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# Polyoxometalates based electrocatalysts for vanadium redox flow battery

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## Abstract

The intermittent nature of renewable energy sources such as wind and solar has increased the demand for suitable storage technologies. The vanadium redox flow battery (VRFB) offers a viable option in this field, demonstrating long life, safety and decoupling of power and energy. Carbon based electrodes are the most commonly deployed electrode for VRFB. The electrode provides an active site for redox reactions to occur, making it a vital cog in the performance of these batteries; however, offer sluggish kinetics towards the redox active species. Modification of the electrode can be utilised to combat this issue. Modification involves the treatment of carbon-based electrodes using different techniques, such as electrocatalyst deposition, to increase the electrochemical activity of the material towards vanadium redox reactions. In this work, a class of metal-oxide materials known as polyoxometalates have been considered as potential catalysts for this purpose. Tetrabutylammonium hexamolybdate, $(C_4H_9N_2)_2Mo_6O_{19}$, has been synthesised and characterised using FTIR, Single Crystal XRD and Powder XRD. Deposition $(C_4H_9N_2)_2Mo_6O_{19}$ onto the electrode was achieved hydrothermally. Deposition was confirmed using SEM, with kinetic improvements subject to electrochemical testing through CV experiments.


## Background

- The intermittent nature of renewable energy sources has increased demand for storage technologies.
- Redox flow batterie are a viable option with abundant potential.
- Current stationary energy storage technique unsuitable for large scale energy grid replacement.

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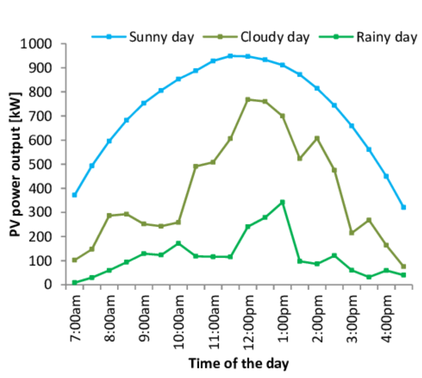


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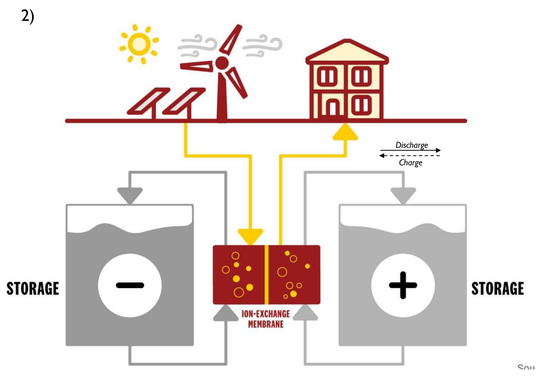
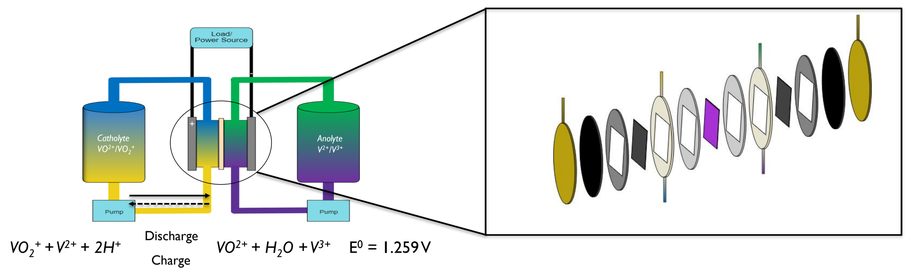


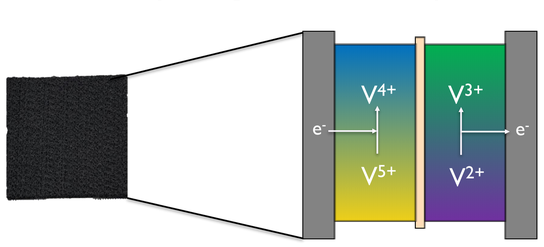

## Redox Flow Battery

- Storage device in which the energy is stored in two redox active species e.g $V^{4+}/V^{5+}$ and $V^{3+}/V^{2+}$.
- Advantages include low maintenance, long life cycle and decoupling of power and energy.
- Disadvantages include high cost, moderate efficiency and low power density.
- Battery performance can be improved through electrode treatment.




## Electrode

- Carbon based electrodes are among the most common.
- High chemical stability and good conductivity.




- Provides active site for electron transfer.
- Sluggish kinetics hinder performance.
- Treatments such as catalyst deposition improve performance.
- Polyoxometalates yet to be explored as electrocatalyst.
- POMs are polyatomic ions composed of three or more transition metal (e.g., Mo, V, W) oxyanions linked together by shared oxygen atoms to form closed three-dimensional frameworks.
- Highly attractive due to high chemical stability, unique redox properties and tunable chemical structure.

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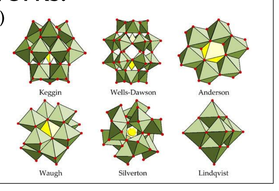
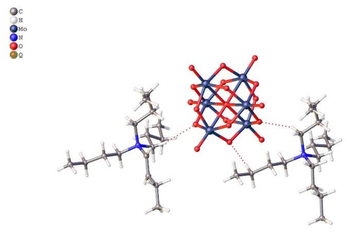



## Future Work

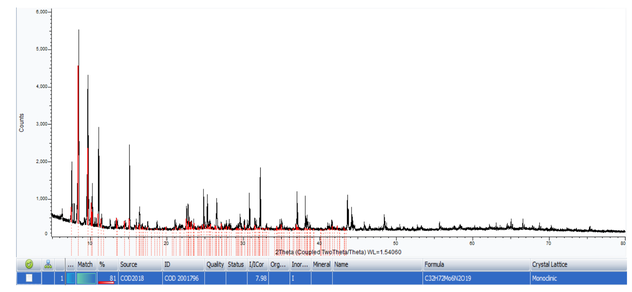
- Characterise treated felts electrochemically through cyclic voltammetry and electrochemical impedance spectroscopy.
- Analyse battery performance through cell tests.
- Translate knowledge from VRFB to all iron redox flow battery.

## Preliminary Results

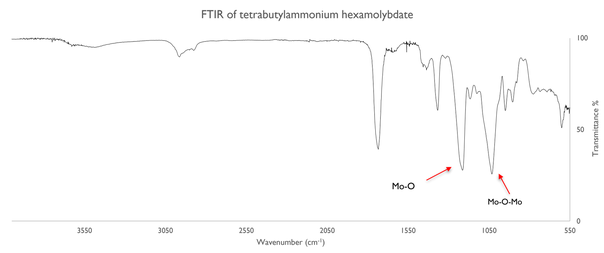
- Tetrabutylammonium hexamolybdate was successfully synthesised per reported method and characterised using FTIR, Single Crystal XRD, Podwer XRD.
- Synthesised product was deposited onto the carbon-based electrode using the hydrothermal method and characterised using SEM.



Single crystal XRD showing 6 MoO6 octahedra.
Each polyanion hydrogen bonded to two counter cations
Exhibits Lindqvist arrangement.

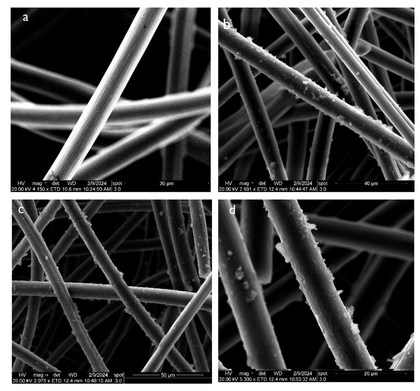



PXRD results detailing present formula and crystal lattice.




FTIR spectrum for synthesised crystals.
Two strong sharp stretches in the M-O range (M=Metal).
Characteristic of bonds present in $[Mo_6O_{19}]^{2-}$.

SEM images of pristine felt (a) compared to treated felt (b-d).Deposition was successfully achieved.
Random arrangement of particles observed.
Uniform arrangement is associated with improved performance.

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3. Gusmão FMB, Mladenović D, Radinović K, Santos DMF, Šljukić B. Polyoxometalates as Electrocatalysts for Electrochemical Energy Conversion and Storage. Energies [Internet]. 2022; 15(23).