

Supplementary Material

Influence of Crystal Disorder in MoS₂ Cathodes for Secondary Hybrid Mg-Li Batteries

Jyah Strachan,^A Lu Chen,^A Thomas Ellis,^A Anthony Masters,^A and Thomas Maschmeyer^{A,B}

^ALaboratory of Advanced Catalysis for Sustainability, School of Chemistry, The University of Sydney, Camperdown, NSW 2006, Australia.

^BCorresponding author. Email: thomas.maschmeyer@sydney.edu.au

Experimental

2 μm MoS₂, 90 nm MoS₂, lithium chloride (LiCl), aluminium chloride (AlCl₃) and *t*-amyl alcohol were purchased from Sigma-Aldrich. LiCl was dried under vacuum in schlenk line at 120 degrees for 12 hours. THF was purchased from Merck and distilled before use to bring the moisture content below 15 ppm. Coin cell components including spacers, springs and cages were purchased from TOB New Energy, China. Whatman glassy fibre separators (GF/D) were purchased from Sigma Aldrich. All chemicals were used without further purification.

The electrode slurry was prepared by mixing 80% (mass ratio) MoS₂, 10% polyvinylidene fluoride (as a binder) and 10% Super P (conductive agent) in N-Methyl-2-pyrrolidone (NMP, solvent). The slurry was subsequently coated on stainless-steel foil at 80 °C. It was further dried at 120 °C overnight before use.

The electrolyte was prepared by adding 2.0 M EtMgCl/THF dropwise to a flask containing *t*-amyl alcohol (*t*-AmOH). An ice bath was used to cool the strongly exothermic reaction. Gas evolution occurred immediately upon adding EtMgCl/THF, as (presumably ethane) gas is generated. EtMgCl/THF was added in slight excess (1.05:1, EtMgCl: *t*-AmOH) to ensure the *t*-AmOH was fully consumed, generating *t*-AmOMgCl. The mixture was stirred for 12 h under an N₂ atmosphere. AlCl₃ powder with the optimized molar ratio of AlCl₃ (*t*-AmOMgCl) of 1:6 was then slowly added into the resultant solution. The milky solution cleared after stirring overnight. The solution was stirred for a further 8 hours and transferred to glovebox for storage. This electrolyte is considered as single ion (Mg²⁺) electrolyte. Dry THF is slowly added into this electrolyte for dilution to reach higher concentration of Li source. Once LiCl is added, the electrolyte is considered as dual ions (Mg²⁺/Li⁺) electrolyte.

Morphological characterization of the MoS₂ was carried out by a Zeiss Scanning Electron Microscope (SEM). Powder X-ray Diffraction (XRD) was collected using a PANalytical X'Pert Powder instrument

using Cu X-ray source. Raman spectra were collected using a Bruker MultiRam FT-Raman Spectrometer with a 512 nm laser. N₂-sorption was performed using a Micromeritics ASAP 2020 Accelerated Surface Area and Porosity.

Ball-milling was performed using a Retsch PM 100 planetary ball mill. MoS₂, 1 g, was loaded into an agate jar with 3 agate balls (diameter = 20 mm) and subject to milling at 450 rpm for the stated time.

Electrochemical operations were carried out inside a glovebox (oxygen and moisture concentrations were maintained below 1 ppm). Voltammetric experiments were carried out on an ADAQ ER466 Integrated Potentiostat System (Edaq, Australia). Cyclic voltammograms were obtained using a 1 mm diameter platinum working electrode (Edaq) with a magnesium wire as both counter and reference electrodes.

Coin cell tests were performed with a Neware Coin Battery Cycler (BTS - 5V 5 mA, Shenzhen, China) using constant current charging/discharging parameters.

Electrolyte development

The dual metal ion electrolyte shows increased reduction and oxidation currents compared to the synthesized 0.8 M Mg electrolyte, using the method above (at all concentrations tested, Figure S 1a). The current continues to increase as the concentration of LiCl increases from 0.25 M to 1.0 M. This is due to the increased conductivity of the electrolyte, as reflected in the slope of the stripping curve.⁵⁴ The overpotential of reduction of the active magnesium species ([Mg₂Cl₃]⁺) reduction and the anodic stability of this dual metal ion electrolyte remains unchanged, suggesting that no additional complexes have been generated by reaction of the Mg electrolyte and LiCl. The role of LiCl is therefore solely a Li⁺ source and supporting electrolyte.

The anodic stability of the electrolyte (2.75V vs Mg) is sufficient for Li⁺ intercalation (which occurs below 2.0 V vs Mg (Figure S 1c)). Cycling tests were performed using coin cells containing a single (Mg²⁺) or dual ion electrolyte (Mg²⁺/Li⁺) to compare the electrolytes (Figure S 1b). The single ion electrolyte cells show a discharge capacity of just 32 mAh/g even under a very small current density of 28.5 mA/g; the dual ion electrolyte cells exhibit significantly improved capacity and power, reaching 138 mAh/g capacity under a higher current density of 250 mA/g. The improved performance was also confirmed by the cyclic voltammetry (Figure S 1c), where the two intercalation peaks (at 1.4 and 1.8 V) have a greater current than when LiCl is omitted.

Current density is defined as the applied current divided by the mass of active material, rather than the total mass of electrode.

Because of its suitable performance, the 0.8 M Mg + 1.0 M LiCl electrolyte was chosen for use in the current study.

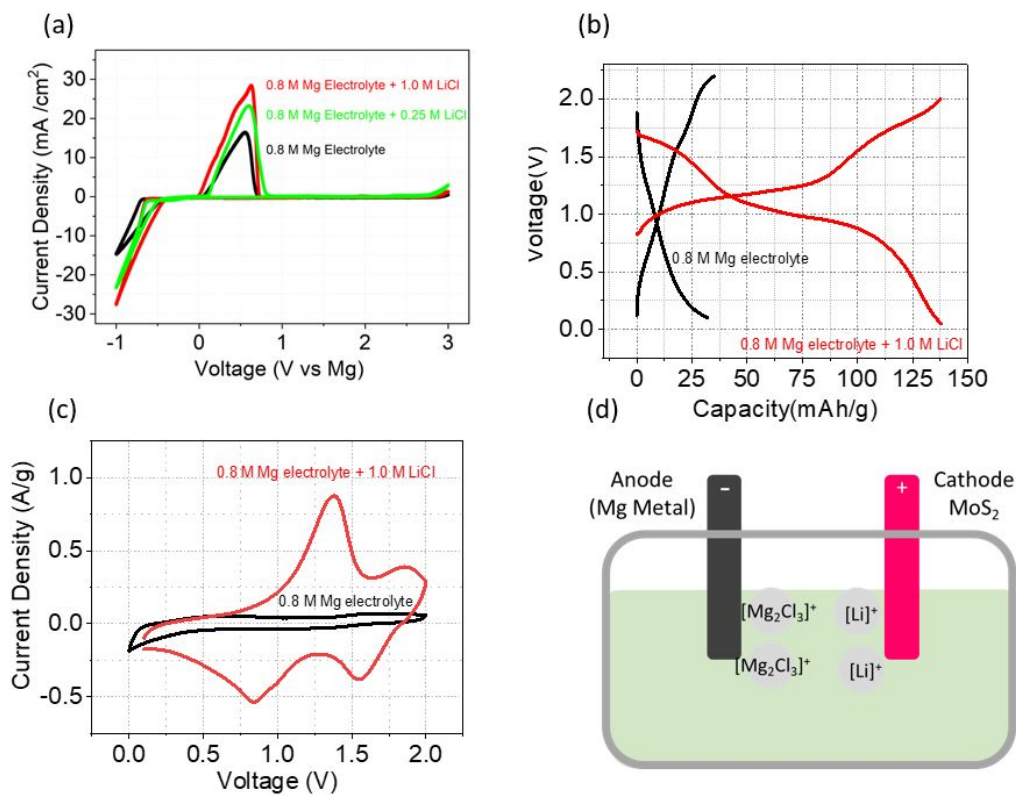


Figure S1 – (a) Cyclic voltammograms obtained with Pt working electrode in electrolyte containing 0.8 M Mg (black) and LiCl with concentration of 0.25 M (green) and 1.0 M (red), respectively. (b) The cycling performance of the battery containing 0.8 M Mg electrolyte only with current density of 28.5 mA/g (black) and battery containing 0.8 M Mg electrolyte and 1.0 M LiCl with current density of 250 mA/g (red). (c) Cyclic voltammogram collected with as-prepared coin cells containing single Mg electrolyte (black) and dual (Mg and Li) metal ion (red) with scan rates of 1.0 mV/s. (d) Illustration of the configuration of the Mg cell containing dual metal ions in the electrolyte.

Supplementary Data

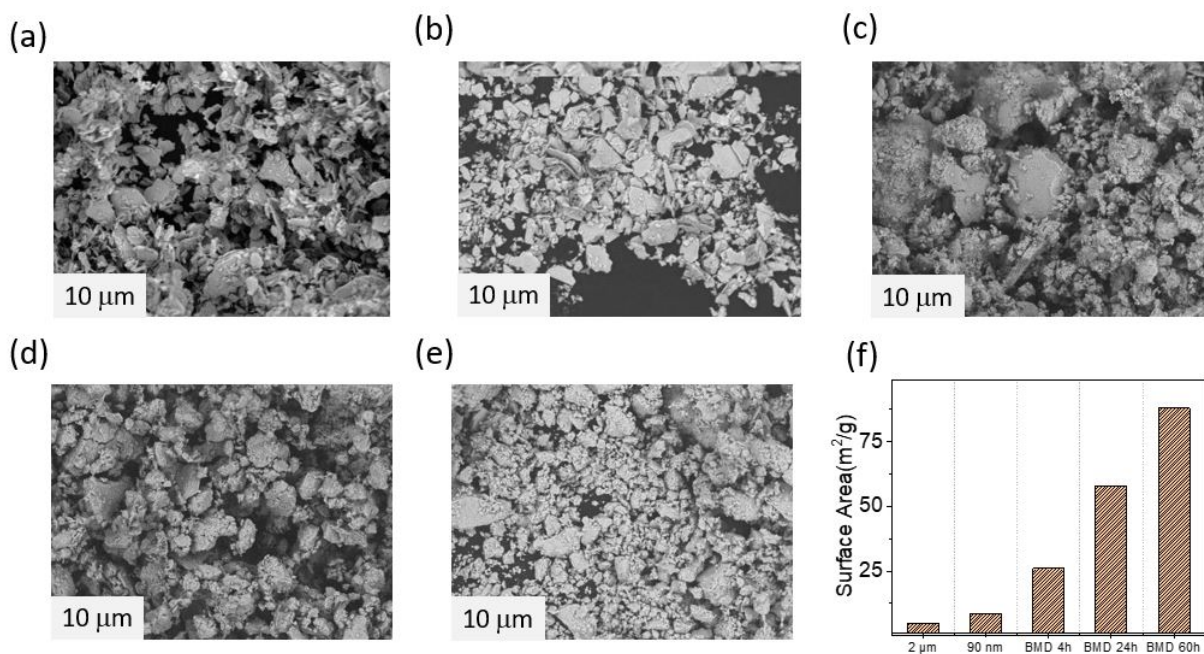


Figure S2 – Scanning electron micrographs of MoS₂ samples before and after ball-milling for various durations. a) 2 μ m-MoS₂; b) 90nm-MoS₂; c) 4h-MoS₂; d) 24h-MoS₂; e) 60h-MoS₂

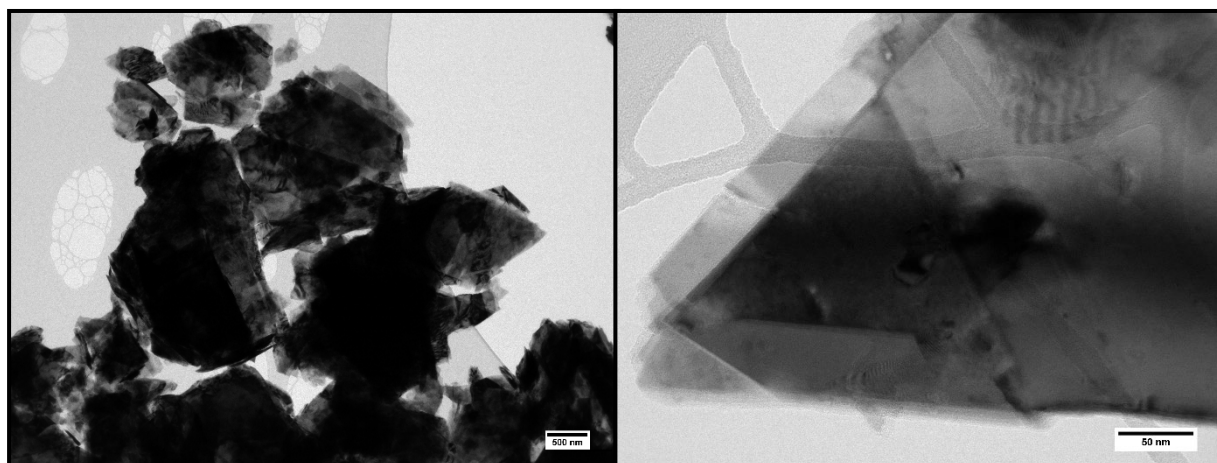


Figure S3 – Transmission electron micrographs of 90nm-MoS₂ showing large, crystalline sheets of MoS₂ that exhibit conventional hexagonal features.

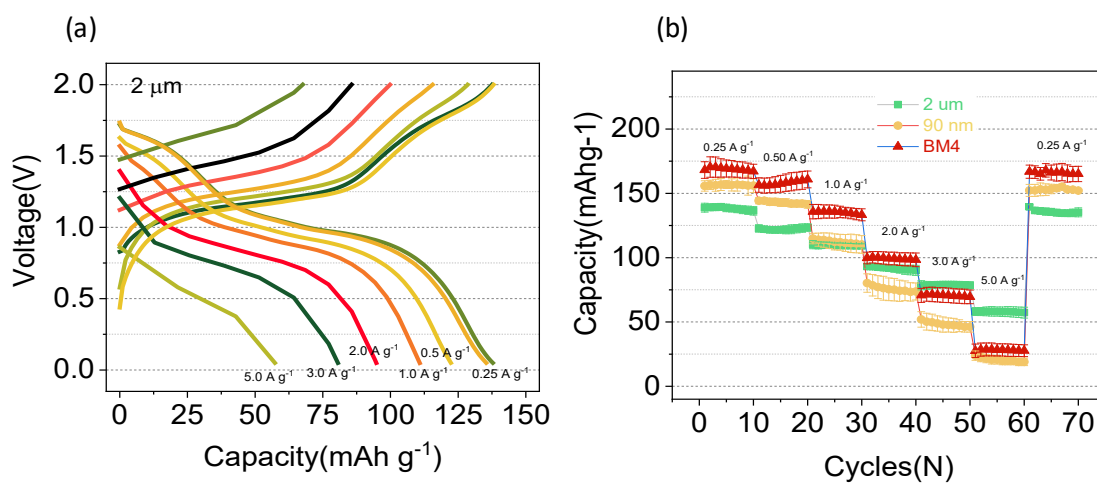


Figure S4 (a) Cycling profile of the coin cell with 2 μ m-MoS₂ as the cathode material at different charging/discharging current. (b) summary of the cathode capacity density with 3 types of cathode material at different current density.