Electronic Supplementary Information

Low Temperature Preparation of Crystalline ZrO₂ Coatings for Improved Elevated-Temperature Performances of Li-Ion Battery Cathodes

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Experimental Section

Preparation of bare composite electrode

The LiMn₂O₄ powders (99.5%) were purchased from Alfa Aesar without any further treatment. The bare composite electrode was composed of 80 % pristine LiMn₂O₄ particles, 10 % acetylene black (conductive carbon, Alfa Aesar, 99.5%) and 10 % poly-vinylidene fluoride (PVDF, Alfa Aesar) as the binder.

Atomic layer deposition of ZrO₂ coating on LiMn₂O₄ particles and bare composite electrode

Atomic layer deposition of ZrO₂ coating on LiMn₂O₄ particles and bare composite electrodes was carried out in a Savannah 100 ALD system (Cambridge NanoTech Inc.) at 120°C using Zr(OC(CH₃)₃)₄ (Zirconium tert-butoxide, ZTB) and H₂O as precursors with exposure time of 0.25 and 0.015 s, waiting time of 5 and 5 s and purge time of 60 and 40 s, respectively. The two self-terminating reactions involved in this ZrO₂ ALD growth are described in the following reactions:

¹
\[
\text{Zr(OH)}^* + \text{Zr(OC(CH}_3)_3)_4 \rightarrow \text{Zr-O-Zr-(O-C(CH}_3)_3)^*+ (CH}_3)_3\text{COH}
\]

\[
\text{Zr-O-(CH}_3)_3)^*+ \text{H}_2\text{O} \rightarrow \text{ZrOH}^*+ \text{CH}_2=\text{C(CH}_3)_2
\]

**Characterizations**

The crystallographic structure of ZrO\(_2\) ALD coated LiMn\(_2\)O\(_4\) particles were examined by using a Rigaku MiniFlex X-ray diffractometer with Cu K\(_\alpha\) radiation at a scan rate of 2\(^\circ\)/min. The particle size of bare LiMn\(_2\)O\(_4\) particles and surface morphology of bare composite electrode 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 instrument microscopy at an acceleration voltage of 200 kV, to investigate the characteristics of the ZrO\(_2\) coatings. Surface compositions of LiMn\(_2\)O\(_4\) particles coated with 6 ZrO\(_2\) ALD layers and LiMn\(_2\)O\(_4\) composite electrode coated with 6 ZrO\(_2\) ALD layers were analyzed via X-ray photoelectron spectroscope (XPS) using an AXIS 165 spectrometer using a twin-anode Al K\(_\alpha\) (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 electrodes were integrated into two-electrode CR2032-type coin cells for electrochemical measurements, with metallic lithium foil as anode, Celgard-2320 membrane as separator; electrolyte was 1 M LiPF\(_6\) dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) and diethyl carbonate (DEC) at a volumetric ratio of 1:1:1. Galvanostatic charge and discharge were performed at different current densities in a voltage range of 3.4 - 4.5 V using an 8-channel battery analyzer (MTI Corporation) at room temperature (25\(^\circ\)C) and elevated temperature (55\(^\circ\)C). The electrochemical impedance spectroscopy (EIS) of different
ZrO$_2$ ALD modified LiMn$_2$O$_4$ electrodes were performed on VersaSTAT MC electrochemical analyzer (Princeton Applied Research) in a frequency range of 100 kHz-10 mHz by applying an AC amplitude of 5 mV.
Fig. S1 XRD patterns of (a) bare LiMn$_2$O$_4$ particles, (b) LiMn$_2$O$_4$ particles coated with 300 ZrO$_2$ ALD layers and (c) composite electrode (LiMn$_2$O$_4$:Carbon:PVDF=8:1:1 in weight ratio) coated with 300 ZrO$_2$ ALD layers. Three XRD patterns only present show spinel cubic LiMn$_2$O$_4$ phase with a $F3dm$ space group (JCPDS: 35-0782). No ZrO$_2$ phase can be detected.
**Fig. S2** Scanning electron microscopy (SEM) image of bare LiMn$_2$O$_4$ particles with an average particle size of ~5 μm.
Fig. S3 SEM image showing surface morphology of the bare composite electrode composed of 80 % pristine LiMn$_2$O$_4$ particles, 10 % acetylene black and 10 % poly-vinylidenefluoride (PVDF) as the binder.
Fig. S4  Cycling performance of bare LiMn$_2$O$_4$ composite electrode and LiMn$_2$O$_4$ composite electrodes coated with 6, 50, and 300 ZrO$_2$ ALD layers corresponding to the thickness of 1.74, 14.5 and 87 nm at a current density of 120 mAh/g in a voltage range of 3.4–4.5 V at room temperature (25°C).
Fig. S5 Electrochemical impedance spectra of different ZrO$_2$-ALD-modified LiMn$_2$O$_4$ electrodes in comparison with bare electrode in a frequency range of 100 kHz - 10 mHz by applying an AC amplitude of 5 mV at 55°C. “B-E”: bare LiMn$_2$O$_4$ composite electrode; “n ZrO$_2$ ALD-E”: LiMn$_2$O$_4$ composite electrode coated with n ALD layers; “6 ZrO$_2$ ALD LMO-E”: electrode composed of LiMn$_2$O$_4$ particles coated with 6 ZrO$_2$ ALD layers and uncoated carbon/PVDF network.
References