Supporting Information

Highly Reversible Zinc-Ion Intercalation into Chevrel Phase Mo_6S_8 Nanocubes and Applications for Advanced Zinc-Ion Batteries

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EXPERIMENTAL

Synthesis of $Cu_2Mo_6S_8$ nanocubes: A graphene-assisted two-step process was used for the synthesis of $Cu_2Mo_6S_8$. In a typical experiment, 40 mg graphene powder (Graphene Laboratories, Inc.) was added to 10 ml dimethylformamide (DMF) and the mixture was sonicated for 20 min. Afterwards, 500 mg $(NH_4)_2MoS_4$ (Aldrich, 99.97%) and 86 mg anhydrous $CuCl_2$ (Aldrich, 99.995%) were added and the resulting solution was heated at 90°C for 4 hours under Ar protection. The choice of DMF is important because it has a relatively high boiling point and provides good solubility for the precursors. The mixture was then cooled to room temperature and 50 ml diethyl ether was added to induce precipitation, and left overnight. The solids that precipitated out were collected using a centrifuge (7000 rpm for 5 min) and were dried. The obtained powder was ground using a pestle and mortar to fine consistency. The second step of the synthesis was solid-state reaction conducted at 1000°C for 7 hours under the flow of 4% H_2 and 96% Ar, at 100 sccm.

Preparation of Mo_6S_8: In order to prepare electrochemically active Mo_6S_8 for intercalation of Zn^{2+}, copper ions in the as-synthesized Chevrel phase were leached out using the acid-leaching method. The leaching procedure was mixing the powders with 1.0 M hydrochloric acid (HCl) and stirring the mixture at room temperature for 12 hours. After leaching, the nanoparticle powders were collected by centrifuge (3000 rpm for 5 min) and were washed with deionized water to remove any residual impurities besides Mo_6S_8. The obtained Mo_6S_8 nanocube powder was dried in a vacuum oven at 90°C for 12 hours.

Characterization and electrochemical tests:

Material characterization: The synthesis and acid-leaching experiments were monitored by X-ray diffraction (XRD) analysis using a Rigaku MiniFlex II instrument. The particle size and morphology were analyzed using a JEOL JSM-7001F scanning electron microscope, a Tecnai G^2 transmission electron microscope, and an aberration-corrected Titan 80-300^{TM} scanning/transmission electron microscope (S/TEM).

Electrochemical tests: The electrodes were prepared by mixing 80 wt% of Mo_6S_8 nanocubes, 10 wt% of Super-C carbon and 10 wt% of poly(vinylidene fluoride) (PVDF) with N-methyl-2-pyrrolidone (NMP) as the dispersant. The slurry was mixed well and coated onto a piece of carbon. Typical active material loading was ~1.0 mg/cm^2. The electrolyte solution was either 1.1 M $ZnSO_4$ in water or 1.1 M $Zn(ClO_4)_2$ in acetonitrile. Cyclic voltammograms were measured using a CHI660C electrochemical work station using a three electrode configuration, with two pieces of Zn foil working as the reference and counter electrodes. Galvanostatic charge-discharge tests and cycle life tests were conducted using a BT2000 Arbin battery tester with coin cells (or H-cells for full-cell tests). The coin cells were assembled with a piece of Zn foil as the anode and the separator was a glass fiber membrane. The separator for the H-cell was a piece of cation exchange membrane (Nafion, Dupont, DE, USA).

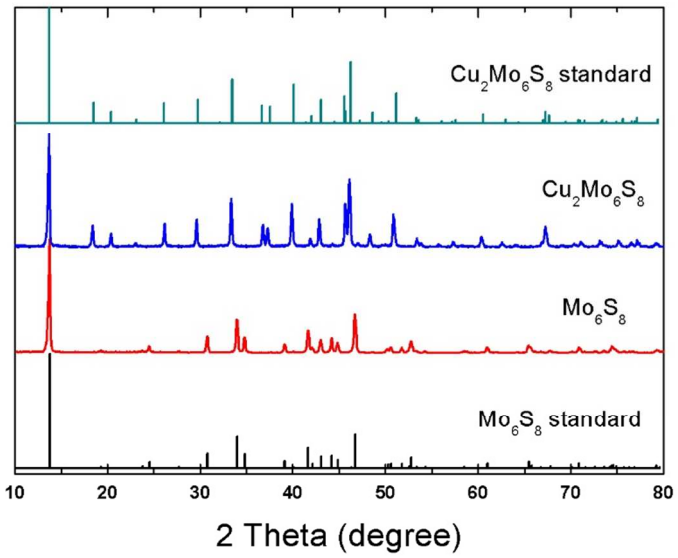

Figure S1: X-ray diffraction pattern of Mo_6S_8 nanocubes after acid leaching (the red line). The standard data is also shown for reference (the black line). The XRD pattern from the $Cu_2Mo_6S_8$ nanocubes is also shown for comparison (the blue line); note that the XRD pattern from Mo_6S_8 after acid leaching matches well with that of the standard, and therefore the acid-leaching process was successful.

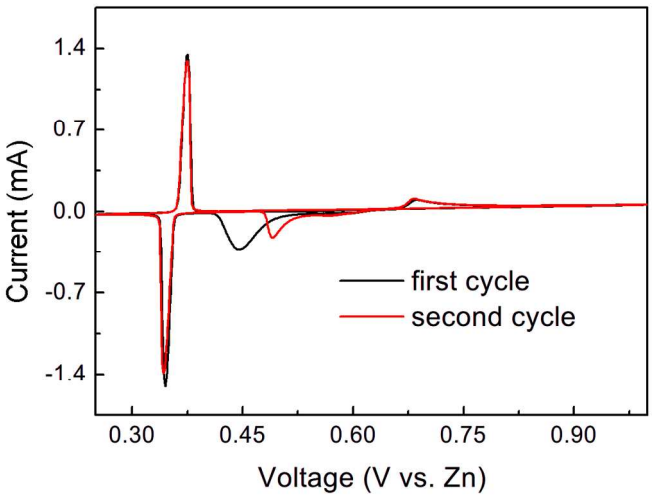

Figure S2: CV profiles for the first and second cycles that exhibit irreversible capacity; the scan rate was 0.05 mV/s. This phenomenon is similar to Mg^{2+} intercalation and is an intrinsic property of Mo_6S_8 that is related to partial cation trapping (see detailed discussion in the main text).

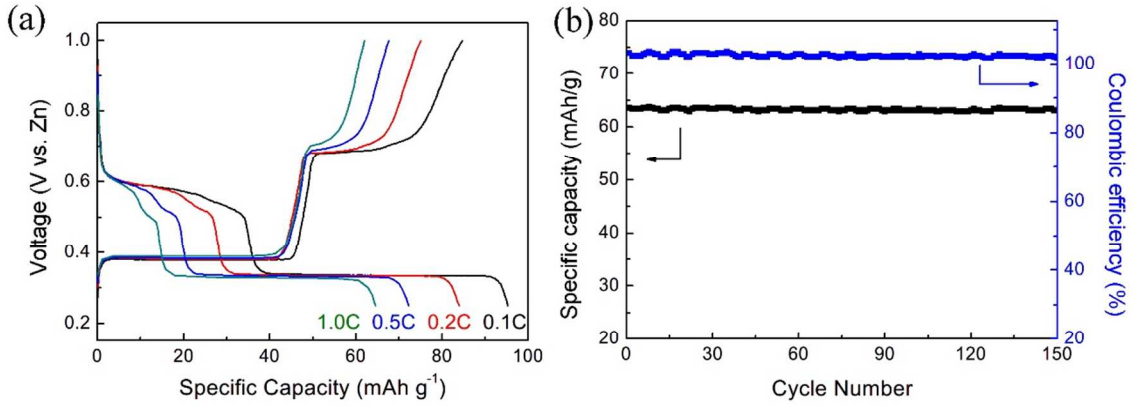

Figure S2: (a) Charge-discharge profiles and (b) cyclic stability (at 1.0C) of Mo_6S_8 electrodes in 1.0 M $Zn(ClO_4)_2$ in acetonitrile.

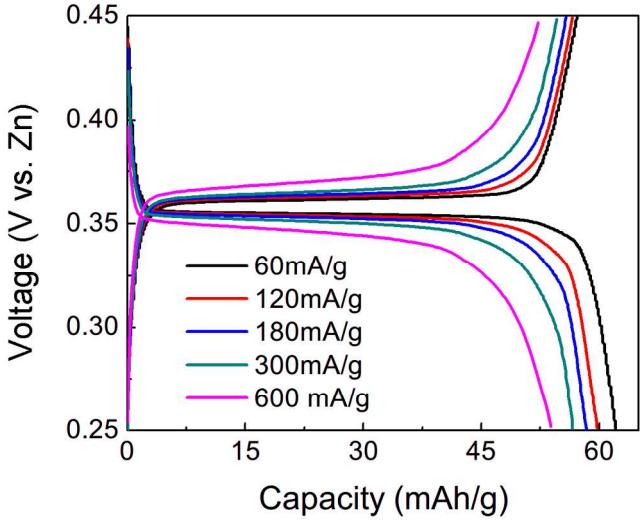

Figure S4: Charge-discharge profiles of Mo_6S_8 electrodes in an electrolyte of 1.0 M $ZnSO_4$ in water at different current densities. A voltage window of 0.25 ~ 0.45 V was used in this test in order to evaluate the application for full cells.

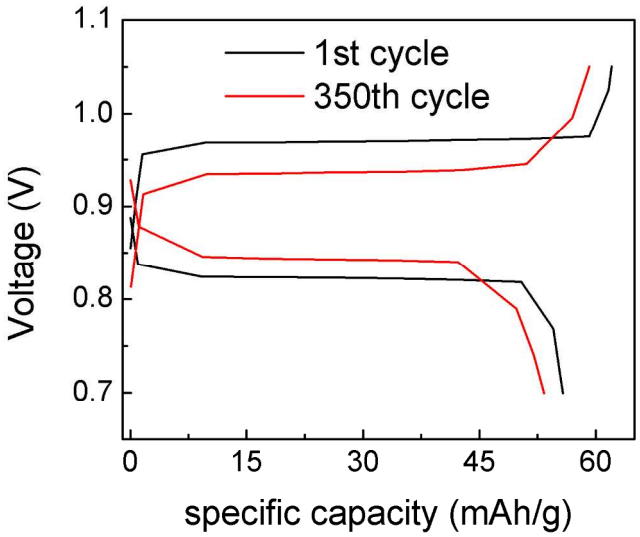

Figure S5: Comparison of the voltage profiles for the first cycle and the 350th cycle for a full cell that shows the cell had remarkable cyclic stability.