Electronic Supplementary Information

Low Temperature Preparation of Crystilline ZrO_2 Coatings for Improved Elevated-Temperature Performances of Li-Ion Battery Cathodes

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Experimental Section

Preparation of bare composite electrode

The $LiMn_2O_4$ powders (99.5%) were purchased from Alfa Aesar without any further treatment. The bare composite electrode was composed of 80 % pristine $LiMn_2O_4$ particles, 10 % acetylene black (conductive carbon, Alfa Aesar, 99.5%) and 10 % poly-vinylidenefluoride (PVDF, Alfa Aesar) as the binder.

Atomic layer deposition of ZrO_2 coating on $LiMn_2O_4$ particles and bare composite electrode

Atomic layer deposition of ZrO_2 coating on $LiMn_2O_4$ particles and bare composite electrodes was carried out in a Savannah 100 ALD system (Camabridge NanoTech Inc.) at 120°C using $Zr(OC(CH_3)_3)_4$ (Zirconium tert-butoxide, ZTB) and H_2O 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 ZrO_2 ALD growth are described in the following reactions:[1]

$$Zr(OH)^* + Zr(OC(CH_3)_3)_4 \rightarrow Zr\text{-}O\text{-}Zr\text{-}(O\text{-}C(CH_3)_3)_3{}^*+ (CH_3)_3COH$$

$$Zr\text{-}O\text{-}(CH_3)_3{}^*+ H_2O \rightarrow ZrOH^*+ CH_2{=}C(CH_3)_2$$

Characterizations

The crystallographic structure of ZrO_2 ALD coated $LiMn_2O_4$ particles were examined by using a Rigaku MiniFlex X-ray diffractometer with Cu K_α radiation at a scan rate of 2^o/min. The particle size of bare $LiMn_2O_4$ 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 $LiMn_2O_4$ particles coated with 6 ZrO_2 ALD layers and $LiMn_2O_4$ 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_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 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 (25ºC) and elevated temperature (55°C). The electrochemical impedance spectroscopy (EIS) of different

ZrO_2 ALD modified $LiMn_2O_4$ 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.

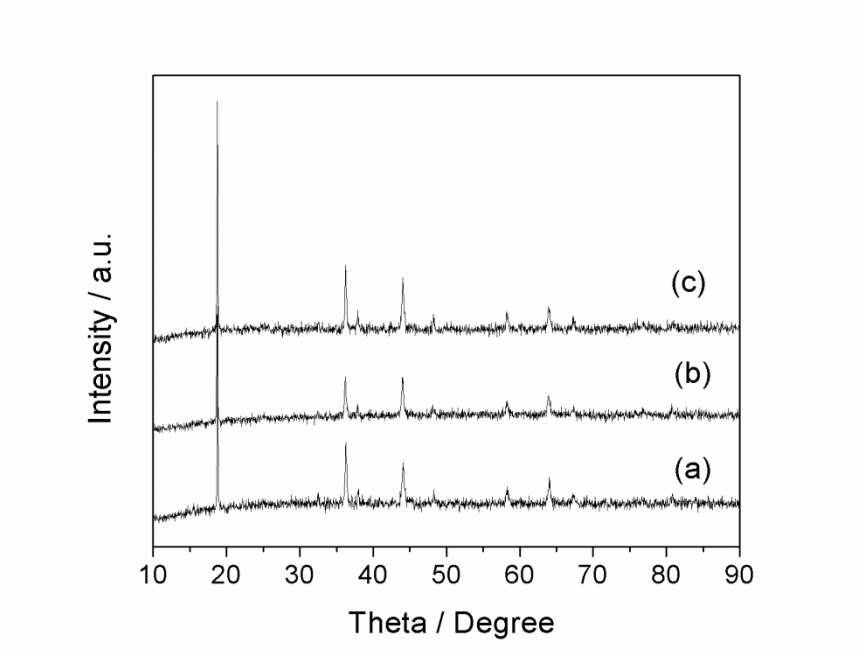

Fig. S1 XRD patterns of (a) bare $LiMn_2O_4$ particles, (b) $LiMn_2O_4$ particles coated with 300 ZrO_2 ALD layers and (c) composite electrode ($LiMn_2O_4$:Carbon:PVDF=8:1:1 in weight ratio) coated with 300 ZrO_2 ALD layers. Three XRD patterns only present show spinel cubic $LiMn_2O_4$ phase with a *F3dm* space group (JCPDS: 35-0782). No ZrO_2 phase can be detected.

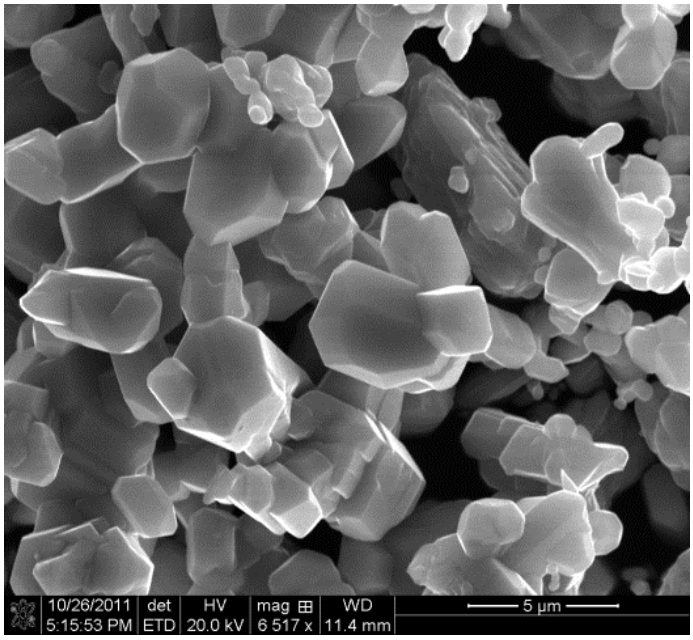

Fig. S2 Scanning electron microscopy (SEM) image of bare $LiMn_2O_4$ particles with an average particle size of ~5 µm.

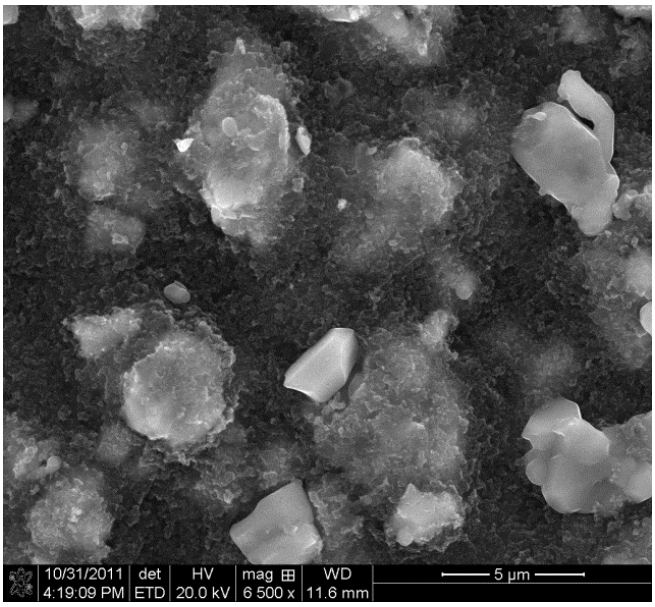

Fig. S3 SEM image showing surface morphology of the bare composite electrode composed of 80 % pristine $LiMn_2O_4$ particles, 10 % acetylene black and 10 % poly-vinylidenefluoride (PVDF) as the binder.

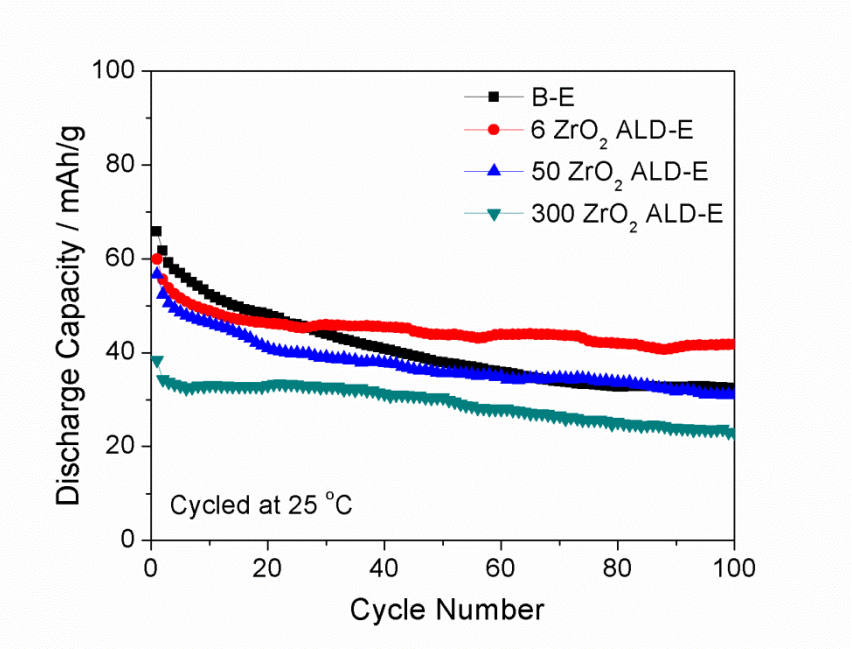

Fig. S4 Cycling performance of bare $LiMn_2O_4$ composite electrode and $LiMn_2O_4$ composite electrodes coated with 6, 50, and 300 ZrO_2 ALD layers corresponding to the thickness of 1.74, 14.5 and 87 nm at a current density of 120 mAh/g in a voltage range of 3.4-4.5 V at room temperature (25°C).

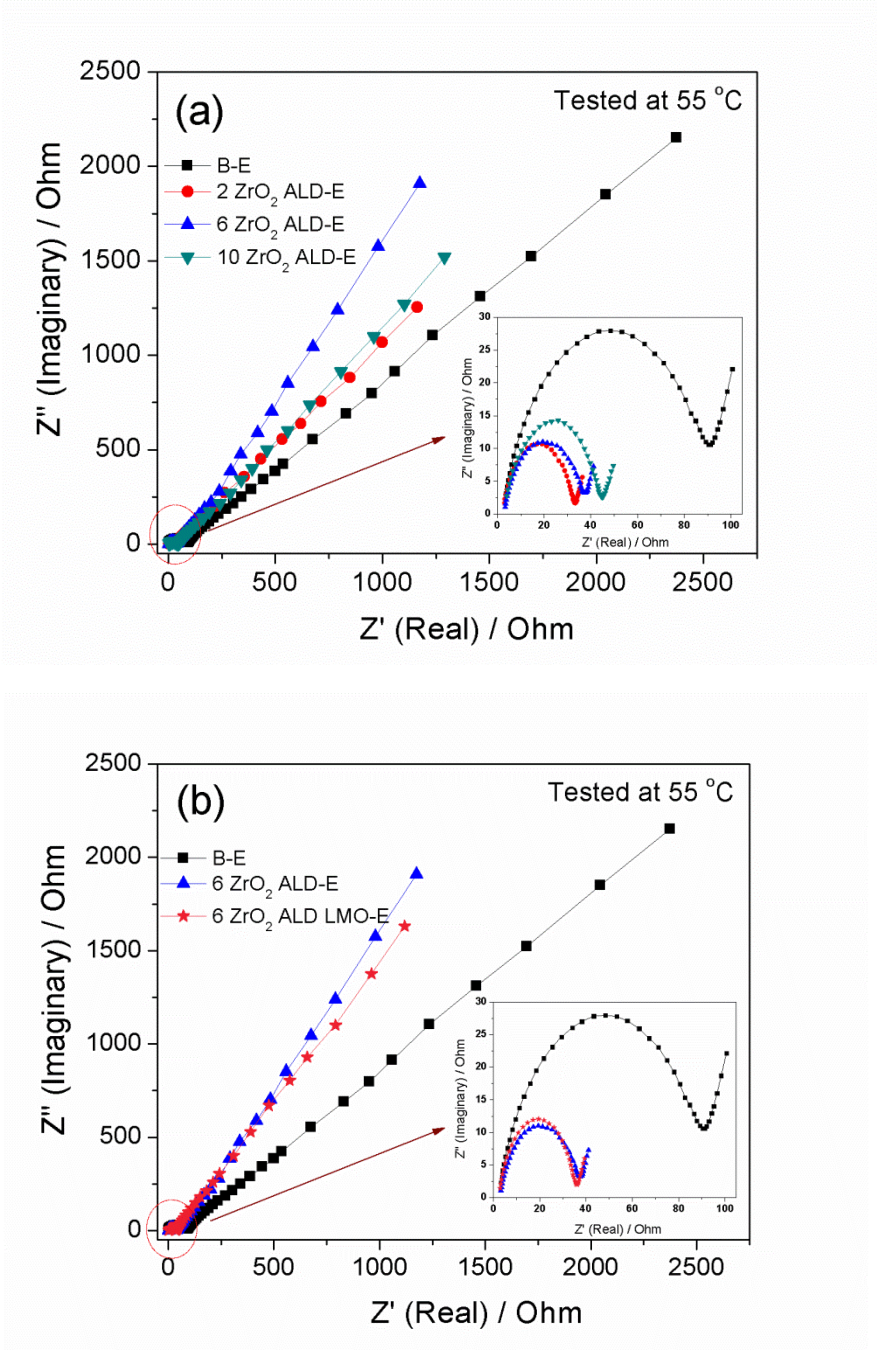

Fig. S5 Electrochemical impedance spectra of different ZrO_2-ALD-modified $LiMn_2O_4$ electrodes in comparison with bare electrode in a frequency range of 100 kHz - 10 mHz by applying an AC amplitude of 5 mV at 55°C. "B-E": bare $LiMn_2O_4$ composite electrode; "*n* ZrO_2 ALD-E": $LiMn_2O_4$ composite electrode coated with *n* ALD layers; "6 ZrO_2 ALD LMO-E": electrode composed of $LiMn_2O_4$ particles coated with 6 ZrO_2 ALD layers and uncoated carbon/PVDF network.

References

1 M. A. Cameron and S.M. George, *Thin Solid Films*, 1999, **348**, 90.