Supporting Information

Mesoporous \( \text{Al}_2\text{O}_3 \) zincophilic sieve enables ultra-long lifespan of Zn-ion batteries

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Material synthesis processes

Preparation of different pore size of mesoporous \( \text{Al}_2\text{O}_3 \) powder: LA-MA was prepared according to previous reports.\(^\text{[1]}\) All chemicals were used directly without purification and bought from Macklin. Aqueous solutions of \( \text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \), carboxylic acid and triethanolamine (TEA) with a molar ratio of 1:0.1:3 were mixed to create the precursors. \( \text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) (14.716 g) was dissolved in water (20 mL) and warmed at 80 °C to make an aqueous solution of aluminum nitrate. The mixture of lactic acid (0.36 g) and TEA (16 mL) was dissolved in water (30 mL) to get a clear solution. At 80°C, this mixture was then added into aluminum nitrate solution to produced white precipitate. After that, the reaction mixture was stirred for 12 hours at room temperature and then transferred into the teflon container and aged for 24 hours at 90 °C. After filtering, the precursor powder is created by washing with distilled water and drying at 90 °C. After that, the precursor was calcined for three hours in air at 550 °C to produce porous alumina powder. Lactic acid was substituted for other carboxylic acids such as lauric acid, hexanoic acid and stearic acid. Alumina formed by reacting just with aluminum nitrate and TEA is known as MA, while alumina prepared
by reacting with stearic acid, lauric acid, hexanoic acid and lactic acid are referred to C18-MA, C12-MA, C6-MA and LA-MA, respectively.

**Preparation of LA-MA@Zn layer:** The obtained LA-MA and PVDF powder were mixed at the radio of 9:1, and then add appropriate amount of N-methyl pyrrolidone solvent. The slurry was cast onto Zn foil after 12 hours of ball milling, and dried at 60°C for 12 hours in vacuum.

**Cathode preparation:** According to previous reports,\(^2\) CNT/MnO\(_2\) composite cathode material was obtained. A mixture of 70wt% CNT/MnO\(_2\) powder, 20wt% Ketjenblack, 10wt% PVDF and several droplets of NMP was used to create the CNT/MnO\(_2\) cathode. The slurry is poured onto titanium mesh and dried in vacuum for 12h at 60°C.

**Material characterization**

X-ray diffraction (XRD) experiments were performed using Cu Kα (λ=1.54182Å) radiation on a Philips X'Pert Super diffractometer. Scanning electron microscopy (SEM, Zeiss Gemini 450) image and transmission electron microscopy (TEM, Hitachi H7650.) were used to characterized the surface morphologies of samples. The Brunauere–Emmette–Teller (BET) specific surface and pore size distributions of samples were measured by using a Micromeritics Tristar II 3020 instrument. FT-IR were tested on Hyperion 3000 system. A Thermo ESCALAB 250 X-ray photoelectron spectrometer (Perkin-Elmer) was used to collect X-ray photoelectron spectroscopy (XPS). Raman spectra were performed by a HORIBA LabRAM HR Evolution Invia confocal laser micro-Raman spectrometer at 733 nm.\(^3\) Atomic force microscope (AFM) images were obtained by NanoScope IIIa (Bruker, USA).

**Electrochemical measurements**

CR2016 coin cells with a glass fiber separator (Whatman, GF/C) and ZnSO\(_4\) (2 M) electrolyte were used to measure the electrochemical performance of symmetric cells and half cells. And full cell used ZnSO\(_4\) (2 M) + MnSO\(_4\) (0.2 M) as electrolyte and CNT/MnO\(_2\) as cathode. The performance of the galvanostatic charge/discharge was evaluated by NEWARE CT4008T and LAND CT2001A. The electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), Tafel plots, chronoamperometry (CA) and cyclic voltammetry (CV) were tested on a CHI 660E electrochemical workstation. The frequency range of EIS is 100KHz to 1Hz. And the voltage window of CV is 0.8-1.8V.
Fig. S1 Diagrams of (a) synthesis mechanism of different pore sizes mesoporous Al$_2$O$_3$ with zincophilic groups and (b) Zn deposition behavior on LA-MA@Zn anode.
Fig. S2 Pore-size distribution of (a) LA-MA, (b) C6-MA, (c) C12-MA, (d) C18-MA, (e) MA powder.

Fig. S3 Nitrogen adsorption/desorption isotherm plots of (a) LA-MA, (b) C6-MA, (c) C12-MA, (d) C18-MA, (e) MA powder.
Fig. S4 (a) TEM images and corresponding SAED pattern, (b) HRTEM images, (c) XRD patterns of LA-MA powder.

Fig. S5 SEM images and EDS mapping images of (a) LA-MA@Zn surface, (b) the cross-sectional of LA-MA@Zn.
**Fig. S6** ν-SO$_4^{2-}$ band of Raman spectroscopy of 2M ZnSO$_4$ solutions in different pore size of mesoporous Al$_2$O$_3$.

**Fig. S7** Nyquist plots of (a) LA-MA@Zn, (b) bare Zn symmetric cell under different temperatures.
Fig. S8 (a) Linear polarization curves, (b) LSV curves (c) Chronoamperometry curves of LA-MA@Zn and bare Zn.

Fig. S9 The cycling stability of different pore size of mesoporous Al₂O₃ symmetrical cells at current densities of (0.25, 1, 2, and 5 mA cm⁻², respectively) and capacities (0.25, 1, 2, and 5 mA h cm⁻², respectively).
**Table S1.** Electrochemical performance comparison of full-cell in this work and other reported works.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Current density</th>
<th>Capacity</th>
<th>Cycle number</th>
<th>Capacity retention</th>
<th>Reference</th>
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<tbody>
<tr>
<td>LA-MA@Zn</td>
<td></td>
<td>CNT/MnO₂</td>
<td>1 A g⁻¹</td>
<td>Over 3500</td>
<td>94.2%</td>
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<tr>
<td>APTESZn</td>
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<td>ZVO</td>
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<tr>
<td>ZnO-rich ASEI@Zn</td>
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<td>MnO₂</td>
<td>0.5A g⁻¹</td>
<td>1000</td>
<td>70%</td>
</tr>
<tr>
<td>ZnOMMT-4</td>
<td></td>
<td>MnO₂</td>
<td>2 A g⁻¹</td>
<td>1000</td>
<td>76.7%</td>
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<tr>
<td>Zn@PDMS/TiO₂−x</td>
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<td>MnO₂</td>
<td>1C</td>
<td>400</td>
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<tr>
<td>MCM41- Zn</td>
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<td>K-NVO</td>
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<td>500</td>
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<tr>
<td>Zn@CaF₂</td>
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<td>V₂O₅O₂₄</td>
<td>2 A g⁻¹</td>
<td>1000</td>
<td>70%</td>
</tr>
<tr>
<td>Zn@TiO₂/NC</td>
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<td>MnO₂</td>
<td>0.5 A g⁻¹</td>
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<td>75%</td>
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<td>g-C₃N₄-Zn</td>
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</table>

**Fig. S10** Long-term cycling performance of different full cells.

**References**


