Molybdenum sulfide clusters as capacity enhancing additives in lithium sulfur batteries

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Introduction

With the huge demand for batteries due to increase with the transition to renewable energy, new battery technologies are needed. Li-S batteries are a proposed solution to this due to their theoretical energy density of 2700 Wh.kg-1$_{(a)}$ and low cost as compared to Li-ion batteries currently on the market.

- Li-S cells have not yet reached this theoretical energy density in part due to issues with **polysulfide shuttling,** whereby **the polysulfide intermediates** release during discharge and **react irreversibly** with the Li cations leading to **surface passivation** and **loss of active material**. **Catalysts** are one of the proposed solutions.

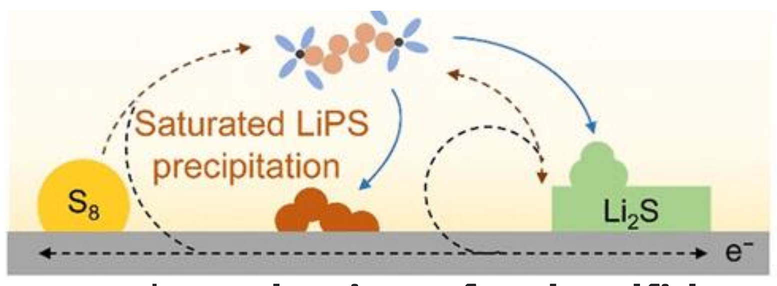

Figure 1: Passivation of an electrode via lithium polysulfide formation

- The **catalysts** make **reduction of polysulfides** to Li_2S faster **by accelerating kinetic bottlenecks** in the polysulfide pathway, hence reducing the amount left passivating the electrode, unreacted.

Aims & Objectives

- **Aims:**
  - **Synthesize** both clusters in a stable salt form.
  - **Record cyclic voltammograms** to establish redox activity in cell potential range.
  - **Test performance** in Li-S cells.

- In this project **two molybdenum sulfide** clusters, **$[Mo_2S_{12}]^{2-}$** and **$[Mo_3S_{13}]^{2-}$** were **synthesised** and investigated via **voltammetry** to investigate if the had any capability as **catalysts** . They were also put into coin cells for **cell cycle analysis**.

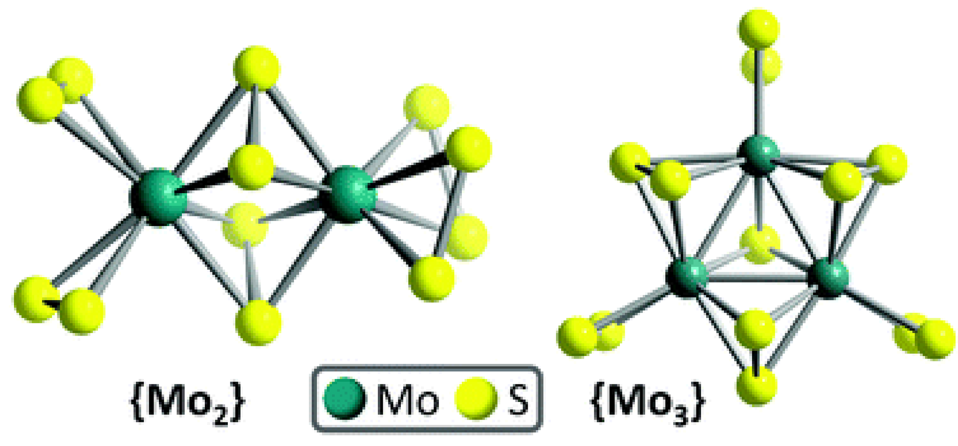

Figure 2: Structures of $[Mo_2S_{12}]^{2-}$ ({Mo$_2$}) and $[Mo_3S_{13}]^{2-}$ ({Mo$_3$})

Synthesis

- **$(NH_4)_2(Mo_2S_{12}).2H_2O$** was synthesized as a black powder with a low yield of **19.5%** probably due to the synthesis being air-sensitive, and upon analysis via **MS no characteristic peak** corresponding to the cluster was seen, although the IR did show expected peaks.
- A red powder of **$(NH_4)_2(Mo_3S_{13}).2H_2O$** **(0.62g, 68.5%)** was also synthesized and did show the **expected peak for [H $(Mo_3S_{13})]^+$** indicated in red with the correct isotope pattern. The IR was also as expected.

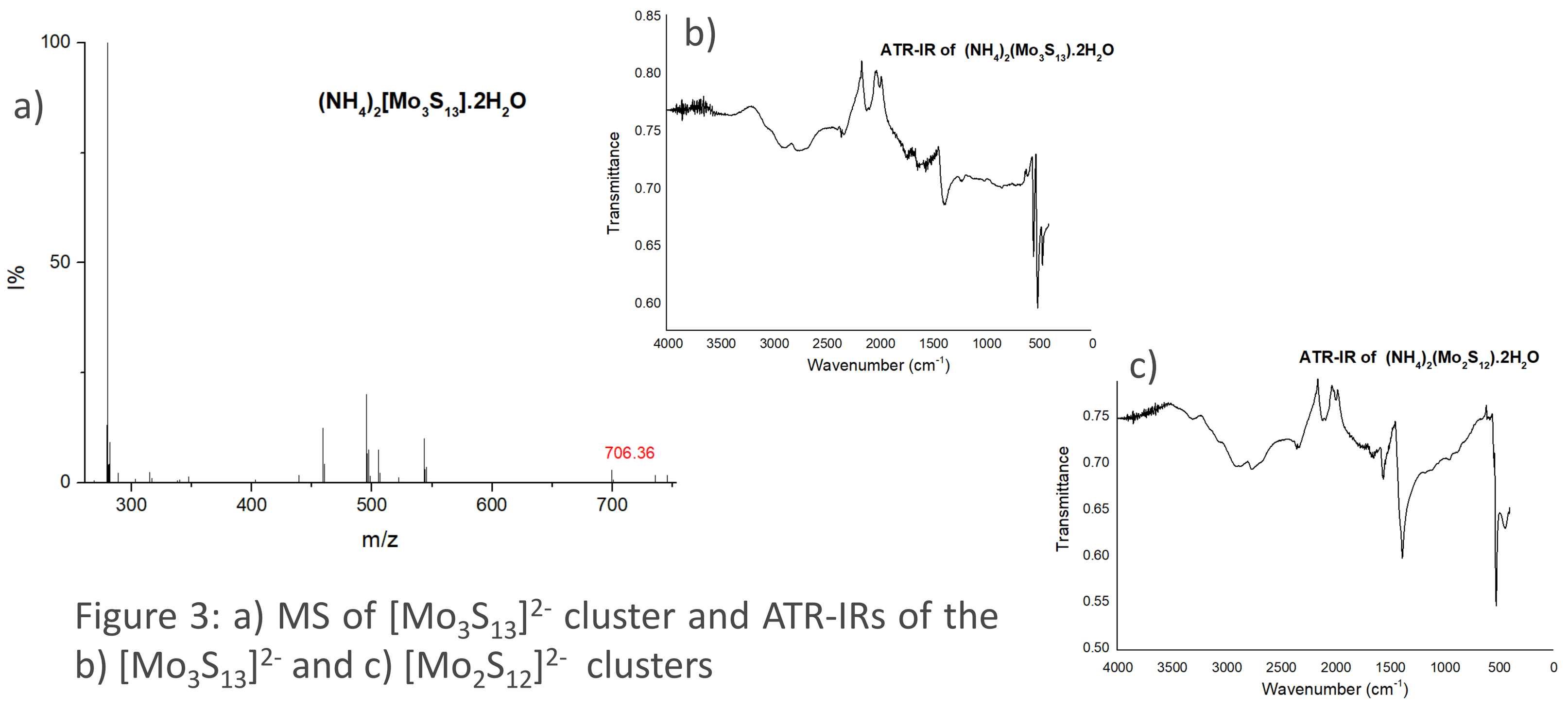

Figure 3: a) MS of $[Mo_3S_{13}]^{2-}$ cluster and ATR-IRs of the b) $[Mo_3S_{13}]^{2-}$ and c) $[Mo_2S_{12}]^{2-}$ clusters

Cyclic Voltammetry (CVs)

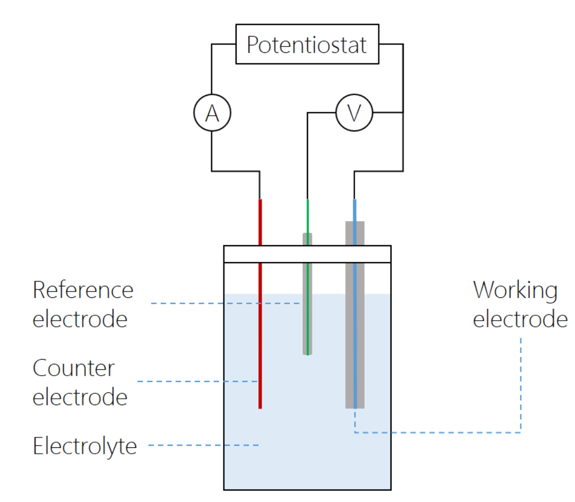

Figure 4: A diagram of a voltammogram setup

- **Cyclic voltammograms (CVs)** were taken with the clusters both in **solution** and **dropcast onto a GDL** cathode in the **solid state.**
- In part due to **issues with solubility, solid state** voltammetry led to the **most reproducible CVs** upon multiple cycles.
- The clusters were formulated into an **ink** which was **70% cluster**, 20% carbon black and 10% PVDF and **80µl was dropcast** onto a GDL strip.

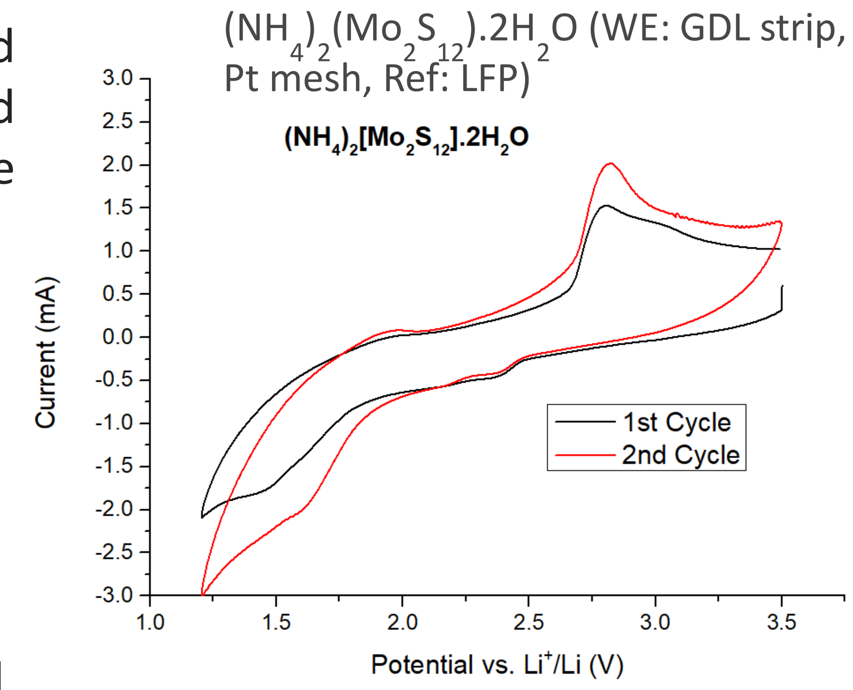

Figure 5: Voltammetry of $(NH_4)_2(Mo_2S_{12}).2H_2O$ (WE: GDL strip, CE: Pt mesh, Ref: LFP)

- **$(NH_4)_2(Mo_2S_{12}).2H_2O$** showed **multiple reduction** peaks and **one strong oxidation** peak. There are no clear redox couples.

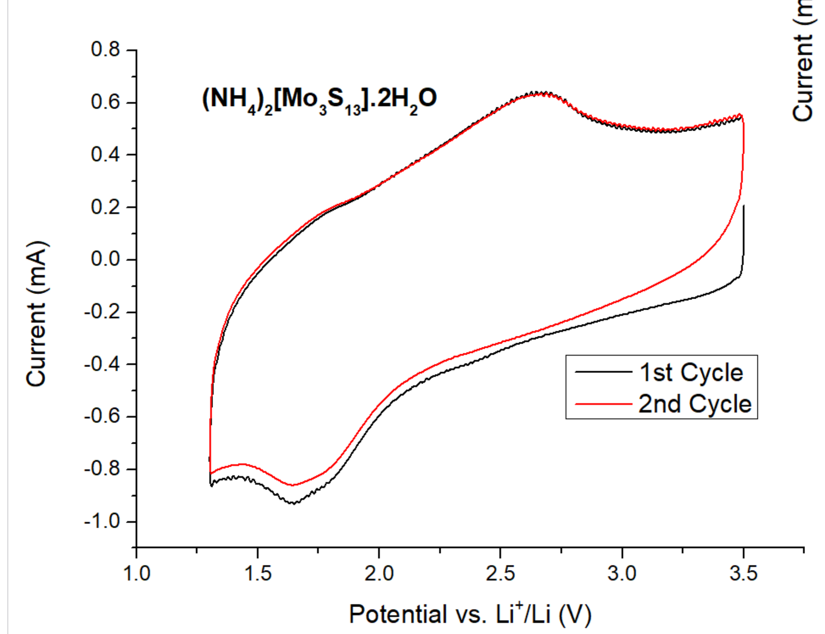

Figure 6: Voltammetry of $(NH_4)_2(Mo_3S_{13}).2H_2O$ (WE: GDL strip, CE: Pt mesh, Ref: LFP)

- **$(NH_4)_2(Mo_3S_{13}).2H_2O$** has **one clear redox couple** that is **irreversible**, with no other peaks visible, but this may be due to the **high capacitance** masking them.

Cell cycling

- Only cells **$[Mo_2S_{12}]^{2-}$** dropcast on the electrode were have been cycled so far, due to time constraints.
- After 48 cycles, they show **improved charge and discharge capacity** as compared to standards cycled without the additive, and a **similar columbic efficiency** after multiple cycles.

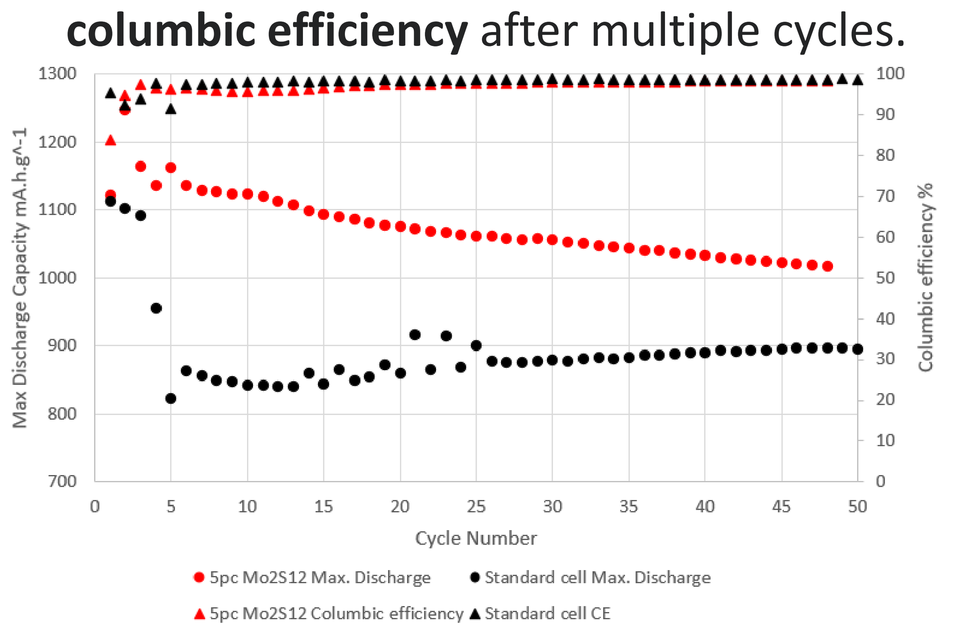

Figure 7: Max Discharge and columbic efficiency plotted against cycle number for the $[Mo_3S_{13}]^{2-}$ cell and a standard cell

Conclusions

- Two clusters were **synthesised and characterised**.
- Both clusters have shown **redox activity** within the **range of the Li-S battery**, and one featuring an **irreversible redox couple** and both showing **multiple reduction** peaks.
- The **$[Mo_2S_{12}]^{2-}$** cluster when in a **Li-S cell** shows **improved charge and discharge characteristics.**

Future work

- Further solubility tests to see whether the clusters are soluble in any relevant solvents including concentration limits.
- More coin cell cycling, especially with the $[Mo_3S_{13}]^{2-}$ cluster which has not yet been tested in Li-S cells.
- Further CVs including scan rate studies to gain more insight into what redox processes are occurring.

References

- Figure 1: M. Zhao, B. Li, X. Zhang, J. Huang, and Q. Zhang, *ACS Central Science*, 2020, **6 (7)**, 1095-1104
- Figure 2: A. Rajagopal, F. Venter, T. Jacob, L. Petermann, S. Rau, S. Tschierlei and C. Streb, *Sustainable Energy Fuels*, 2019,**3**, 92-95
- Figure 4: Forrister, T., 2022. Analyzing Cyclic Voltammetry at a Microdisk Electrode with Simulation. [online] COMSOL. Available at: https://www.comsol.com/blogs/analyzing-cyclic-voltammetry-at-a-microdisk-electrode-with-simulation/
- (a) – S. Gifford and J. Robinson, 2020. Lithium-Sulfur Batteries: Advantages. [online] The Faraday Institution. Available at: <https://www.faraday.ac.uk/lis-advantages/> [Accessed 8 September 2022].

Intern bio

I am studying Chemistry at University of Nottingham, entering my 3rd year in September. I have a specific interest in inorganic and sustainable chemistry, and this project has definitely peaked my interest into cluster synthesis and batteries as well as increasing my confidence in the labs. I am aspiring to do a PhD in chemistry.

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