Surface Zn doped $LiMn_2O_4$ for an improved high temperature performance

Supporting Information

Material and Methods

Material synthesis

The pristine $LiMn_2O_4$ (LMO) was received from Pulead Technology Industry Co.,Ltd. without further treatment. All of the other chemicals were of analytical purity and purchased from Sinopharm Chemical Reagent Co.,Ltd. All chemicals were purchased and used as received without further purification. Milli-Q water (resistance > 18 MΩ) was used for all experiments.

The ZnO coated LMO was synthesized by a wet chemistry method. 6.0/1.3/0.4 g of pristine LMO powders were dispersed in 300 ml of distilled water containing 133 mg of ascorbic acid, 420 mg of hexamethylenetetramine, and 330 mg of zinc acetate dihydrate. After heated at 80ºC for 4 hours with stirring followed by drying at 80ºC to obtain the sample of LMO@2/10/32 nm ZnO. The thickness of the coating layer could be tuned by adjusting the amount of pristine LMO. The surface Zn doped $LiMn_2O_4$ sample (Zn-LMO or 10-Zn-LMO) was prepared by sintering the LMO@2 nm ZnO or LMO@10 nm ZnO at 700ºC for 2 hours.

Characterizations

TEM characterization was performed using a JEOL-2100F electron microscope with a field-emission gun, operated at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data were taken on an ESCA Lab 220i-XL electron spectrometer from VG Scientific using 300 W Al K_α radiation. XRD patterns were obtained using a Bruker D8 Advance diffractometer with a Cu K_α radiation source (λ_1 = 1.54056 Å, λ_2 = 1.54439 Å). The experiments of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) were carried out on a Shimadzu type instrument (ICPE-9000).

Electrochemical measurements were tested with CR2032 coin cells assembled in an argon-filled glove box using lithium metal as the counter and reference electrodes. The cathodes were prepared by mixing the active materials, acetylene black (Super-p), and poly(vinyldifluoride) (PVDF, Aldrich) at a weight ratio of 8:1:1, pasting on a pure Al foil (99 %, Goodfellow) and cutting into circular electrodes with diameter of 1.2 cm. Polypropylene membrane (Celgard) was used as a separator. The electrolyte, 1 M $LiPF_6$ in ethylenecarbonate (EC) / dimethyl carbonate (DMC) / diethyl carbonate (DEC) (1:1:1, in vol%), was purchased from Kishida

Chemical Co. Ltd. Galvanostatic tests of the assembled cells were performed with a Land CT2001A battery test system between 3.2 and 4.5 V. Cyclic voltammetry (CV) as well as the electrochemical impedance spectroscopy (EIS) spectra were performed on Autolab PGSTAT302N electrochemistry workstation.

Calculations of the chemical diffusion coefficient of Li^+ (D_{Li})

In CV tests, the peak current (I_p) shows a linear relation with the square root of scanning rate ($v^{-1/2}$), indicating a typical diffusion controlling response. The chemical diffusion coefficient of Li^+ (D_{Li}) was measured on CV according to a standard method. For a homogeneous system, the chemical diffusion coefficient can be calculated from the Randles–Sevcik equation:

$$I_p = 0.4463 n^{3/2} F^{3/2} c S R^{-1/2} T^{-1/2} D_{Li}^{1/2} v^{1/2} \qquad \textbf{(1)}$$

where I_p is the peak current (A), n is the charge transfer number, F is the Faraday's constant (96487 C mol^{-1}), c is the concentration of Li^+ (mol m^{-3}), S is the surface area of the electrode (m^2), R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), D_{Li} is the chemical diffusion coefficient of Li^+ (m^2 s^{-1}) measured by CV, and v is the scanning rate (V s^{-1}). It was presumed that the apparent D_{Li} values should be constant in the whole charge or discharge process while the system was regarded as a homogeneous system. Therefore, the apparent D_{Li} could be calculated by Eq. (1) from the slope of $dI/dv^{1/2}$.

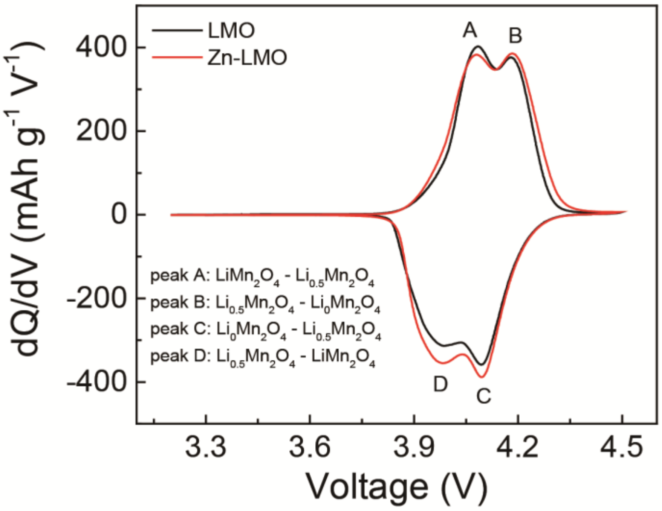

Fig. S1 CV curves of LMO and Zn-LMO.

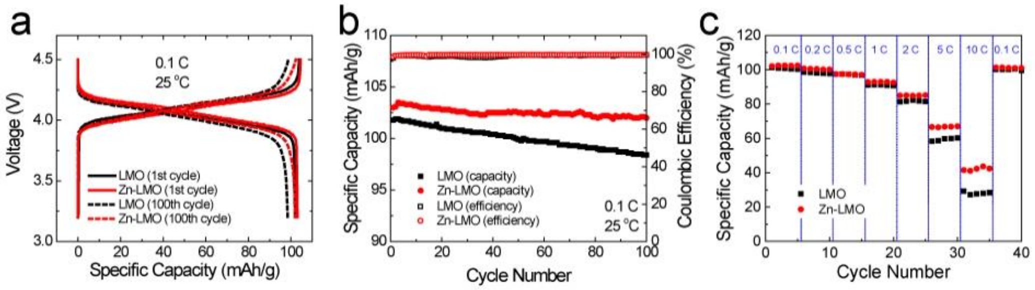

Fig. S2 (a) Charge and discharge profiles of 1st and 100th cycle. The data was collected at 0.1 C, 25ºC. (b) Cycling performance of LMO and Zn-LMO at 0.1 C, 25ºC. (c) Rate performance of LMO and Zn-LMO.

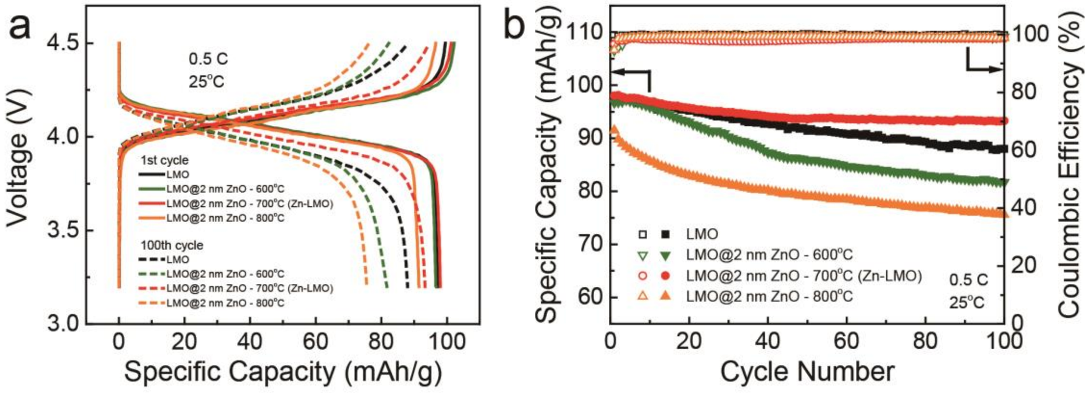

Fig. S3 Battery performance of Zn treated sample annealed at different temperature. (a) Charge and discharge profiles of 1st and 100th cycle. The data was collected at 0.5 C, 25ºC. (b) Cycling performance at 0.5 C, 25ºC.

Table S1 Elemental analysis tested by ICP-AES (based on the mass).

Amount	Li (wt%)	Mn (wt%)	Zn (wt%)
LMO	3.84	60.77	-
Zn-LMO	3.83	60.05	0.77
10-Zn-LMO	3.70	58.43	3.81

Table S2 Calculated chemical diffusion coefficient of Li^+ (D_{Li}) of LMO and Zn-LMO.

D_{Li} (cm^2/s)	Charge	Discharge
LMO	1.68×10^{-10}	1.34×10^{-10}
Zn-LMO	1.63×10^{-10}	1.25×10^{-10}

Table S3 Mn dissolution amount tested by ICP-AES (based on the mass).

Dissolution Amount	Mn (wt%)
LMO	0.64
Zn-LMO	0.22

Table S4 Relative intensity of (220), (400), (311) XRD peaks, based on the intensity of (111) XRD peak.

XRD peak	(111)	(220)	(311)	(400)	(400)/(311)
LMO	1	0.00214	0.42595	0.43527	1.0219
Zn-LMO	1	0.00179	0.47149	0.47647	1.0106