

New cathode materials for rechargeable Mg batteries: fast Mg ions transport and reversible copper extrusion in $\text{Cu}_y\text{Mo}_6\text{S}_8$ compounds

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Brief description of the synthesis of the precursor

The Chevrel phase precursor with the composition $\text{Cu}_{-2}\text{Mo}_6\text{S}_8$ was synthesized by reaction of the powdered elements mixture in an evacuated, sealed quartz tube. The procedure consisted of four sequential stages: (i) Heating at 450 °C for 24 h; (ii) heating at 700 °C for 24 h; (iii) heating at 1050 °C for 48 h; (iv) cooling down to room temperature at the rate of 120 °C/h. The synthesis product (1.8 g) was partially leached under an ambient air atmosphere in a 6 M aqueous HCl solution.

Typically, several days were required to accomplish the partial leaching. In order to accelerate the rate of leaching oxygen bubbling was used. In this case, the partial removal of Cu was performed until the composition of the leached material reached the composition $\text{Cu}_{-1}\text{Mo}_6\text{S}_8$. After leaching, the powder was filtered using a fine glass frit, washed with water, and dried in an oven at 120 °C. The morphologies of the initial $\text{Cu}_2\text{Mo}_6\text{S}_8$ and the leached $\text{Cu}_1\text{Mo}_6\text{S}_8$ phases were studied by scanning electron microscopy (SEM) with JSM-6300 JEOL Inc. equipment (Japan) and by ex-situ XRD (Bruker Inc., Germany, AXS D8 ADVANCE diffractometer, Cu K_α radiation).

Details about the synthetic procedures, leaching mechanisms and precursors' characterizations can be found elsewhere (E. Lancry, E. Levi, Y. Gofer, M. Levi, G. Salitra, and D. Aurbach, *Chem. Mater.* 2004, **16**, 2832).

Rietveld analysis of the product of chemical Mg intercalation into $\text{Cu}_2\text{Mo}_6\text{S}_8$ (the air-stored sample):

9% Cu + 75% $\text{Mg}_2\text{Mo}_6\text{S}_8$ ($a_h = 9.763 \text{ \AA}$, $c_h = 10.372 \text{ \AA}$, $a_r = 6.612 \text{ \AA}$, $\alpha = 95.16^\circ$)

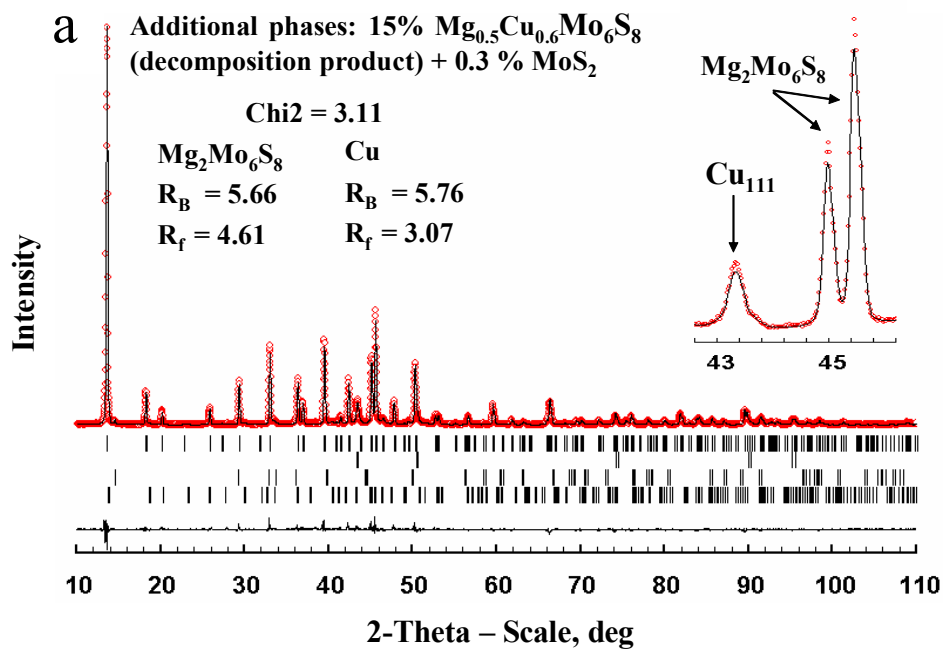


Figure 1S: Rietveld analysis of the product of chemical Mg intercalation into $\text{Cu}_y\text{Mo}_6\text{S}_8$ (the air-stored sample).

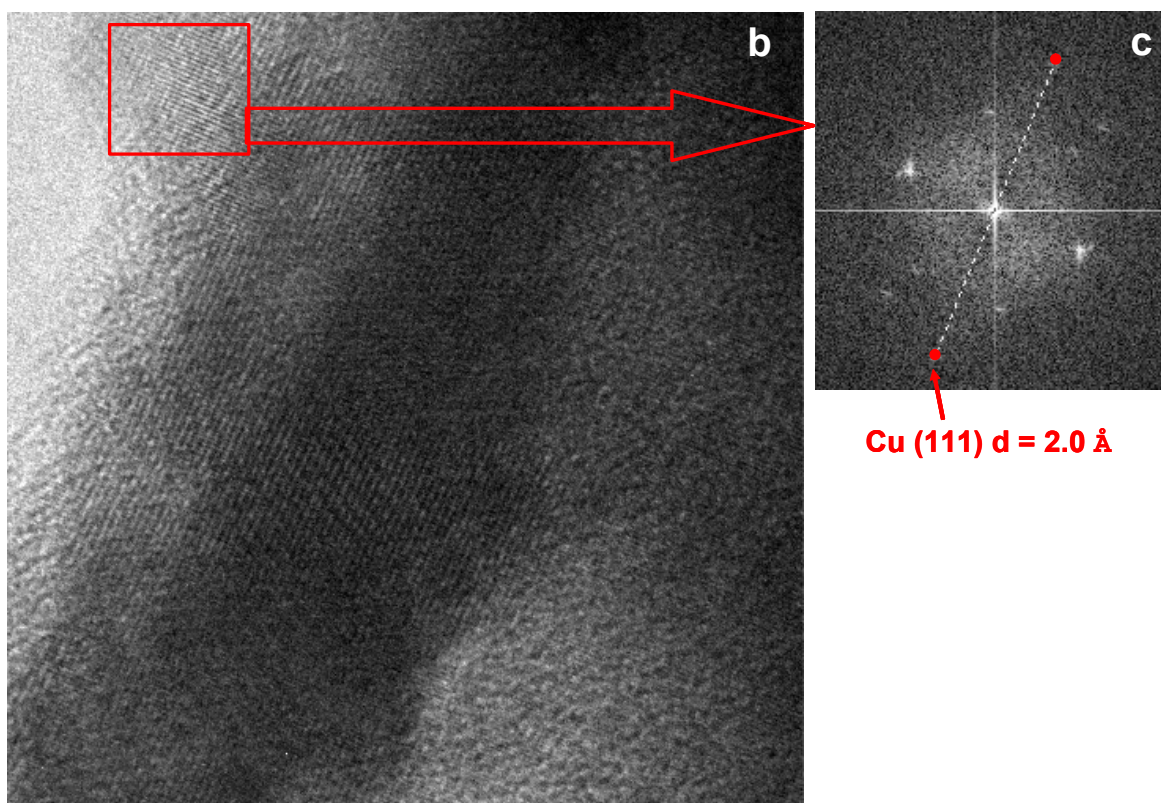


Figure 1S: (b) HRTEM micrograph for the fully discharged product of the composition $\text{Cu}^0 + \text{Mg}_2\text{Mo}_6\text{S}_8$ (obtained at 0.3 V vs. Mg). The red square marks the area assigned to metallic Cu lattice; (c) The FFT analysis of the marked area in panel b. The d value between the red circles was found to be 2 Å in good agreement with the literature data for Cu (111).

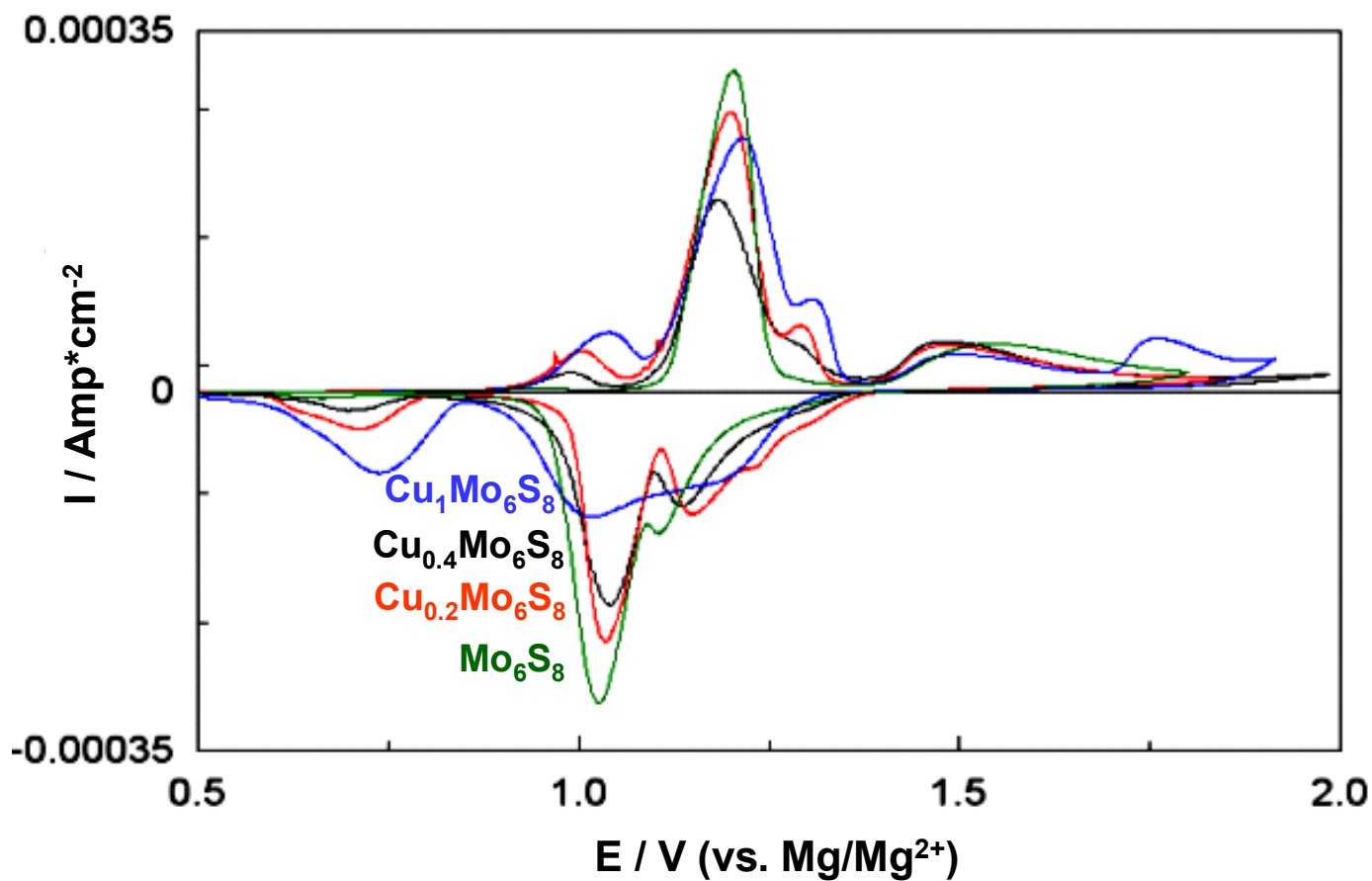
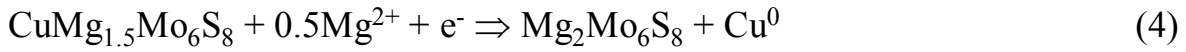
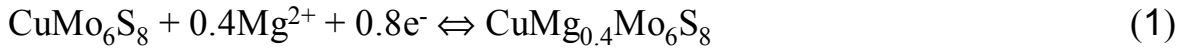


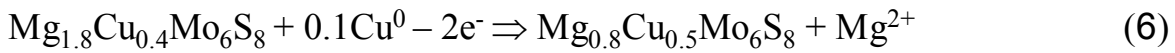
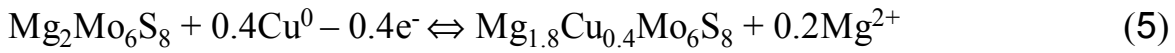
Figure 2S: Cyclic voltammetry for the $\text{Cu}_y\text{Mo}_6\text{S}_8$ electrodes containing different initial amount of copper as indicated. Scan rate $10 \mu\text{Vs}^{-1}$.

Scheme 1S: Stoichiometries of the cathodic and anodic reactions obtained by combined integration of the cyclic voltammetry curve in figure 2 and the curves obtained by intermittent reversal linear voltammetry

Cathodic reactions (discharge):



Anodic reactions (charge):



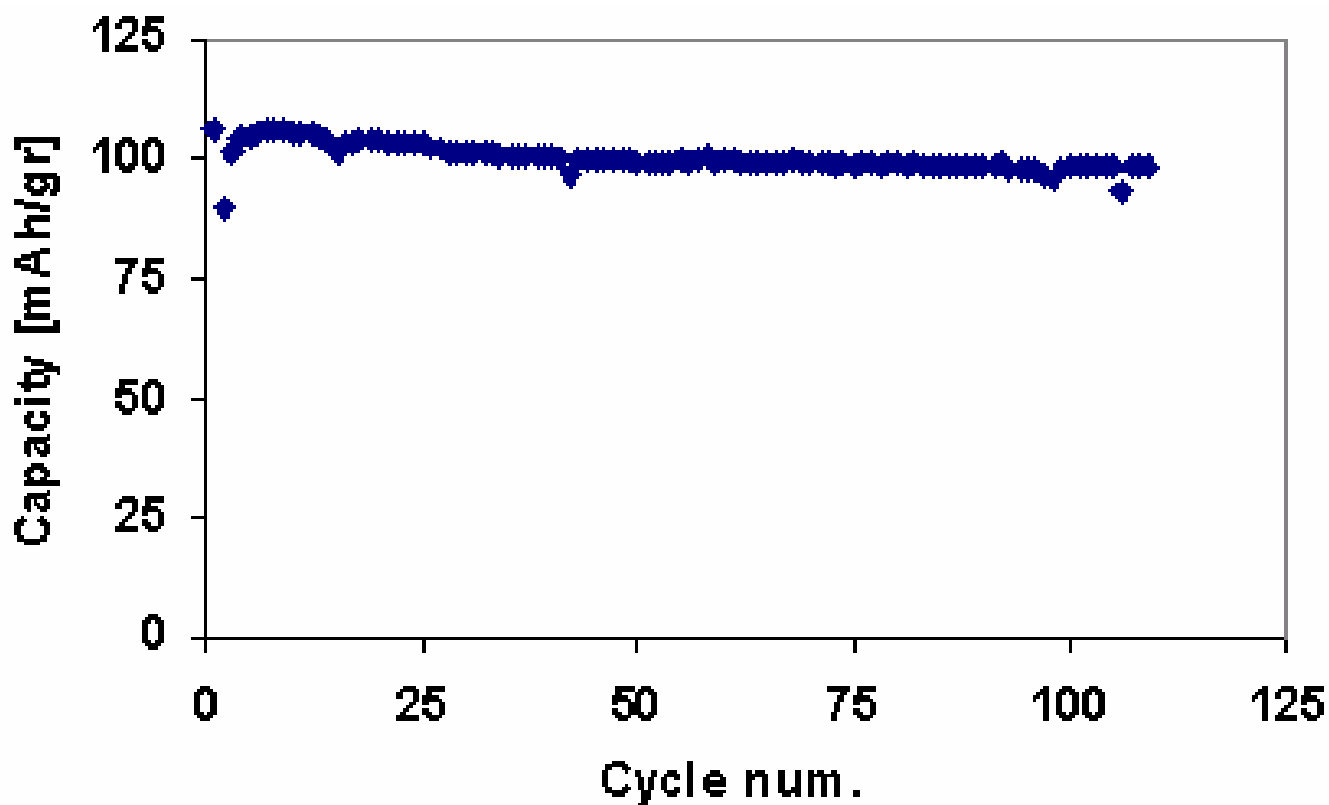


Figure 3S: Cycling ability of a coin-type cell with $\text{Cu}_1\text{Mo}_6\text{S}_8$ cathode and Mg anode measured at C/6 rate at 30° C.