

Supporting Information

## High Performance Batteries Based on Hybrid Magnesium and Lithium Chemistry

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Experimental details:

### Material synthesis:

The  $\text{Mo}_6\text{S}_8$  cathode material was synthesized using a two-step process: synthesis of  $\text{Cu}_x\text{Mo}_6\text{S}_8$  by the molten salt method and acid leaching.

The synthesis protocol for  $\text{Cu}_x\text{Mo}_6\text{S}_8$  was adapted from Aurbach et al., but with some modifications in order to yield phase pure product. KCl was used as the solvent; it was dried for 3 hours at  $150^\circ\text{C}$  under vacuum prior to use and was stored inside a glove box. In a typical synthesis,  $\text{MoS}_2$  (1 g), CuS (0.398 g), Mo (0.602 g) and KCl (4 g) powders were mixed and hand-grounded using a mortar and

pestle inside a glove box, and was then transferred into a crucible. The crucible was quickly transferred to a tube furnace and the reaction proceeded under slow flow of argon ( $\sim 1$  sccm). The synthesis protocol was as follows: ramp to  $150^{\circ}\text{C}$  at a rate of  $2^{\circ}\text{C}/\text{min}$  from room temperature; stay at  $150^{\circ}\text{C}$  for 2 hours; ramp to  $850^{\circ}\text{C}$  at a rate of  $2^{\circ}\text{C}/\text{min}$ ; dwell at  $850^{\circ}\text{C}$  for 60 hours; cool to room temperature naturally. The product was washed twice with hot deionized water to dissolve KCl and was sonicated for 10 min to completely dissolve unreacted salts. The obtained powder was then dried at  $100^{\circ}\text{C}$  for 2 hours.

In order to prepare electrochemically active  $\text{Mo}_6\text{S}_8$ , acid leaching was used to extract the copper ions in the synthesized Chevrel phase. The leaching was performed using 8.0 M HCl with a few drops of  $\text{HNO}_3$ . The mixture was stirred for 24 hours in order to complete the reaction.

### **Characterization and cell assembly**

The synthesis and acid leaching processes were monitored by X-ray diffraction analysis using a Rigaku MiniFlex II instrument. The size and morphology of  $\text{Mo}_6\text{S}_8$  particles were studied using SEM and TEM (FEI Tecnai G2).

The cathodes for battery assembly were prepared as follows: 80 wt%  $\text{Mo}_6\text{S}_8$ , 10 wt% Super-P and 10 wt% polyvinylidene fluoride were mixed as slurry using NMP as the dispersant. The slurry was coated onto a piece of stainless steel (SS) foil (on Mo foil for electrodes used for cyclic stability test). After drying, the SS foil (with active material coating) was punched into  $\frac{1}{2}$  inch discs and typical active material loadings were  $1 \sim 3 \text{ mg}/\text{cm}^2$ . The electrolyte solution was prepared by following a reported protocol and was filtered through a membrane (200 nm pore size) prior battery assembly.<sup>16</sup> The batteries were assembled inside a Ar-filled glove box as CR2032 coin cells, using glass fiber paper as the separator. CV tests were conducted using a CHI660C electrochemical workstation. Charge-discharge tests and cyclic stability tests were conducted using an Arbin multichannel battery analyzer.

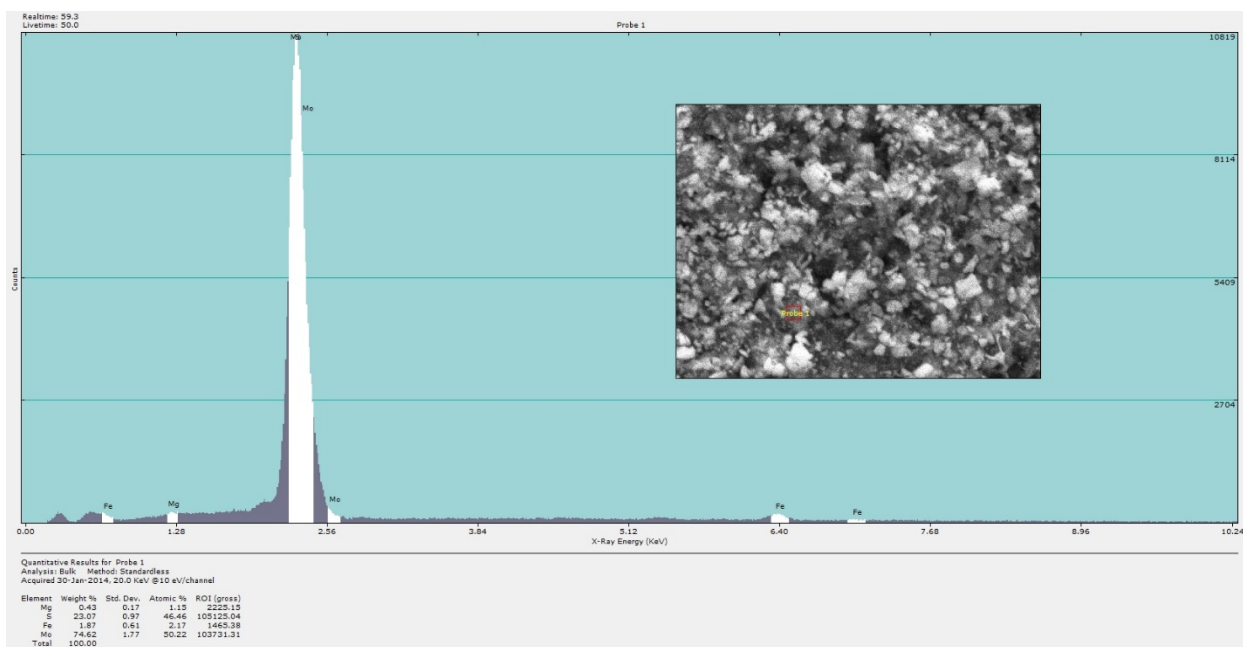


Figure S 1: EDS spectrum of the  $\text{Mo}_6\text{S}_8$  cathode after a full discharge process in a hybrid cell. Note that the atomic ratio of Mg to Mo was very low ( $\sim 0.02$ ). If  $\text{Mg}^{2+}$  ions had been intercalated into  $\text{Mo}_6\text{S}_8$ , this ratio would be much higher.

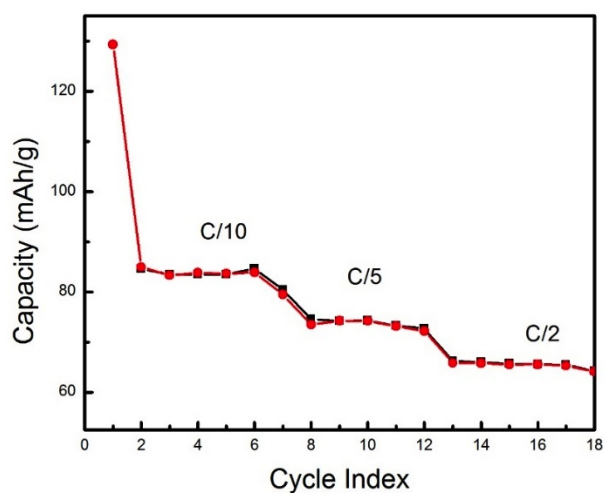


Figure S2: Rate performance of a cell assembled with electrolyte that did not contain  $\text{Li}^+$  ions (i.e., pure magnesium intercalation performance). Note that the capacities were much lower than those of the hybrid cells.

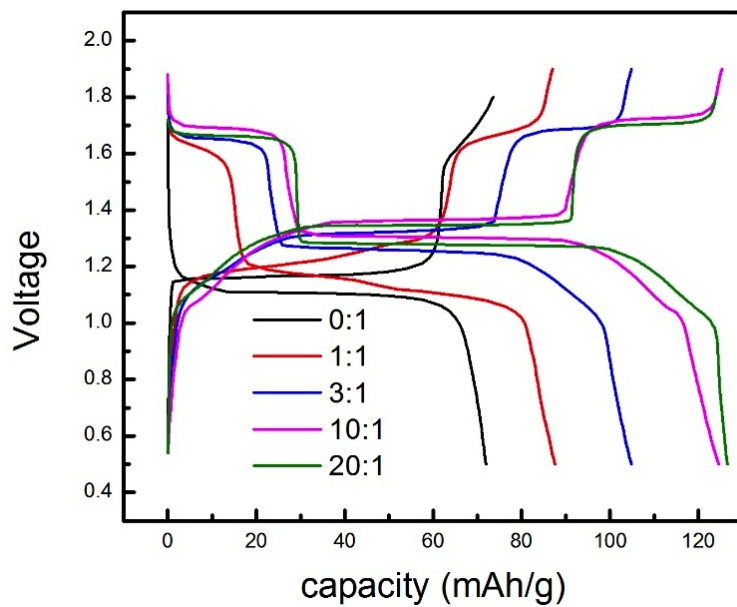


Figure S3: Charge-discharge profiles of cells assembled with electrolytes that have different LiCl concentrations. The ratios labeled in the figure refer to the ratio between the amount of available Li ions in the electrolyte and the amount of Li ions required for complete cathode reaction. The amounts of required Li ions were determined based on the theoretical capacity of  $\text{Mo}_6\text{S}_8$ .

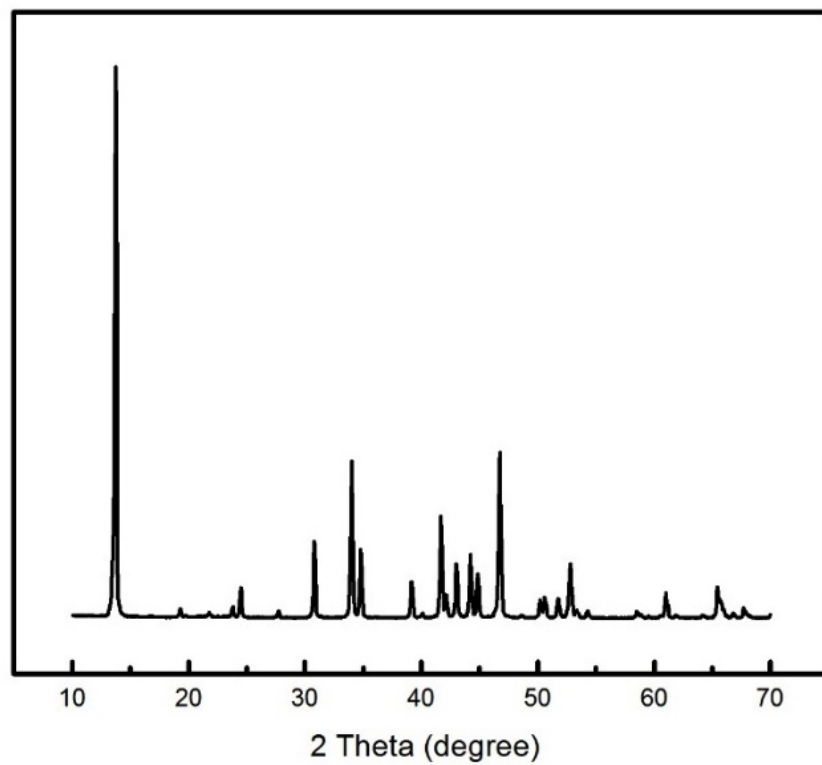


Figure S4: X-ray diffraction pattern of the  $\text{Mo}_6\text{S}_8$  particles synthesized by the molten salt method.

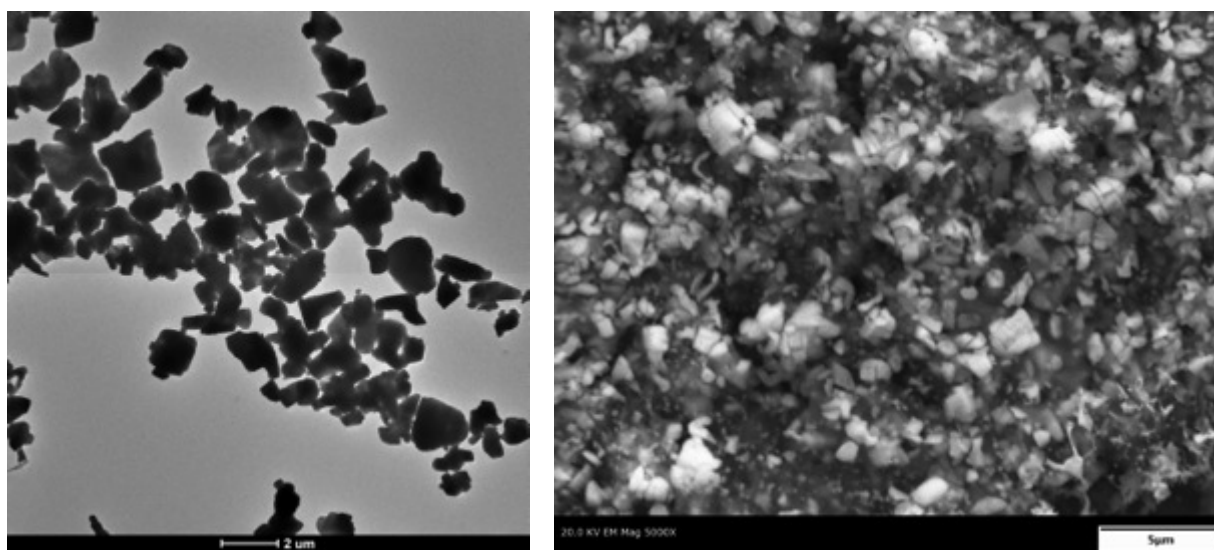


Figure S5: (left) TEM and (right) SEM images of the  $\text{Mo}_6\text{S}_8$  particles synthesized using the molten salt method.



Figure S6: Cross section SEM image for Mg metal anode after 3000 cycles. The arrows indicate the thickness of Mg sponge layers at the surface.