Electronic Supplementary Material (ESI) for ChemComm.

Supplementary information for:

Screening for Positive Electrodes for Magnesium Batteries: A Protocol for Studies at Elevated Temperatures

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Experimental Details

Synthesis: Tetrahydrofuran (THF) (99.9 %, Sigma-Aldrich) and tetraglyme (G4) (99 %, Sigma Aldrich) were distilled over sodium and stored over 4 Å molecular sieves (Sigma-Aldrich) prior to use. Synthesis of the electrolytes was carried under an Ar atmosphere with H_2O and O_2 concentration < 0.1 ppm using an MBraun glovebox.

Electrolyte solutions of the All Phenyl Complex (APC) were prepared as previously described.[1] Briefly, anhydrous $AlCl_3$ (99.99 %, Sigma-Aldrich) was dissolved in THF and a solution of phenylmagnesium chloride (2 M, Sigma-Aldrich) was slowly added under vigorous stirring. The volume was corrected by addition of THF, yielding a transparent brown solution with a final concentration of 0.4 M of 2:1 PhMgCl:$AlCl_3$. In order to obtain the APC-G4 solution, standard APC solutions were evaporated under vacuum (~5×10^{-2} mbar) at room temperature for 12h. The white precipitate was dissolved in the necessary amount of G4 and filtered before use.

CuS was synthesized from the elements in a stoichiometric ratio, which were sealed in an evacuated (~5×10^{-2} mbar) quartz ampule heated at 450 °C for 2 days, followed by another 2 day heat treatment at 600 °C. $Fe[Fe(CN)_6]_{0.95}.0.4H_2O$ was obtained by stirring microcrystalline $Na_xFe[Fe(CN)_6]_{0.94}$, synthesized according to previously reported procedure,[2] in 0.25 M NO_2BF_4 in acetonitrile at room temperature for 24 hours under inert atmosphere. It was then vacuum dried (~5×10^{-2} mbar) at 160 °C overnight. MoS_2 (K & K Laboratories Inc.) was used without further purification.

Electrochemistry: Positive electrodes were prepared by mixing the active materials with Super P carbon and polyvinylidene fluoride (PVDF) (Sigma-Aldrich, average Mw ~ 534,000) in 8:1:1 weight ratio in N-methyl-2-pyrrolidone (NMP) (99.5%, Sigma-Aldrich, 99.5%) and casting the slurry onto molybdenum foil. The resulting electrodes with a loading of ~2-5 mg cm^{-2} were punched into 10 mm disks and dried overnight at 90 °C under vacuum.

Negative electrodes were prepared in the glovebox by sanding magnesium ribbons (99.5%, Sigma-Aldrich) immediately before assembling the cell.

Galvanostatic and potentiostatic experiments were carried out using a VMP3 potentiostat (Biologic) with Swagelok® cells (See Fig. S1) placed in a Heratherm oven (Thermoscientific). The cell were assembled in the glovebox and loaded in the preheated oven; acquisition was started after 1h.

Characterization: Phase purity was checked by X-ray powder diffraction (XRD) using a PANalytical Empyrean diffractometer in θ-θ Bragg-Brentano geometry, utilizing Cu Kα radiation, a Ni filter and a 2D PIXcel^{3D} detector.

Morphologies were obtained with a Zeiss Ultra field emission scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy detector (EDX).

List of Supplementary Figures

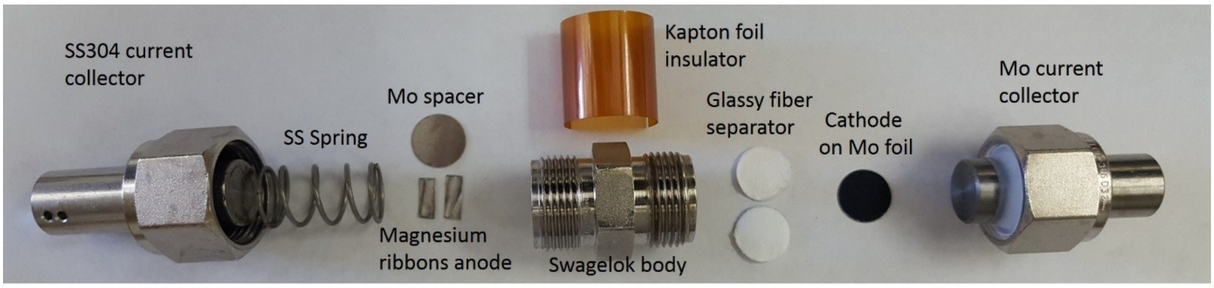

Figure S1: Modified Swagelok® cell using a Mo current collector rod on the positive electrode side; all other metallic parts of the cell are made of SS304 stainless steel.

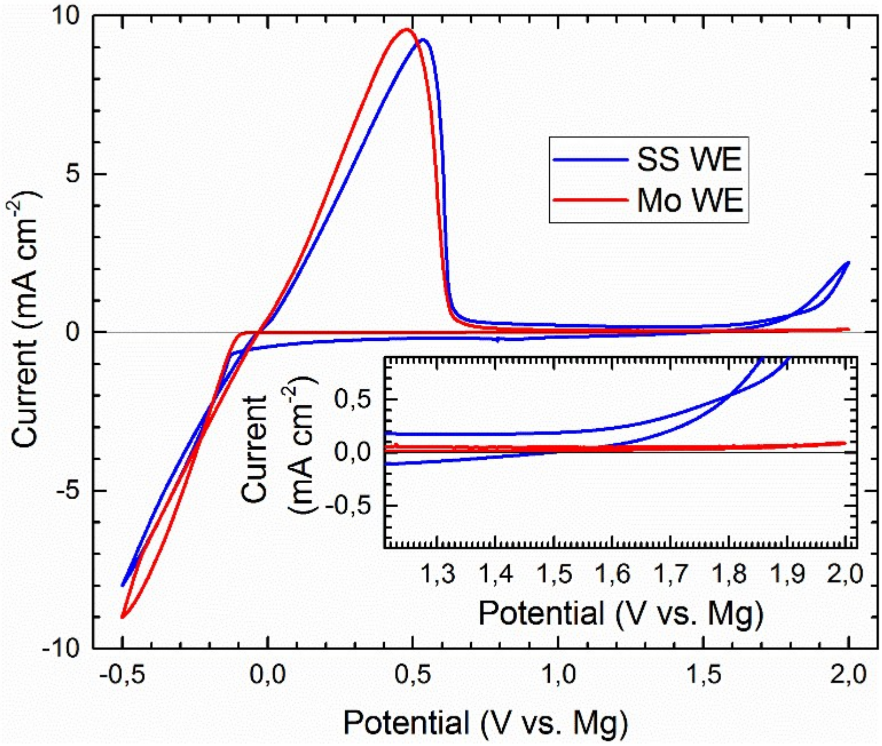

Figure S2: Cyclic voltammogram showing magnesium stripping and plating in a solution of APC-G4 using a Mo WE at 180 °C or a SS304 WE at 150 °C. For the sake of comparison, only the 10th cycle was plotted in each case.

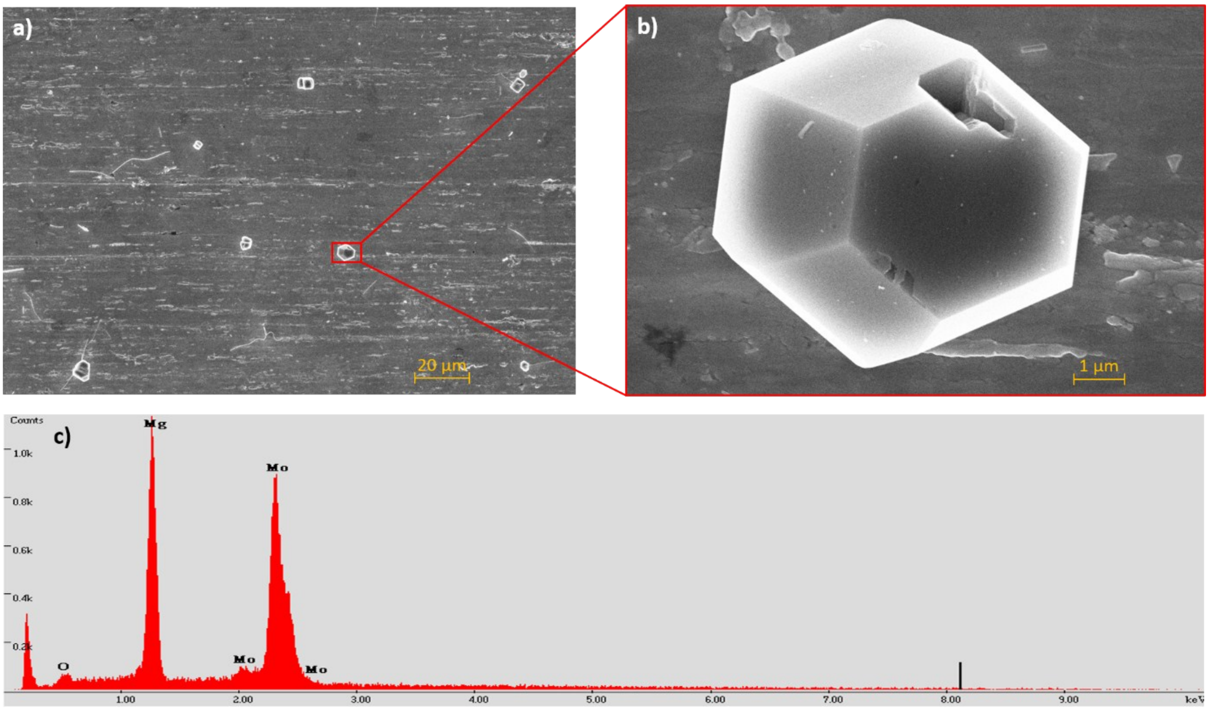

Figure S3: Scanning electron image of a magnesium electrodeposited particle from a solution of APC-G4 at 180 °C; a) low magnification view, b) high magnification view and c) EDX analysis of the high magnification view, showing the absence of contamination by aluminum or chlorine.

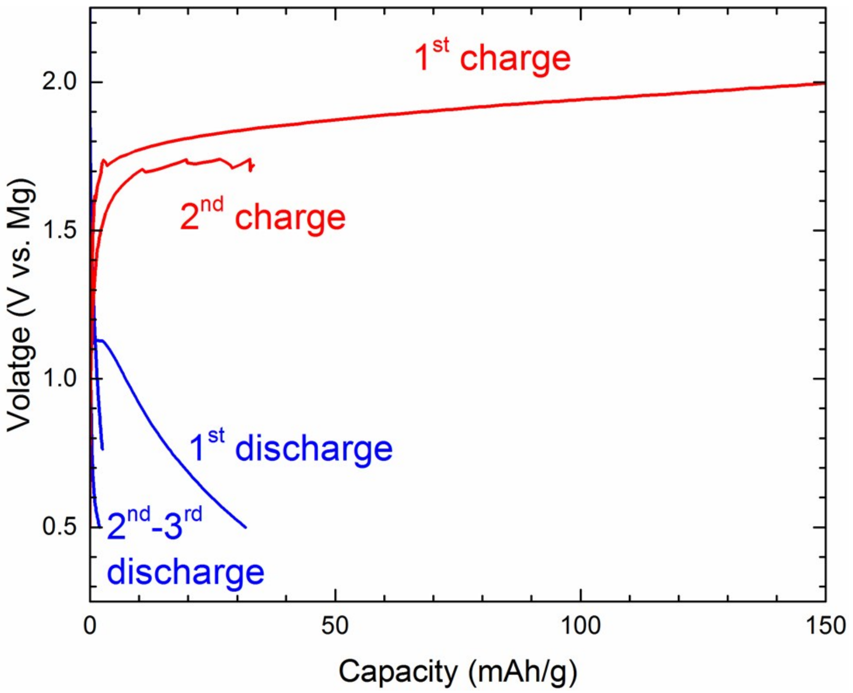

Figure S4: Galvanostatic cycling of $Fe[Fe(CN)_6]_{0.95}.0.4H_2O$ at 150 °C and C/10 in APC-G4, showing limited anodic stability.

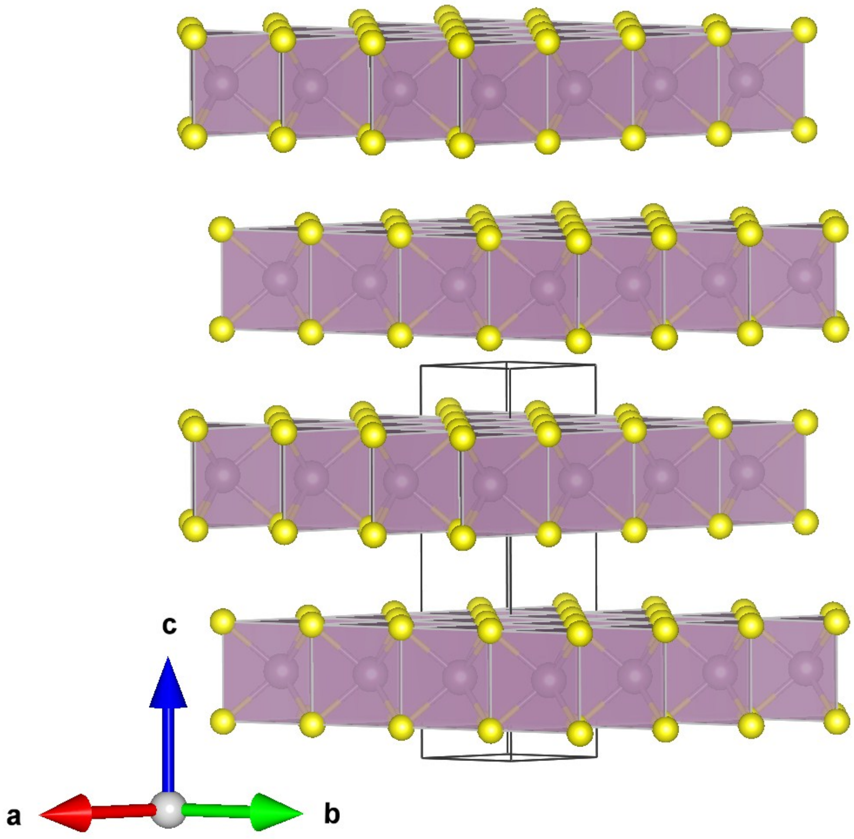

Figure S5: Structure of MoS_2. Molybdenum atoms (purple) are at the center of trigonal prisms made of sulfur atoms (yellow).

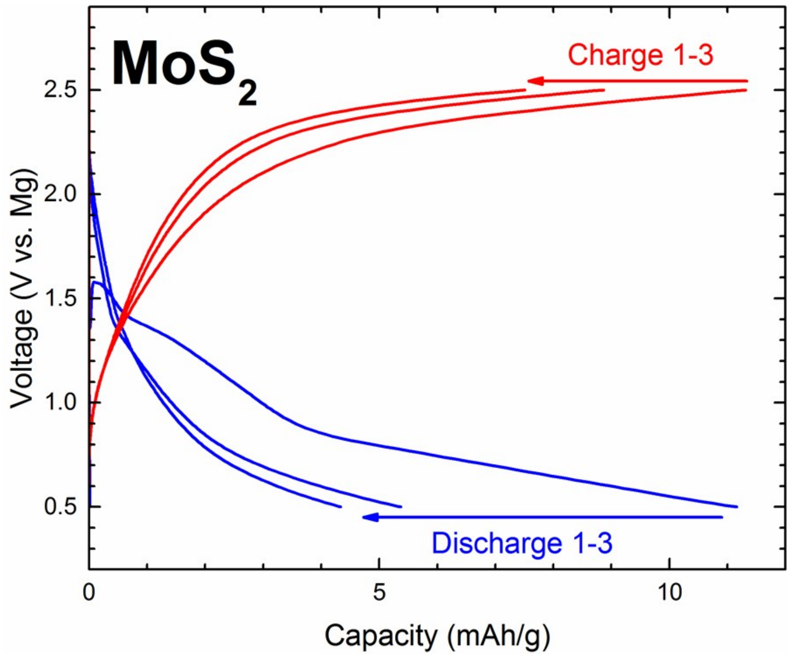

Figure S6: Galvanostatic cycling of MoS_2 at 150 °C and C/10 in APC-G4, showing negligible discharge capacity.

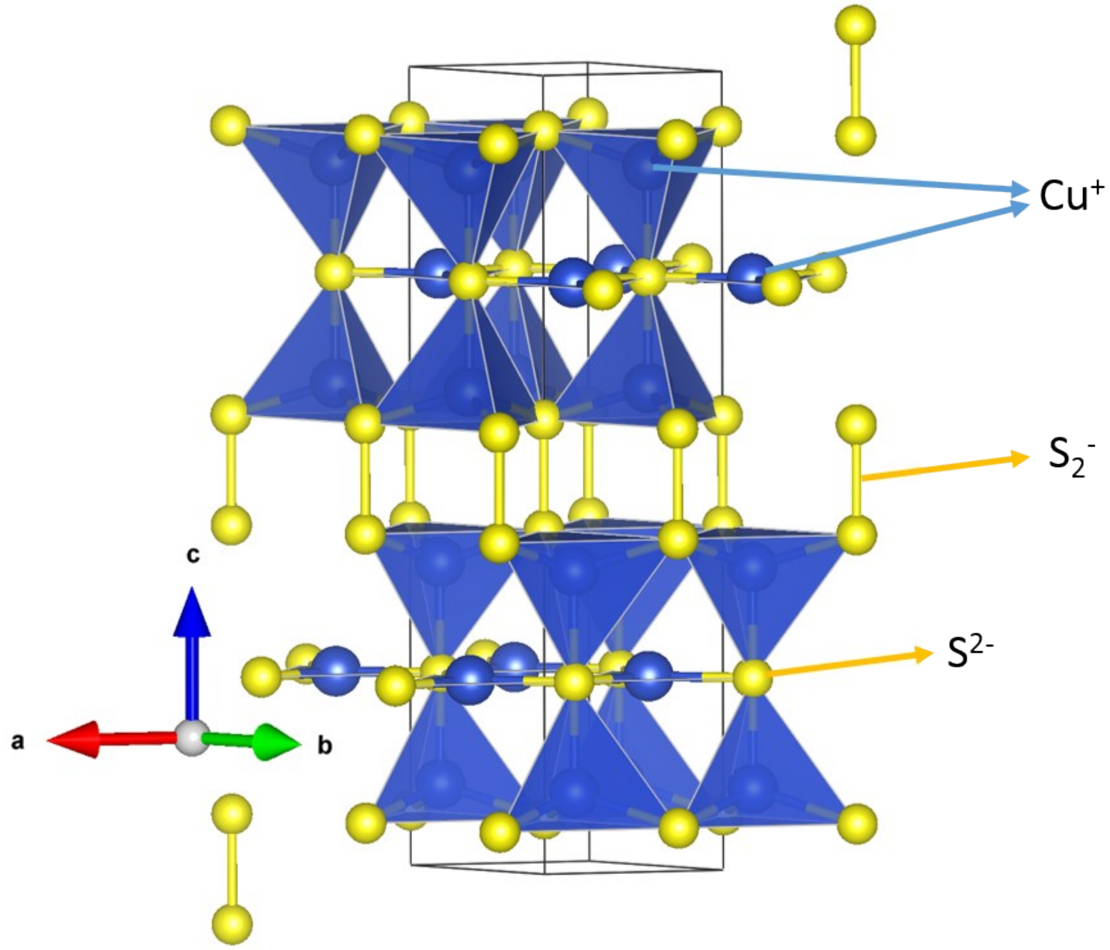

Figure S7: Structure of covellite, CuS.

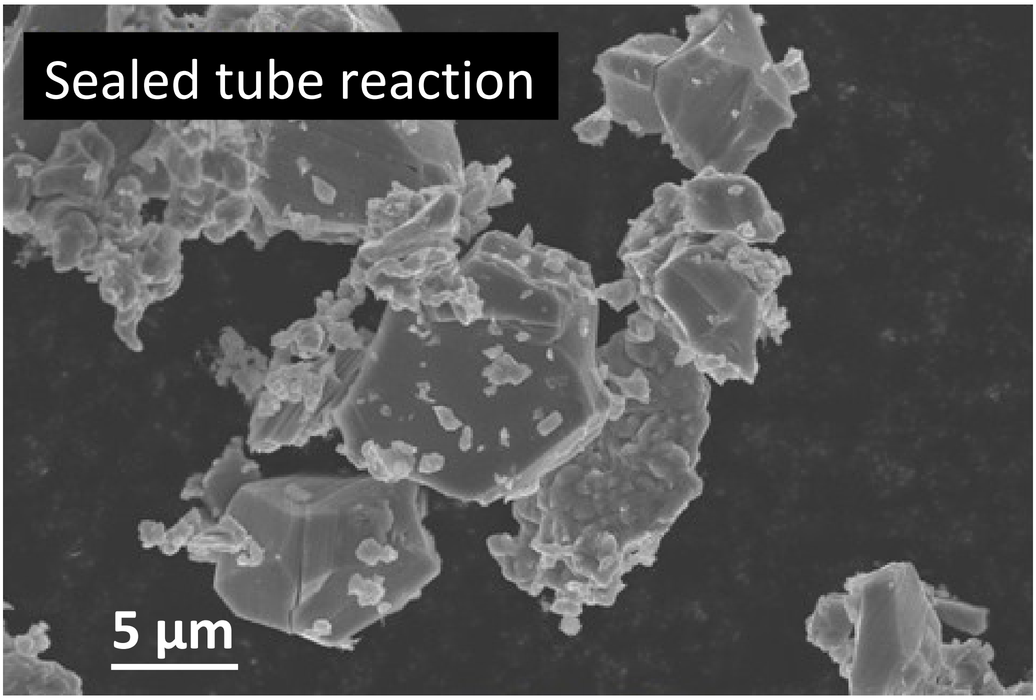

Figure S8: SEM micrograph of the as-synthesized CuS grains.

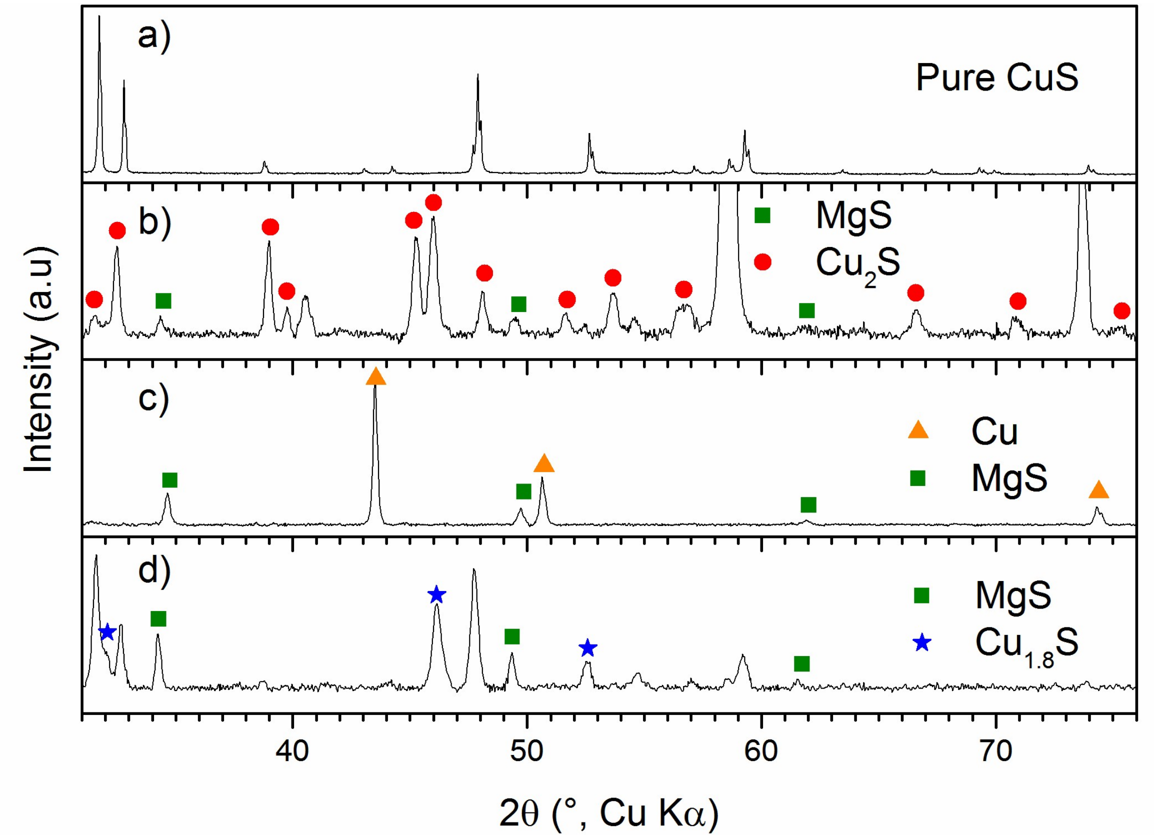

Figure S9: Diffractograms of a) pristine CuS, b) electrode discharged at 0.9 V, c) electrode discharged at 0.5 V and d) electrode recharged at 1.7 V. The cells were cycled at 120 °C in order to (partially) reform Cu_2S at the end of charge.

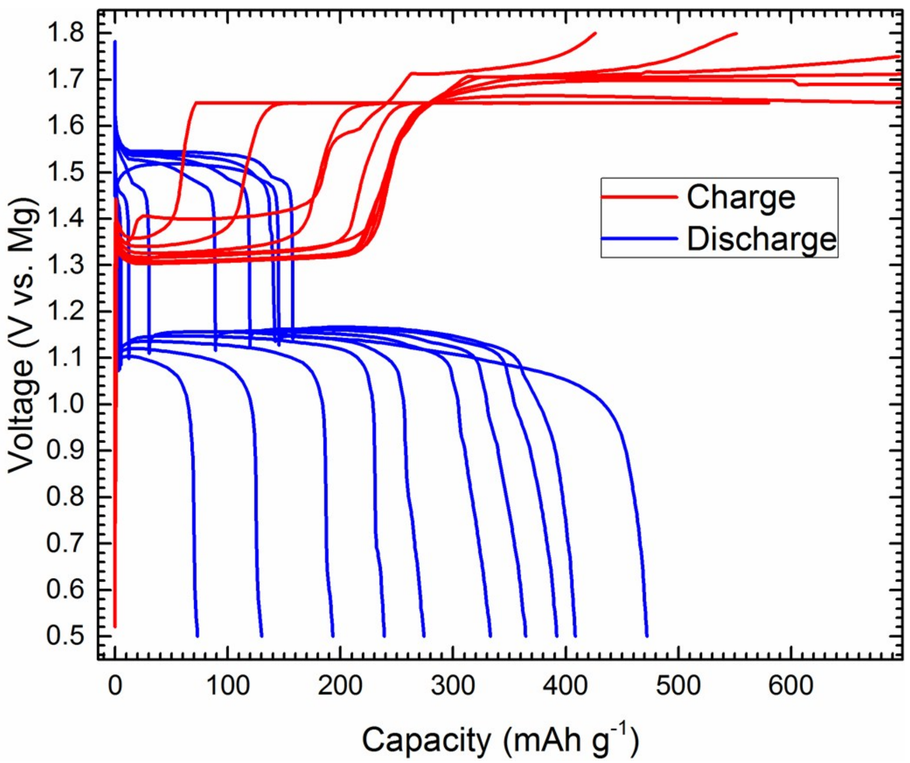

Figure S10: Galvanostatic discharge (blue) and charge (red) curves of CuS at 120 °C in APC-G4 electrolyte.

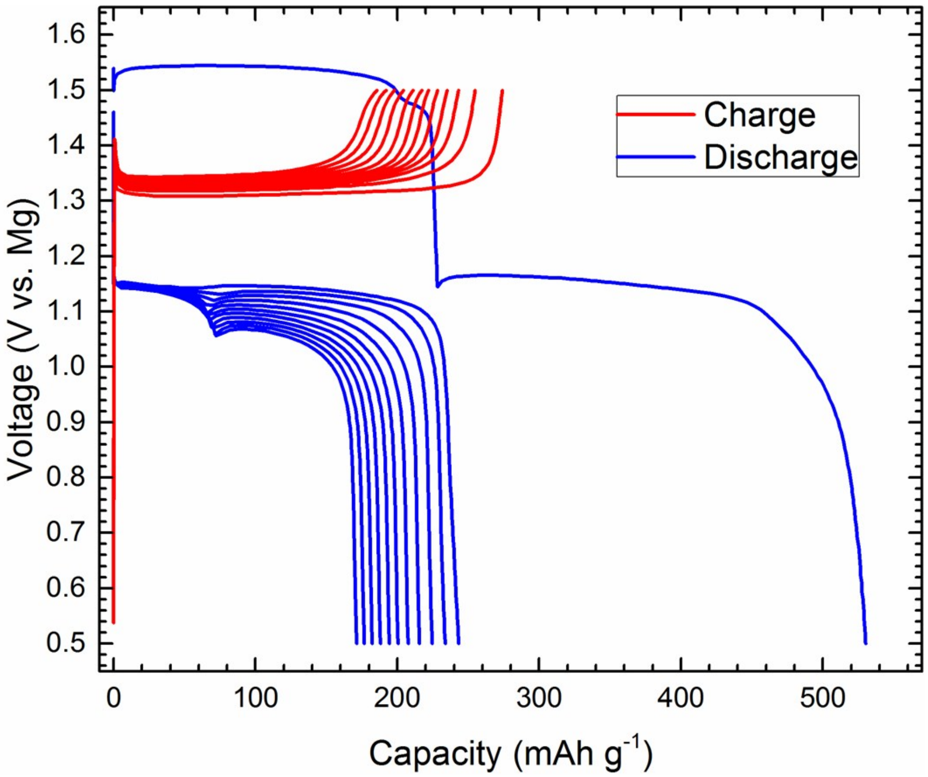

Figure S11: Galvanostatic discharge (blue) and charge (red) curves of CuS at 150 °C in APC-G4 electrolyte. A cutoff voltage of 1.5 V was selected to avoid the high voltage processes.

References:

1 O. Mizrahi, N. Amir, E. Pollak, O. Chusid, V. Marks, H. Gottlieb, L. Larush, E. Zinigrad, and D. Aurbach, *J. Electrochem. Soc.*, 2008, **155**, A103.
2 Y. You, X.-L. Wu, Y.-X. Yin, and Y.-G. Guo, *Energy Environ. Sci.,* 2014**,** *7*, 1643.
3 K. Momma, and F. J. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272.