The study of POMs as heterogeneous catalysts in lithium-sulfur batteries

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Abstract

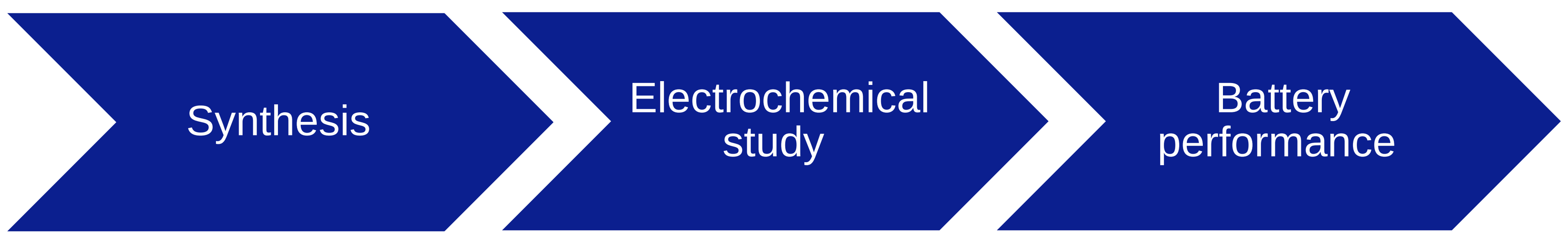
- The demand for energy storage is rapidly increasing and, as we approach the theoretical energy limit of Li-ion batteries, **next generation batteries** will be essential for the global transition to more sustainable energy sources.
- The **high theoretical energy density** of lithium sulfur batteries and the **natural abundance** of sulfur makes them an attractive alternative. [1] However, the current energy density performance of lithium sulfur batteries is much lower than what is theoretically expected.
- An electrochemical study of four **polyoxometalates as additives** was carried out to investigate their ability to act as **heterogeneous catalysts** in lithium sulfur batteries, with the aim of increasing the energy density and cycle stability of the battery.

Motivation

- The main challenges in commercialising lithium sulfur batteries are the **low-rate capability** and a **low capacity** due to the incomplete conversion of the terminal charge and discharge products S_8 and Li_2S. [2]
- **Polyoxometalates** have reversible multielectron capability and this project focuses on the impact they can have as **heterogeneous catalysts** in LSBs.

Methods

- The **synthesis** and characterisation of two POMs, **$[SiMo_{12}O_{40}]^{4-}$** and **$[PMo_{12}O_{40}]^{3-}$**, that could have suitable properties for catalysis in LSBs.
- The **electrochemical study** of four POMs to assess redox activity in the potential range of LSBs (1.6-2.8 V vs Li^+/Li) and to evaluate their suitability as catalysts.
- Cathode fabrication with POM additives for cell testing to test their cyclability and capacity **performance** as heterogeneous catalysts in LSBs.



Synthesis

- Two POMs, **TBA_4 $[SiMo_{12}O_{40}]$** and **TBA_3 $[PMo_{12}O_{40}]$**, were synthesised and the following characterisation methods were used: elemental analysis, NMR and infrared spectroscopy.
- Elemental analysis:

a)

TBA_4 $[SiMo_{12}O_{40}]$		
Element	Expected %	Measured %
C	27.56	27.51
H	5.20	5.13
N	2.01	1.98

b)

TBA_3 $[PMo_{12}O_{40}]$		
Element	Expected %	Measured %
C	22.61	22.70
H	4.27	4.31
N	1.65	1.58

Figure 1: Elemental analysis of TBA_4 $[SiMo_{12}O_{40}]$ (a) and TBA_3 $[PMo_{12}O_{40}]$ (b)

- Phosphorous NMR of TBA_3 $[PMo_{12}O_{40}]$:

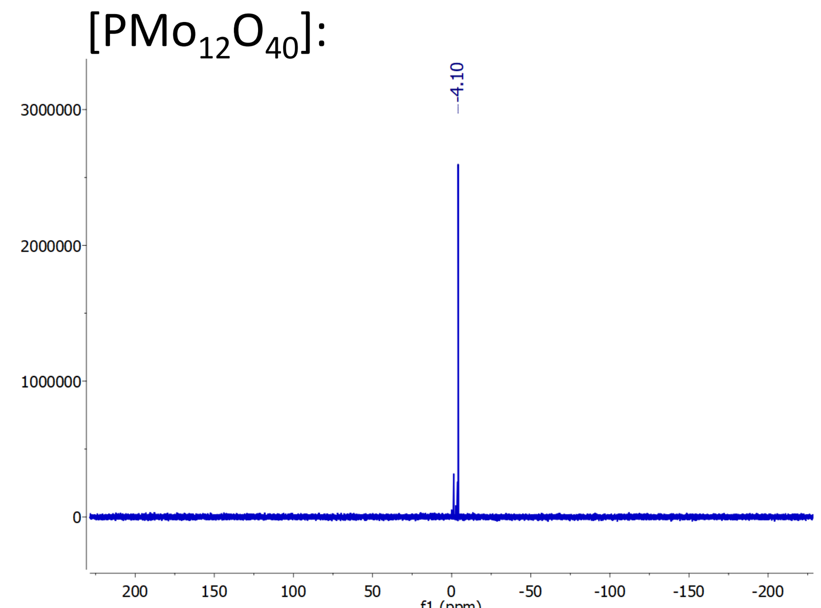
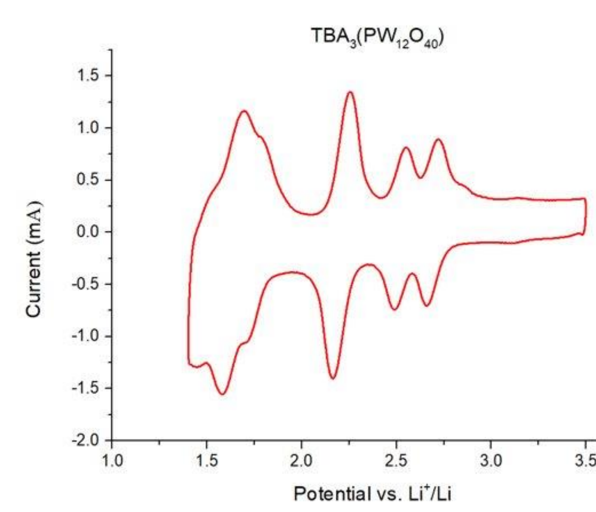


Figure 2: Phosphorous NMR ofTBA_3 $[PMo_{12}O_{40}]$

Electrochemical Study

- An electrochemical study was completed for four POMs, **TBA_4 $[SiMo_{12}O_{40}]$**, **TBA_3 $[PMo_{12}O_{40}]$**, **TBA_3 $[PW_{12}O_{40}]$** and **TBA_4 $[SiW_{12}O_{40}]$**. Voltammograms were recorded in solution, solid state and under the presence of sulfur.

a)



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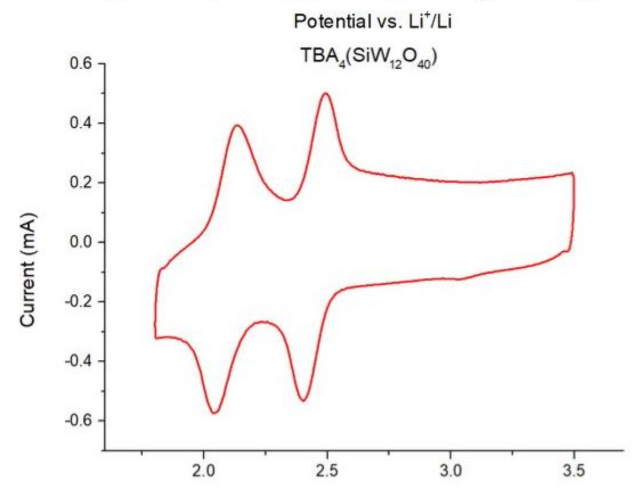

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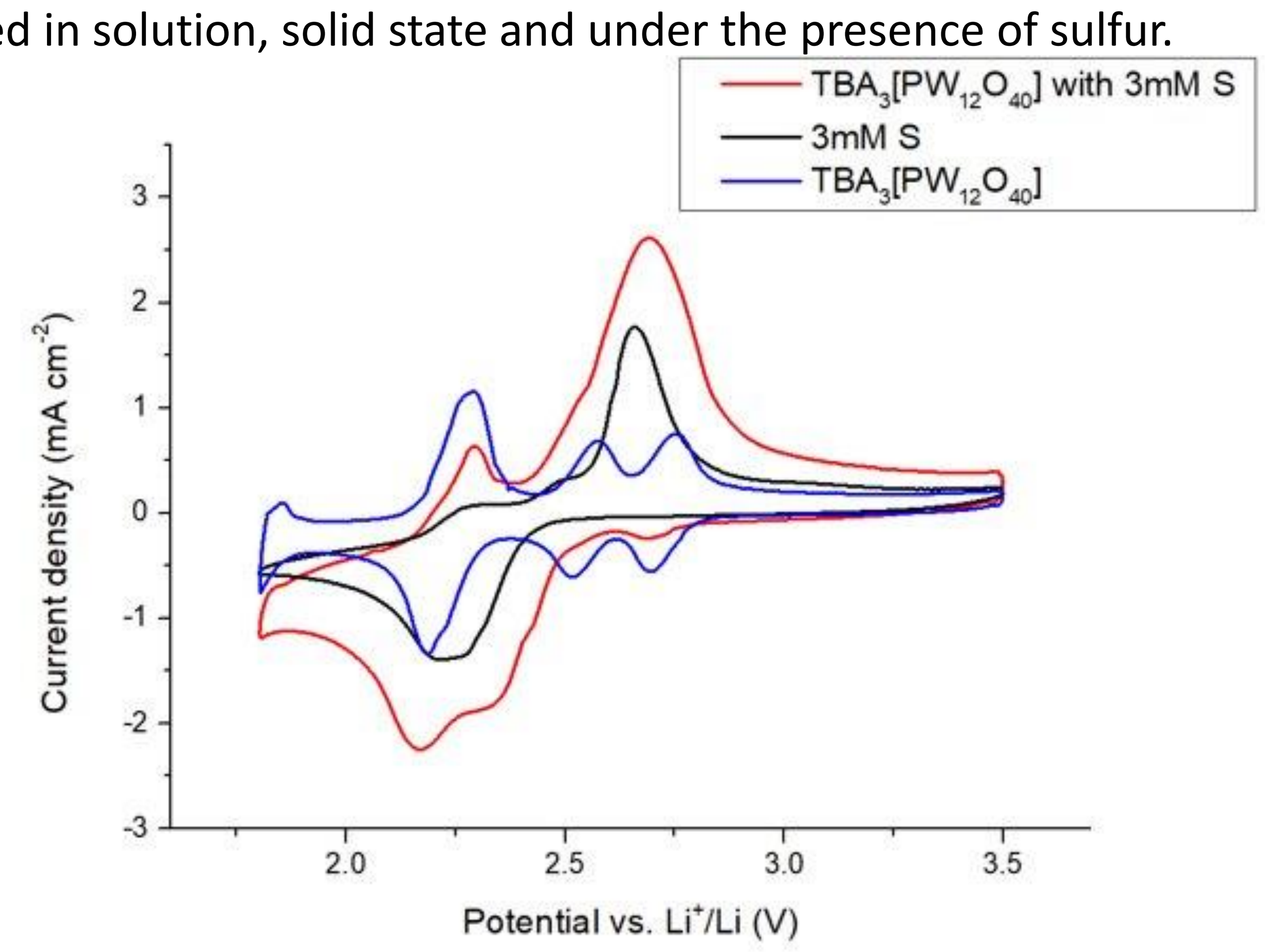


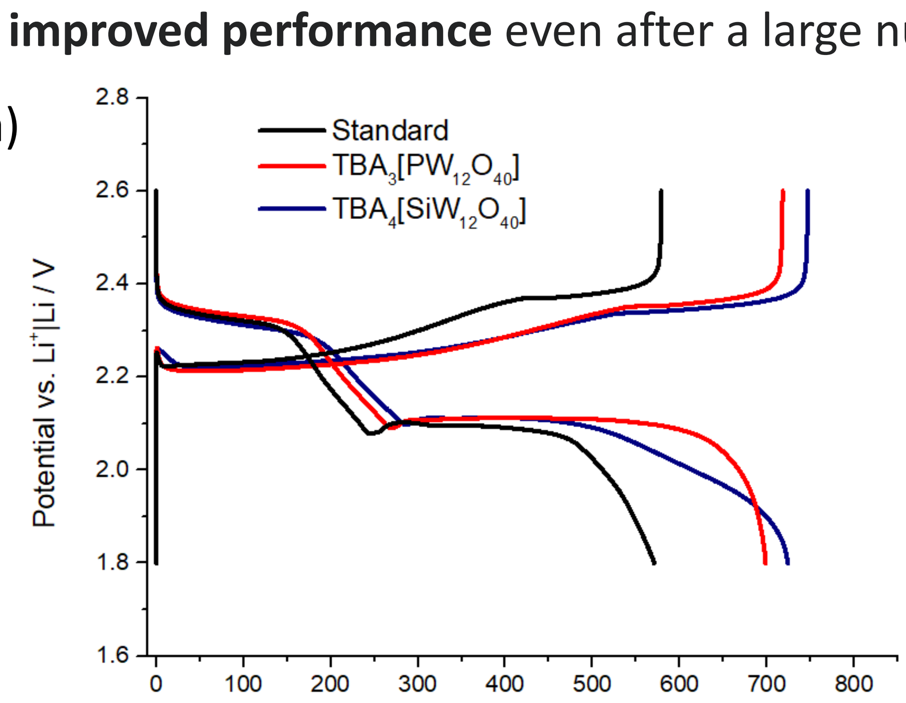
Figure 3: Cyclic voltammograms recorded at 100 mv/s of TBA_3 $[PW_{12}O_{40}]$ in solid state (a) of TBA_4 $[SiW_{12}O_{40}]$ in solid state (b) and TBA_3 $[PW_{12}O_{40}]$ under the presence of sulfur (c)

- TBA_3 $[PW_{12}O_{40}]$ and TBA_4 $[SiW_{12}O_{40}]$ showed the most promising redox activity in solution and their solubility in electrolyte allowed solid state voltammetry to be carried out.
- Both POMs were **redox active,** with quasi reversible peaks, in the potential range of 1.8-2.6 V vs Li^+/Li which is required for catalysis of Li_2S oxidation and S reduction in Li-S batteries.
- The sulfur voltammetry for TBA_3 $[PW_{12}O_{40}]$ shows an **enhanced reduction current** at 2.2-2.3 V vs Li^+/Li which suggests **catalysis**.

Battery Performance

- Standard lithium-sulfur cells achieved ~660 mAh g_s^{-1} on first discharge, the **TBA_3 $[PW_{12}O_{40}]$** and **TBA_4 $[SiW_{12}O_{40}]$** POMs increase capacity by ~140 and 160 mAh g_s^{-1} respectively. This **increased capacity** originates from the lower charge and discharge plateaus showing that the POMs are catalysing the low order polysulfide reduction of Li_2S.
- Although the standard cells have a very low-capacity fade, the cells containing the additives give an **improved performance** even after a large number of cycles.

a)



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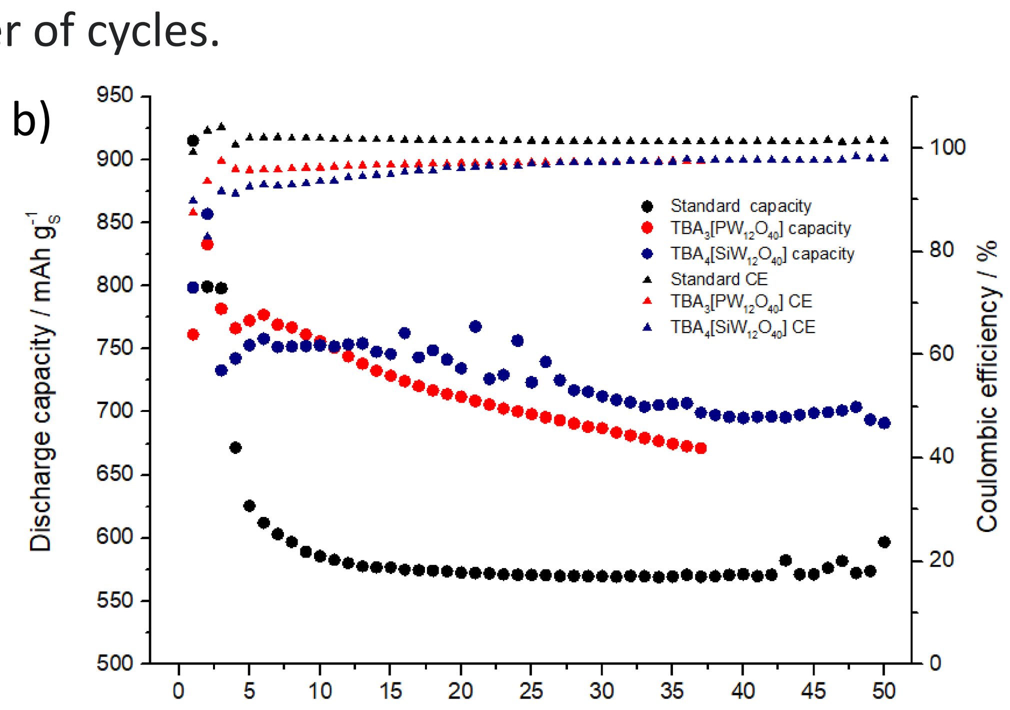

Figure 2: Comparison of the capacity of the first cycle (a) and capacity fade over 50 cycles (b) of standard lithium-sulfur cells and lithium sulfur cells containing TBA_3 $[PW_{12}O_{40}]$ and TBA_4 $[SiW_{12}O_{40}]$

Conclusion, Impact and Next steps

- The use of POMs as additives in lithium sulfur batteries lead to an **increase in capacity** and **promising cyclability** compared to standard lithium sulfur cells, addressing two of the main challenges in LSBs.
- These results have resulted in future work on the four POMs as heterogeneous catalysts in lithium sulfur batteries.
- POM stability will be checked using Li/Cu cells to **monitor degradation** in battery and **mechanistic details** behind the POM's behavior in the battery will be investigated.

I have just finished my second year of MSc Chemistry at the University of Nottingham. The role that Li-S technology could have on the global energy transition has inspired me throughout this project and I am aspiring to work in the energy industry to support the transition to net zero.

References

[1] Seh, Z.W., Sun, Y., Zhang, Q. and Cui, Y., 2016. Designing high-energy lithium–sulfur batteries. *Chemical society reviews*, *45*(20), pp.5605-5634.

[2] Han, Z., Li, Sd key parameters in exploring the cyclability limitation of practical lithium–sulfur batteries. *Journal of Materials Chemistry A*, *9*(43), pp.24215-24240, Wu, Y., Yu, C., Cheng, S. and Xie, J., 2021. Challenges an

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