O_4 composite electrode. Both of these two types of ALD-modified cathodes show enhanced cycleability compared to bare cathodes at room temperature and elevated temperature. Furthermore, cycling performances of coated cathodes are optimized by manipulating the coating thickness via varying ALD growth cycles. Electrode composed of LiMn_2O_4 particles coated with 6 ZnO ALD layers shows the best cycling performance even at the elevated temperature (55 °C), which can be considered as a very promising electrode applied to the elevated temperature environment.

■ EXPERIMENTAL SECTION

Sample Preparation. Atomic layer deposition of ZnO coatings on LiMn_2O_4 particles (Alfa Aesar, 99.5%) was carried out in a Savannah 100 ALD system (Cambridge NanoTech Inc.) at 120 °C using $\text{Zn}(\text{CH}_2\text{CH}_3)_2$ (diethylzinc, DEZ) and

H_2O as precursors with exposure time of 0.015 s, waiting time of 5 s, and purge time of 40 s. The principle of ZnO ALD growth from H_2O and DEZ is subjected to the two self-terminating reactions as follows:^{36,40,41}

LiMn_2O_4 particles were coated with 2, 6, 10, and 50 ZnO ALD layers via corresponding ALD growth cycles, respectively.

Electrode Fabrication. The bare composite electrodes (abbreviated as B-E) were composed of 80% bare LiMn_2O_4 particles, 10% acetylene black (conductive carbon, Alfa Aesar, 99.5%), and 10% polyvinylidene fluoride (PVDF, Alfa Aesar) as the binder, dissolved in *N*-methyl-2-pyrrolidone (NMP) solvent. The resultant viscous slurry was coated onto the aluminum current collector using the AFA-III automatic film applicator (MTI) with the thickness setting of 500 μm and then dried at 120 °C overnight under vacuum. The dried electrodes were pressed to an effective thickness of 50 μm by using the EQ-MR100A rolling press machine (MTI). Approximately 10 mg of active material was loaded in the circular working electrode with a diameter of 18.9 mm. The bare composite electrodes were coated with 2, 6, and 10 ZnO ALD layers, respectively (abbreviated as 2 ZnO ALD-E, 6 ZnO ALD-E, and 10 ZnO ALD-E). Other comparative composite electrodes were prepared by mixing LiMn_2O_4 particles coated with 2, 6, and 10 ZnO ALD layers with conductive carbon and PVDF binder at the same weight ratio of 80:10:10, respectively (abbreviated as 2 ZnO ALD LMO-E, 6 ZnO ALD LMO-E, and 10 ZnO ALD LMO-E).

Characterizations. The crystallographic structure of bare and ZnO ALD coated LiMn_2O_4 powders were examined by using a Rigaku MiniFlex X-ray diffractometer with Cu K_α radiation at a scan rate of 4°/min. The particle size and surface morphology were observed using a FEI Quanta 3D FEG field emission scanning electron microscopy (FESEM). Transmission electron microscopy (TEM) images were captured on a JEM-2010 microscopy at an acceleration voltage of 200 kV, to investigate the characteristics of the ZnO coatings. Surface compositions of LiMn_2O_4 particles coated with 6 ZnO ALD layers and LiMn_2O_4 composite electrode coated with 6 ZnO ALD layers were analyzed via X-ray photoelectron spectroscopy (XPS) using an AXIS 165 spectrometer with a twin-anode Al K_α (1486.6 eV) X-ray source. All the XPS spectra were calibrated according to the binding energy of the C1s peak at 284.8 eV.

Electrochemical Measurements. Different LiMn_2O_4 -based composite electrodes were integrated into two-electrode CR2032-type coin cells for electrochemical measurements, with LiMn_2O_4 -based composite electrode as cathode, metallic lithium foil as anode, and Celgard-2320 membrane as separator; the electrolyte was 1 M LiPF_6 dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) at a volumetric ratio of 1:1:1. The coin cells were assembled in an argon-filled glovebox (OMNI-Lab system, Vacuum Atmosphere Co.). Galvanostatic charge and discharge were performed in a voltage range of 3.4–4.5 V at a current density of 120 mA/g using an 8-channel battery analyzer (MTI Corporation) at room temperature (25 °C) and elevated temperature (55 °C). Electrochemical specific storage

Figure 1. Schematic representation for ZnO ALD growth on the surface of LiMn_2O_4 particle using $\text{Zn}(\text{CH}_2\text{CH}_3)_2$ and H_2O as precursors.

capacities of working electrodes were calculated based on the mass of cathode materials. In addition, cyclic voltammetry (CV) curves of 6 ZnO ALD LMO-E were measured at a scan rate of 0.1 mV s^{-1} between 3.4 and 4.5 V using an electrochemical analyzer (CHI605C) at 25 and 55 $^\circ\text{C}$, respectively.

RESULTS AND DISCUSSION

Ultrathin ZnO coatings can be deposited onto the surface of LiMn_2O_4 particles via ALD with high conformality and exquisite thickness control at the Angstrom or monolayer level. As shown in the schematic representation of ZnO ALD growth in Figure 1, ZnO film grows monolayer by monolayer due to the sequential and self-limiting surface reactions. The self-limiting aspect of ALD leads to excellent step coverage and conformal deposition on high aspect ratio structures. Another advantage of ALD approach is that it allows for direct deposition of ZnO on either as-prepared composite electrodes or individual electrode material particles, providing commercial feasibility for mass industrial production for lithium ion batteries.^{6,28,32}

X-ray diffraction (XRD) pattern of LiMn_2O_4 particles coated with 6 ZnO ALD layers (via 6 ALD growth cycles) is displayed in Figure 2 in comparison with that of bare LiMn_2O_4 particles. All distinct XRD peaks from the sample of 6 ZnO ALD LMO (LiMn_2O_4 particles coated with 6 ZnO ALD layers) are well indexed to the spinel cubic structure of LiMn_2O_4 with a $F3dm$ space group (JCPDS, 35-0782). The ZnO phase is not detectable even when 50 ZnO ALD layers are coated on pristine LiMn_2O_4 particles (Figure S1, Supporting Information), which can be ascribed to the amorphous phase and low weight ratio of ZnO.⁷

Figure 2. XRD patterns of (a) bare LiMn_2O_4 particles and (b) LiMn_2O_4 particles coated with 6 ZnO ALD layers.

Figure 3 reveals the morphology and composition of LiMn_2O_4 particles before and after ZnO ALD coatings. Figure 3a,b present SEM images of bare LiMn_2O_4 particles and LiMn_2O_4 particles coated with 6 ZnO ALD layers, respectively. As can be seen from Figure 3a, LiMn_2O_4 particles have an average particle size of $\sim 5 \mu\text{m}$ with smooth polyhedron profile. Figure 3b shows the shape and morphology of LiMn_2O_4 particles coated with 6 ZnO ALD layers, which are almost identical to bare LiMn_2O_4 particles in Figure 3a. There is no visible difference in the SEM image after the LiMn_2O_4 particles are coated with ZnO ALD film, possibly because the ALD coating is ultrathin and highly conformal and thus preserves the

Figure 3. SEM images of (a) bare LiMn_2O_4 particle and (b) LiMn_2O_4 particle coated with 6 ZnO ALD layers; HRTEM images of (c) bare LiMn_2O_4 particle, (d) LiMn_2O_4 particle coated with 6 ZnO ALD layers, and (e) LiMn_2O_4 particle coated with 50 ZnO ALD layers; and (f) TEM image of LiMn_2O_4 particle coated with 50 ZnO ALD layers (insets, EDS captured at the center and edge of this particle).

morphology of LiMn_2O_4 particles. Even when LiMn_2O_4 particles are coated with 50 ZnO ALD layers, the coated particles retain the same morphology and shape of bare particles as observed under SEM (Figure S2, Supporting Information), suggesting the high conformality of ALD coating.

To study the details of ALD coatings, high-resolution TEM (HRTEM) is used to examine uncoated and ALD-coated LiMn_2O_4 particles. Figure 3c,d present HRTEM images of a bare LiMn_2O_4 particle and a LiMn_2O_4 particle coated with 6 ZnO ALD layers. It is noted that bare LiMn_2O_4 particle is crystalline, as lattice fringes are observed in Figure 3c with $d_{(222)} = 0.238$ nm, while TEM image of the ZnO coated LiMn_2O_4 (Figure 3d) reveals that a very thin and amorphous ALD coating fully and conformally enwraps around the crystalline LiMn_2O_4 particle. To obtain more information about ALD coatings, LiMn_2O_4 particles are coated with thicker ZnO ALD

film (50 ALD layers using 50 ALD growth cycles) and are examined under HRTEM, as presented in Figure 3e,f. Figure 3e clearly shows that an amorphous and homogeneous ALD film is conformally coated on the crystalline LiMn_2O_4 particle. Thickness of the coating is estimated to 8.7 nm, corresponding to an ALD growth rate of 1.7 Å/cycle. In order to confirm the deposition of ZnO on the surface of LiMn_2O_4 , energy dispersive X-ray spectroscopy (EDS) is used to examine the compositions at the center and the edge of coated LiMn_2O_4 , respectively, as shown in the inset graphs of Figure 3f. Both EDS spectra reveal the elements of O, Mn, Zn, and Cu. The Cu peaks are from the copper grid where the TEM sample is placed on. It is noted that the atomic percent of Zn on the edge is 10.9%, larger than 7.1% in the center, confirming the formation of ZnO coating on the surface of LiMn_2O_4 particle. Therefore, from the SEM and TEM results in Figure 3, we can

Figure 4. (a) Cross-section SEM image, (b) surface view, (c) enlarged cross-section SEM image, and (d) schematic representation of bare LiMn_2O_4 composite electrode.

conclude that ZnO ALD coatings are ultrathin, dense, uniform, highly conformal, and provide full coverage of LiMn_2O_4 particles.

Before integrating into lithium ion battery cells, LiMn_2O_4 cathode is fabricated by mixing 80% LiMn_2O_4 particles, 10% acetylene black as conducting material, and 10% polyvinylidene-fluoride (PVDF) as a binder. Figure 4a–c show the SEM images of cross-section view, surface view, and enlarged cross-section view of LiMn_2O_4 cathode, respectively. The cathode shows an even thickness of $\sim 43 \mu\text{m}$ (Figure 4a). As seen from the surface morphology (Figure 4b) and the cross-section profile of LiMn_2O_4 cathode (Figure 4c), LiMn_2O_4 particles are immersed in a porous network composed of smaller carbon and PVDF particles. Figure 4d exhibits a schematic illustrating this morphology and structure of LiMn_2O_4 cathode.

We have prepared three types of LiMn_2O_4 -based electrodes as shown in the schematics in Figure 5. One is a bare electrode consisting of bare LiMn_2O_4 particles, carbon, and PVDF, denoted by B-E. The second type of electrode is composed of ALD-coated LiMn_2O_4 particles, carbon and PVDF, denoted by ALD LMO-E. The third is obtained by depositing ALD coating onto the entire bare electrode, which is marked with ALD-E. Since ALD allows for the growth of conformal films even on substrates with complex surface geometries,^{6,32,35,36} ZnO film will penetrate into the porous electrode, and coat onto both micrometer-sized LiMn_2O_4 particles and porous framework bridged by carbon and PVDF in the case of “ALD-E”, as illustrated in the right picture of Figure 5. LiMn_2O_4 particles are partially covered by ALD coatings because LiMn_2O_4 particles

Figure 5. Schematic representations of bare LiMn_2O_4 composite electrode (left), electrode composed of ALD-coated LiMn_2O_4 particles and uncoated carbon/PVDF (center), and ALD-coated LiMn_2O_4 composite electrode (right).

are tightly enwrapped by carbon and PVDF network as shown in the cross-section SEM image of the electrode (Figure 4c). Therefore, in these three different electrodes, there are various interfaces between LiMn_2O_4 particles, ALD coatings, carbon and PVDF composites, and surrounding electrolyte, to affect electron transport and Li ion diffusion during delithiation and lithiation reactions, resulting in different electrochemical behaviors of these electrodes. It is noted that SEM images captured from an electrode composed of LiMn_2O_4 particles coated with 6 ZnO ALD layers and uncoated carbon/PVDF network, LiMn_2O_4 composite electrode coated with 6 ZnO ALD layers, and LiMn_2O_4 composite electrode coated with 50 ZnO ALD layers (Figure S3, Supporting Information) are all similar to the SEM image of bare LiMn_2O_4 composite

electrode, indicating that ZnO ALD coatings on the composite electrodes are ultrathin, homogeneous, and highly conformal.

To confirm the formation of ZnO on the surface of LiMn_2O_4 particles and LiMn_2O_4 electrode, X-ray photoelectron spectroscopy (XPS) is used to analyze the surface compositions of LiMn_2O_4 particles coated with 6 ZnO ALD layers and LiMn_2O_4 composite electrode coated with 6 ZnO ALD layers, respectively, as shown in Figure 6. Both spectra show the Zn

Figure 6. XPS spectra of (a) LiMn_2O_4 particles coated with 6 ZnO ALD layers and (b) LiMn_2O_4 composite electrode coated with 6 ZnO ALD layers.

$2p_{3/2}$ and $2p_{1/2}$ peaks from ZnO, indicating the existence of ZnO on the surface of the samples. However, the binding energies of the Zn $2p_{3/2}$ and $2p_{1/2}$ in XPS spectrum of 6 ZnO ALD LMO are 1019.4 and 1042.5 eV (Figure 6a), respectively, shifting ~ 2 eV to the lower binding energy in comparison with the standard values of ZnO (1021.7 and 1044.7 eV) in NIST XPS Database, while the binding energies of Zn $2p_{3/2}$ of 1021.7 eV and $2p_{1/2}$ of 1044.6 eV observed for 6 ZnO ALD-E sample in Figure 6b are consistent with standard values of ZnO. This difference is possibly due to different chemical and bonding environments of ZnO ALD coatings on LiMn_2O_4 particles and

LiMn_2O_4 composite electrode. In ALD coating, substrate material and ZnO coating film are bridged by the chemical bond, oxygen bond (substrate–O–ZnO) illustrated in Figure 1. In 6 ZnO ALD-E, the ZnO is mainly deposited on conductive carbon due to the hydrophobic selection property of PVDF to hydroxyl groups (Figure 5),³⁵ while in 6 ZnO ALD LMO, the ZnO is grown tightly on LiMn_2O_4 particles. We speculate that the different electronic distribution and polarity of substrate materials (LiMn_2O_4 and carbon) influence the chemical environment of ZnO coating via oxygen bond, contributing to the peak shift of Zn 2p in 6 ZnO ALD LMO.

The three types of electrodes shown in Figure 5 are then integrated into CR2032-type coin cells with lithium as anode for electrochemical testing. Electrochemical measurements are performed for bare electrode (B-E), electrodes coated with ALD films of various thicknesses (2, 6, and 10 ZnO ALD layers) (samples denoted by 2 ZnO ALD-E, 6 ZnO ALD-E, and 10 ZnO ALD-E), and electrode composed of LiMn_2O_4 particles coated with 2, 6, and 10 ZnO ALD layers and carbon/PVDF (marked with 2 ZnO ALD LMO-E, 6 ZnO ALD LMO-E, and 10 ZnO ALD LMO-E). Figure 7 summarizes cycling performances of these electrodes cycled at a current density of 120 mA/g in a voltage range of 3.4–4.5 V at 25 and 55 °C. All ALD-modified LiMn_2O_4 electrodes exhibit higher final capacities than bare cathode after 100 electrochemical cycles. ZnO coatings have been reported as the most effective HF scavenger among Al_2O_3 , ZrO_2 , and SnO_2 to protect LiMn_2O_4 particles from the detrimental Mn dissolution.¹⁵ The ZnO thin film can serve as an amorphous interphase between electrode and electrolyte to prevent from electrolyte decomposition and formation of the insulating solid electrolyte interphase (SEI) on the surface of working electrode.^{2,28}

It has been estimated from the TEM results in Figure 3 that the growth rate of this ZnO ALD is 1.7 Å/cycle, and thus, one ALD layer is 1.7 Å thick. As shown in Figure 7a,c, the electrode coated with 6 ZnO ALD layers (1.02 nm thick) delivers the best cycling performance and the highest final capacity among the electrodes coated with ZnO ALD films of different thicknesses, either at 25 or 55 °C. This 6 ZnO ALD-E delivers a final capacity of 44.5 mAh/g after 100 electrochemical cycles at 1 C at 55 °C, much higher than the final capacity of 27.0 mAh/g delivered by bare electrode at 55 °C. When ZnO is coated on LiMn_2O_4 particles as shown in Figure 7b,d, 6 ZnO ALD layers are also the optimal thickness for the best cycling performance either at room temperature or elevated temperature. When the ALD coating is too thin, it is not sufficient to scavenge the harmful HF generated during electrochemical cycling and thus the effect of surface coating to enhance the performance of the electrode is less distinct, as observed for electrodes coated with 2 ALD layers. However, an overly thick ZnO ALD coating will slow down the diffusion of lithium ions at the interface between electrode and electrolyte and will thus reduce the capacities of the electrode,²⁷ as observed for electrodes coated with 10 ALD layers. Therefore, it is feasible to accurately tune the thickness of ALD coatings for ultimate optimization of lithium ion battery performances because ALD offers precise thickness control at the atomic level. In addition, the protective effect of ZnO ALD coatings to the LiMn_2O_4 electrode is even more obvious when the electrode is cycled at elevated temperature than cycled at room temperature, by comparing Figure 7a,c for ZnO coated electrodes as well as Figure 7b,d for ZnO modified LiMn_2O_4 particles. In comparison with ALD oxide coatings on different nanosized

Figure 7. Cycling performances of various electrodes at a current density of 120 mA/g in a voltage range of 3.4–4.5 V vs. Li: (a,b,e) cycled at 25 °C; (c,d,f) cycled at 55 °C. B-E, bare LiMn_2O_4 composite electrode; n ZnO ALD-E, LiMn_2O_4 composite electrode coated with n ZnO ALD layers; n ZnO ALD LMO-E, electrode composed of LiMn_2O_4 particles coated with n ZnO ALD layers and uncoated carbon/PVDF network.

cathode materials, such as LiCoO_2 ^{27,35,36} and $\text{Li-Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$,³⁴ the initial capacity drops during the first several cycles in this work are probably due to the micrometer-sized LiMn_2O_4 particles, which have an average size of 5 μm , inevitable Mn dissolution in LiMn_2O_4 -based cathodes and the resultant electrochemical polarization of the cathodes at a relatively high current density of approximate 1 C. It is found in our other work that there is much less distinct initial capacity degradation for nanosized LiMn_2O_4 and this work has been submitted elsewhere. There is also ongoing work in our laboratory to alleviate the initial capacity drops via heat treatments of micro-sized LiMn_2O_4 . Furthermore, at the elevated temperature, LiMn_2O_4 suffers from faster capacity

fading because high temperature accelerates side reactions and electrolyte decomposition in battery cells, which will induce more severe Mn dissolution.⁴²

Figure 7a–d indicate that ZnO coating on LiMn_2O_4 particles is more sensitive for improved electrochemical performance than ZnO depositing on composite electrodes. Figure 7e,f present cycling performances of bare electrode (B-E), LiMn_2O_4 electrode coated with 6 ZnO ALD layers (6 ZnO ALD-E), and the electrode composed of LiMn_2O_4 particles coated with 6 ZnO ALD layers and carbon/PVDF (6 ZnO ALD LMO-E) at 25 and 55 °C, respectively. Differences in the morphology and structure of these three electrodes are illustrated in Figure 5. It is interesting to note that 6 ZnO ALD LMO-E shows even

better cycling performance and higher capacities than 6 ZnO ALD-E. As shown in Figure 7e, 6 ZnO ALD LMO-E delivers an initial discharge capacity of 74.6 mAh/g at 25 °C, higher than the initial capacities of 65.1 mAh/g from 6 ZnO ALD-E and 65.7 mAh/g from B-E at 25 °C. The increased capacity of 6 ZnO ALD LMO-E can be attributed to the following factors: (1) ZnO film is fully coated onto LiMn_2O_4 particles in 6 ZnO ALD LMO-E, while ZnO film is partially coated onto LiMn_2O_4 particles within the ZnO coated carbon/PVDF network in 6 ZnO ALD-E as shown in Figure 5; this difference in ZnO ALD coverage of LiMn_2O_4 particles may contribute to the higher capacities of 6 ZnO ALD LMO-E than 6 ZnO ALD-E; (2) the semiconducting ZnO film can average the distribution of electrons and lithium ions around the whole LiMn_2O_4 surface to take full advantage of the active sites for Li^+ insertion and extraction; the polarization from the concentration difference of Li^+ and electrons can be reduced in the working electrode; (3) the conformal and dense ZnO coatings, as shown in Figures 1 and 3d, can serve as a solid framework to restrain the phase transition of LiMn_2O_4 from cubic to tetragonal structure and thus to prevent the harmful Jahn–Teller effect; (4) dissolution of Mn ions into the internal structure of carbon and PVDF network can be reduced due to the complete ZnO coverage on LiMn_2O_4 particles in 6 ZnO ALD LMO-E, while ZnO coverage on LiMn_2O_4 particles is partial in 6 ZnO ALD-E (Figure 5). Therefore, 6 ZnO ALD LMO-E delivers the highest discharge capacity. However, the capacity retention of 6 ZnO ALD LMO-E after 100 cycles is slightly worse than that of 6 ZnO ALD-E, possibly due to less ZnO content in 6 ZnO ALD LMO-E to rapidly consume the HF. As shown in Figure 5, the composite electrode can be coated with more ZnO than LiMn_2O_4 particles because the electrode composed of micrometer-sized LiMn_2O_4 particles buried in porous carbon/PVDF network has larger surface area than micrometer-sized LiMn_2O_4 particles.

At elevated temperature, LiMn_2O_4 electrode will suffer from faster capacity fading because high temperature accelerates chemical kinetics in the battery cell and aggravates negative factors in terms of Mn dissolution, phase transition, and electrolyte decomposition.⁷ However, higher temperature also leads to enhanced electrical conductivity and faster lithium ion diffusion in LiMn_2O_4 electrode, which can contribute to less polarization and subsequently improved energy and powder densities of LiMn_2O_4 . Figure 7c,d,f illuminates this competitive relationship between such negative and positive influences on different composite electrodes. Bare electrode displays more severe capacity loss at 55 °C compared to that at 25 °C, as shown in Figure 7. The capacity fading of B-E is mainly ascribed to the intensified Mn dissolution, which becomes the predominant factor at elevated temperature without any protective surface coatings on the composite electrode.^{7,16} 2 ZnO ALD-E exhibits similar electrochemical behaviors at 55 and 25 °C without much change in cycleability when the sample is subjected to higher temperature, indicating that the ultrathin ZnO coating (2 ALD layers, 0.34 nm thick) can adequately impede Mn dissolution at elevated temperature. The effect of ALD coatings to enhance performance of LiMn_2O_4 at higher temperature is more phenomenal when thickness of ALD coatings is optimized to be 6 ALD layers (1.02 nm). 6 ZnO ALD-E shows a higher initial capacity (84.9 mAh/g) at 55 °C than that at 25 °C. It is speculated that, when Mn dissolution at elevated temperature is effectively restrained by 6 ZnO ALD layers as it works at room temperature, the enhanced conductivity and Li ion diffusion rate in the electrode

at higher temperature becomes the leading beneficial factor resulting in increased capacity. In the case of 10 ZnO ALD-E, the initial capacity at 55 °C is lower than that at 25 °C because an overly thick ZnO coating may slow down Li^+ diffusion at elevated temperature,^{16,27} though this sample shows very good capacity retention after 100 electrochemical cycles. After 100 electrochemical cycles at 55 °C, the obvious existence of residual ZnO coating in 10 ZnO ALD-E is validated by XPS analysis of Zn 2p peaks in Figure S4a, Supporting Information. The apparently lower Zn 2p peaks can be observed from 6 ZnO ALD-E after 100 electrochemical cycles at 55 °C (Figure S4b, Supporting Information) in comparison with that measured from the primary electrode coated with 6 ZnO ALD layers before cycling (Figure 6b), indicating that 6 ZnO ALD layers can be considered as the critical coating thickness to completely neutralize the HF but not influence the lithium ion diffusivity. In summary, a surface coating composed of 6 ZnO ALD layers (1.02 nm thick) has optimal thickness for enhancing the performance of LiMn_2O_4 electrode, and the positive effect of this coating is more distinct at elevated temperature. Furthermore, when this optimal 6 ZnO ALD layers are coated onto LiMn_2O_4 particles instead of the entire composite electrode, the effect of this coating to enhance the performance of electrode at elevated temperature is even more phenomenal. The sample 6 ZnO ALD LMO-E delivers an initial capacity of 90.8 mAh/g at 55 °C, which is higher than that of 6 ZnO ALD-E (84.9 mAh/g) and 1.7 times larger than that of B-E (52.9 mAh/g) at 55 °C. 6 ZnO ALD LMO-E also delivers the highest final capacity of 56.1 mAh/g at 55 °C, higher than that of 6 ZnO ALD-E (44.5 mAh/g) and that of B-E (27.0 mAh/g) at 55 °C. Moreover, under a low current density of 0.1 C, 6 ZnO ALD LMO-E delivers a high initial discharge capacity of 119.1 mAh/g at 55 °C (Figure S5, Supporting Information), confirming its outstanding electrochemical performance at elevated temperature.

In order to further evaluate the effect of ZnO ALD coating on LiMn_2O_4 particles at elevated temperature, the cyclic voltammetric (CV) measurements of 6 ZnO ALD LMO-E are carried out at a scan rate of 0.1 mV/s between 3.4 and 4.5 V vs. Li, at 25 and 55 °C, respectively, as shown in Figure 8a. It can be seen that the anodic peak current located at 4.18 V at 55 °C is larger than the peak at 4.17 V at 25 °C, indicating that more lithium ions can be extracted from the LiMn_2O_4 structure due to the enhanced electrical conductivity from 3.82×10^{-6} (25 °C) to 3.04×10^{-5} S/cm (55 °C) of 6 ZnO ALD LMO-E when it is subjected to elevated temperature. In the corresponding reduction cycle, the cathodic peak current at a high voltage of 4.06 V at 55 °C is also much higher than that at 4.08 V at 25 °C, suggesting more intercalation of lithium ions into the host LiMn_2O_4 at 55 °C. It should be noted that the improved conductivity and lithium ion diffusion rate at higher temperature stimulate the activity of lithium ions in the high voltage sites, resulting in improved specific capacity. The distinct peak at 4.5 V at 55 °C indicates that decomposition of the electrolyte derived by the higher oxidation of Mn^{4+} due to the deep delithiation reaction is accelerated at elevated temperature. Figure 8b exhibits charge/discharge profiles of 6 ZnO ALD LMO-E from different electrochemical cycles at 25 and 55 °C. As for the second cycle at 55 °C, the charge curve presents two potential plateaus located at 4.03 and 4.16 V, and the corresponding discharge curve displays plateaus at 4.08 and 3.95 V, consistent with the CV curve. In contrast, the two pairs of weak voltage plateaus in charge and discharge curves at 25

Figure 8. Electrochemical performances of the electrode composed of LiMn_2O_4 particles coated with 6 ZnO ALD layers and carbon/PVDF network (6 ZnO ALD LMO-E): (a) CV curves at a scan rate of 0.1 mV/s at 25 and 55 °C and (b) charge/discharge curves from different electrochemical cycles at a current density of 120 mAh/g in a voltage range of 3.4–4.5 V vs. Li at 25 and 55 °C.

°C are not well-matched with the redox peaks in the CV curve. The increased polarization can be attributed to the low conductivity of the working electrode and the usage of high current density in charge/discharge reactions at 25 °C, whereas the CV measurement was performed at a slow scan rate. The extended high-voltage plateaus can be clearly observed in the charge/discharge curves at 55 °C at the second, fifth, 50th, and 100th electrochemical cycles compared to those of charge/discharge curves at 25 °C. The enhanced mobility of lithium ions at high voltage at increased temperature thus contributes to the considerably improved capacity of the 6 ZnO ALD LMO-E at 55 °C.

CONCLUSIONS

We have deposited ultrathin and highly conformal ZnO coatings (as thin as 0.34–1.7 nm) onto LiMn_2O_4 by using the atomic layer deposition method, for enhanced electrochemical performances of electrode materials. Thickness of ZnO ALD coatings can be tuned and precisely controlled by varying ALD growth cycles, with a growth rate of 1.7 Å per

cycle in this study. ZnO ALD coatings are deposited either onto the entire LiMn_2O_4 composite electrode or individual LiMn_2O_4 particles. All the ALD-modified electrodes demonstrate enhanced cycleability compared to bare electrodes at both 25 and 55 °C. Among electrodes coated with ALD films of different thicknesses, LiMn_2O_4 electrode coated with 6 ZnO ALD layers (1.02 nm thick) shows the best cycling performance, demonstrating that it is facile to accurately tune the thickness of ALD coatings and thus optimize the electrochemical performances of ALD-modified electrodes simply via varying ALD growth cycles. Furthermore, the electrode composed of LiMn_2O_4 particles coated with 6 ZnO ALD layers and uncoated carbon/PVDF network shows even better electrochemical performances than the LiMn_2O_4 composite electrode coated with 6 ZnO ALD layers at both 25 and 55 °C, and the effect of ZnO ALD coatings is more phenomenal at the elevated temperature. The electrode composed of LiMn_2O_4 particles coated with 6 ZnO ALD layers delivers the highest final capacity of 56.1 mAh/g after 100 electrochemical cycles at 1 C at 55 °C, much higher than the final capacity of 27.0 mAh/g delivered by bare electrode at 55 °C, showing that the effect of ZnO ALD coatings to enhance the electrochemical performance of LiMn_2O_4 is more phenomenal at elevated temperature. The ultrathin and high-quality ZnO ALD coating can effectively alleviate dissolution of manganese ions into the electrolyte by scavenging HF and retards the electrolyte decomposition by isolating LiMn_2O_4 from the electrolyte. Lastly, the methods presented in this study can be generalized to other cathode materials and other coatings as long as the coatings can be fabricated via ALD. For example, ALD surface coatings will be used to improve electrochemical performances of high-capacity cathodes such as lithium-rich layered oxides $\text{Li}[\text{Li}, \text{Mn}, \text{Ni}, \text{Co}] \text{O}_2$ in our laboratory.

ASSOCIATED CONTENT

Supporting Information

XRD pattern and SEM image of LiMn_2O_4 particles coated with 50 ZnO ALD layers; SEM images of electrode composed of LiMn_2O_4 particles coated with 6 ZnO ALD layers and carbon/PVDF network, composite electrode coated with 50 ZnO ALD layers; XPS spectra of Zn 2p from LiMn_2O_4 composite electrodes coated with 6 and 10 ZnO ALD layers after 100 cycles at 55 °C; cycling performance of the electrode composed of LiMn_2O_4 particles coated with 6 ZnO ALD layers and carbon/PVDF network at 0.1 C at elevated temperature (55 °C). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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