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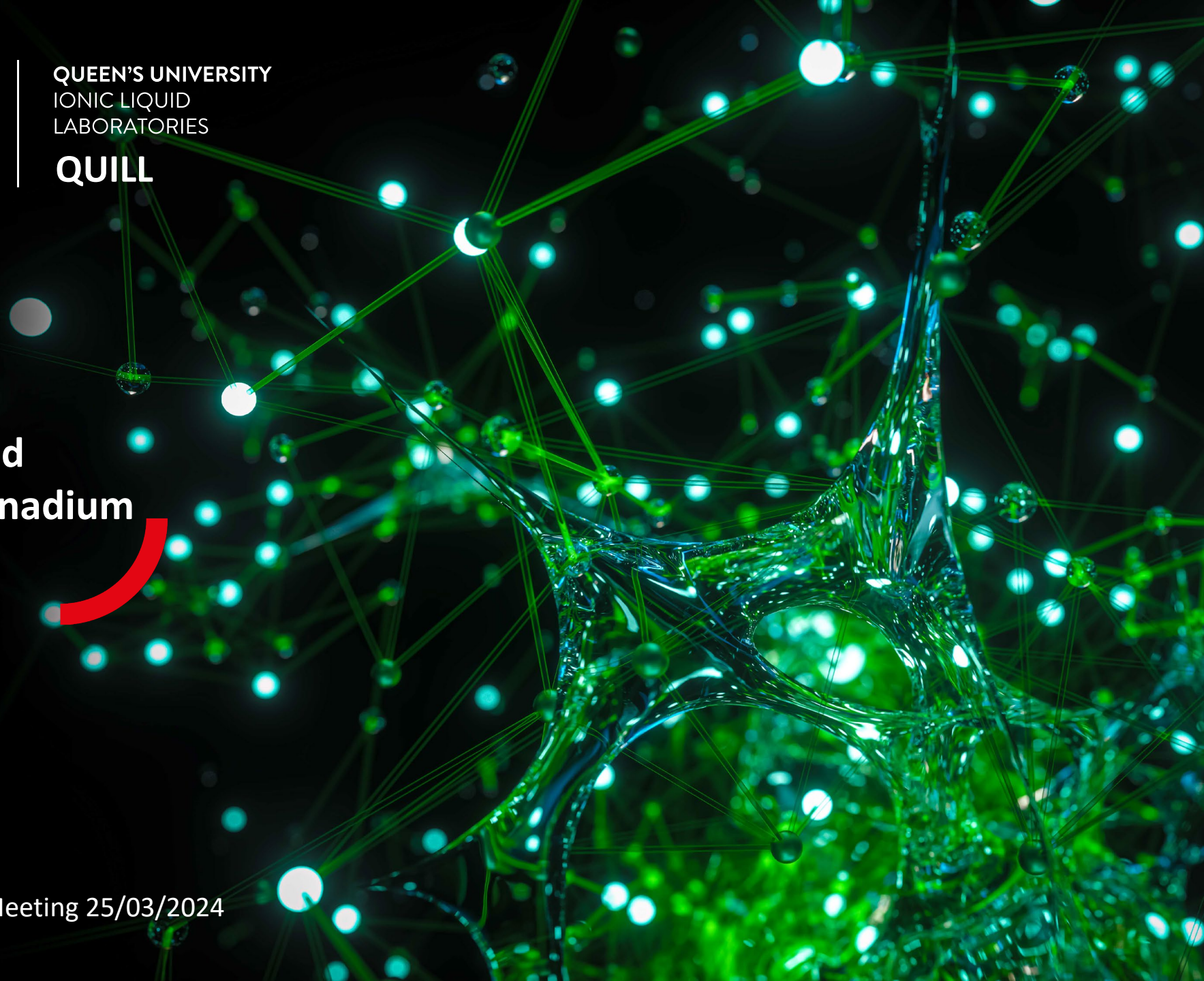

Polyoxometalate-Based Electrocatalysts for Vanadium Redox Flow Batteries

Aodhán Dugan

CONFIDENTIAL – QUILL Spring Meeting 25/03/2024

Contents

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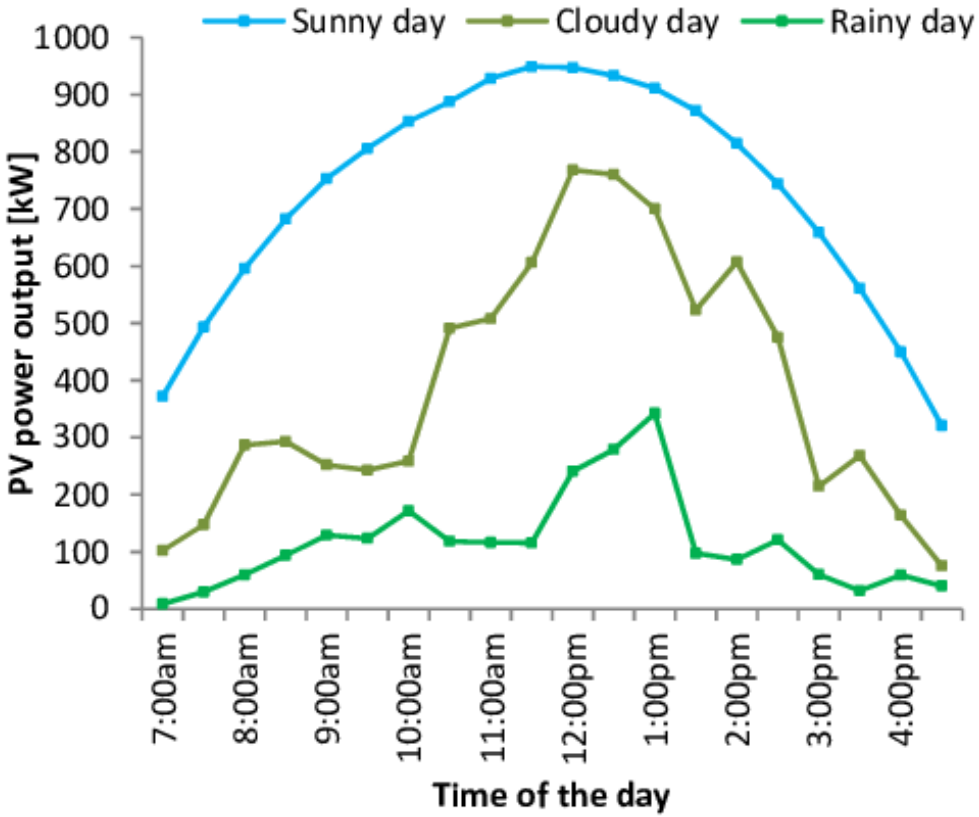
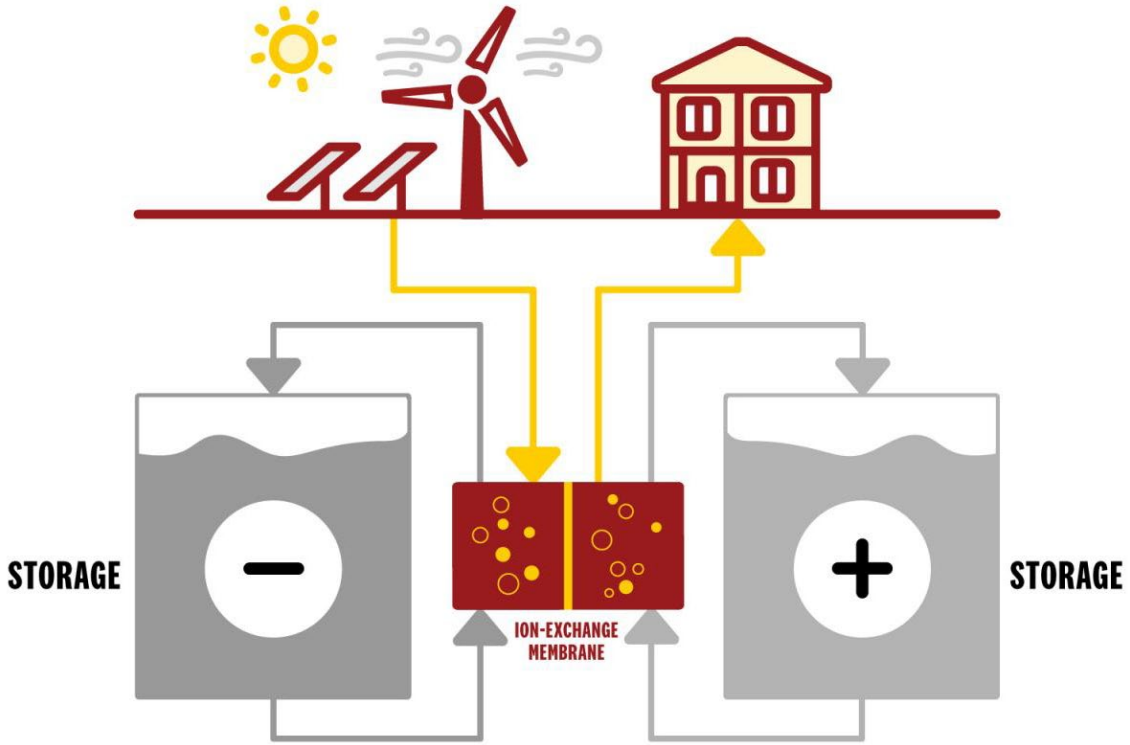
Background

The intermittent nature of renewable energy is a major issue.

Redox flow batteries (RFBs) offer this solution.





Yang B, Murali A, Nirmalchandar A, Jayathilake B, Prakash GKS, Narayanan SR. A Durable, Inexpensive and Scalable Redox Flow Battery Based on Iron Sulfate and Anthraquinone Disulfonic Acid. Journal of The Electrochemical Society. 2020;167(6):060520.
Rana M, Koprinska I, Agelidis VG, editors. Solar power forecasting using weather type clustering and ensembles of neural networks. 2016 International Joint Conference on Neural Networks (IJCNN); 2016 24-29 July 2016.

Redox Flow Battery

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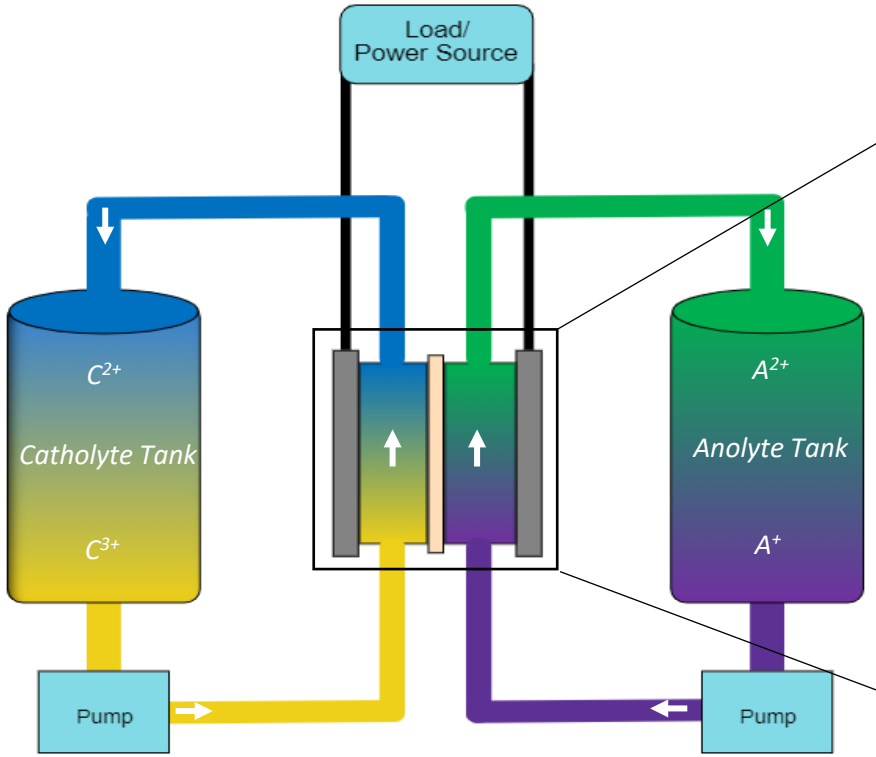

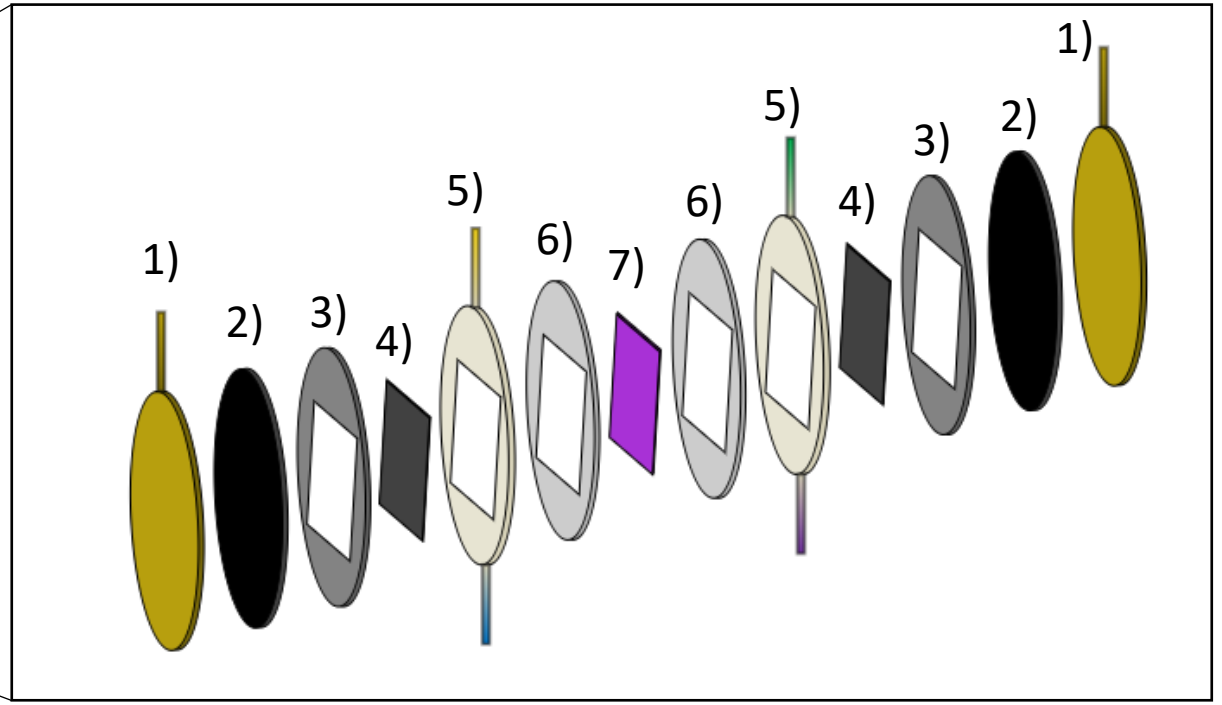

$$A^{2+} + C^{2+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} A^{+} + C^{3+}$$

1) Brass current collector 2) Graphite current collector
3) Electrode gasket 4) Electrode 5) Flow frame
6) Membrane Gasket 7) Ion exchange membrane

Redox Flow Battery

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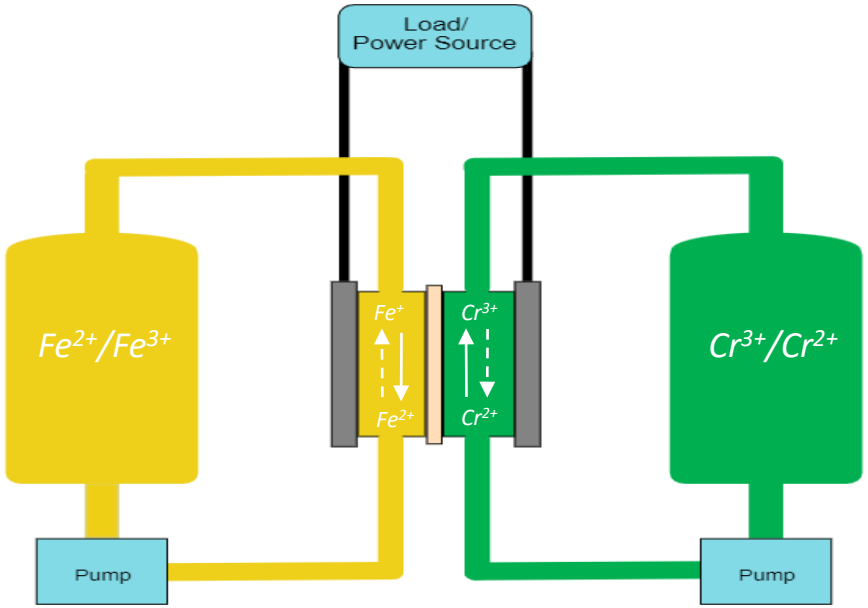
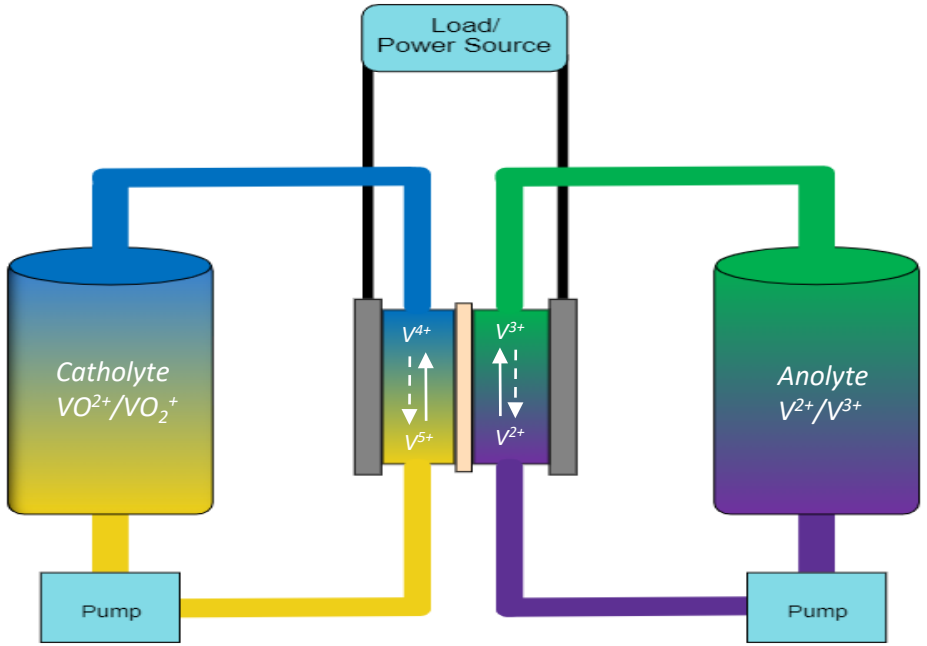
First modern RFB developed by NASA in the 1970's which utilised the Fe^{3+}/Fe^{2+} and Cr^{3+}/Cr^{2+}.



$$Fe^{2+} + Cr^{3+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Fe^{3+} + Cr^{2+}$$

It wasn't until 1986 when RFBs came to the forefront of large-scale energy storage through vanadium RFBs.



$$VO^{2+} + V^{3+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2^{+} + V^{2+}$$

Skyllas-Kazacos M, Rychcik M, Robins RG, Fane AG, Green MA. New All-Vanadium Redox Flow Cell. Journal of The Electrochemical Society. 1986;133(5):1057.

Vanadium Redox Flow Battery

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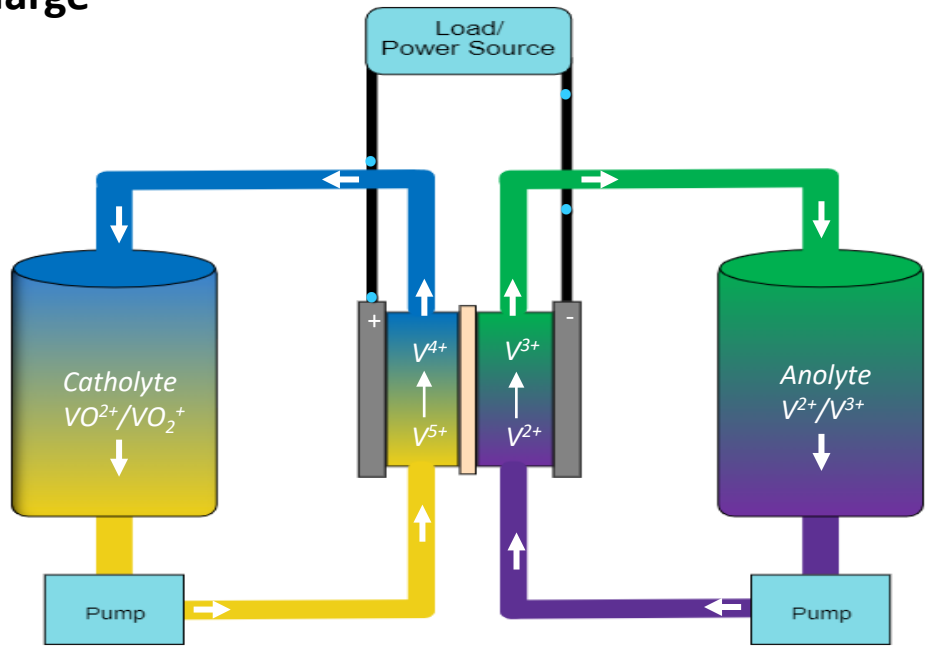
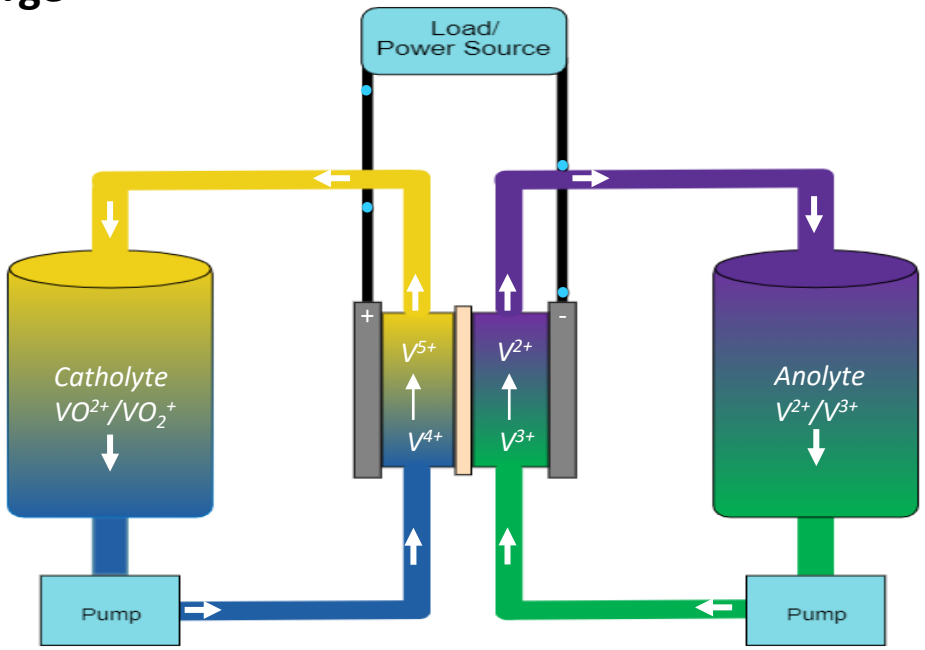
Discharge



Charge



Positive half-cell: $VO_2^+ + e^- + 2H^+ \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} VO^{2+} + H_2O$ $E^0 = 1.004$ V

Negative half-cell: $V^{2+} \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} V^{3+} + e^-$ $E^0 = -0.255$ V

Overall equation: $VO_2^+ + V^{2+} + 2H^+ \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} VO^{2+} + H_2O + V^{3+}$ $E^0 = 1.259$ V

Ruiyong C, Sangwon K, Zhenjun C. Redox Flow Batteries: Fundamentals and Applications. In: Mohammed Awad Ali K, editor. Redox. Rijeka: IntechOpen; 2017. p. Ch. 5.

Electrode The Process

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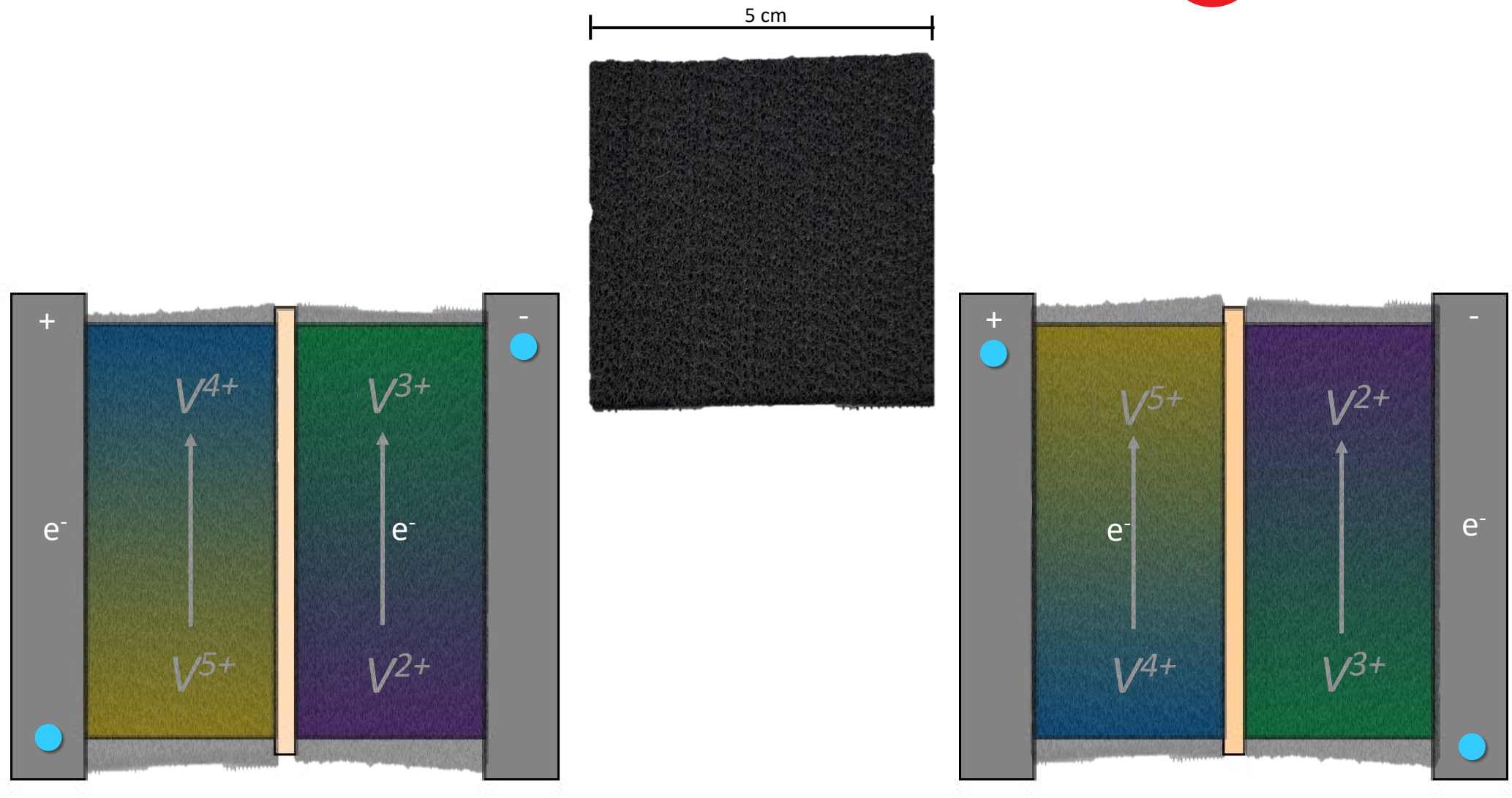
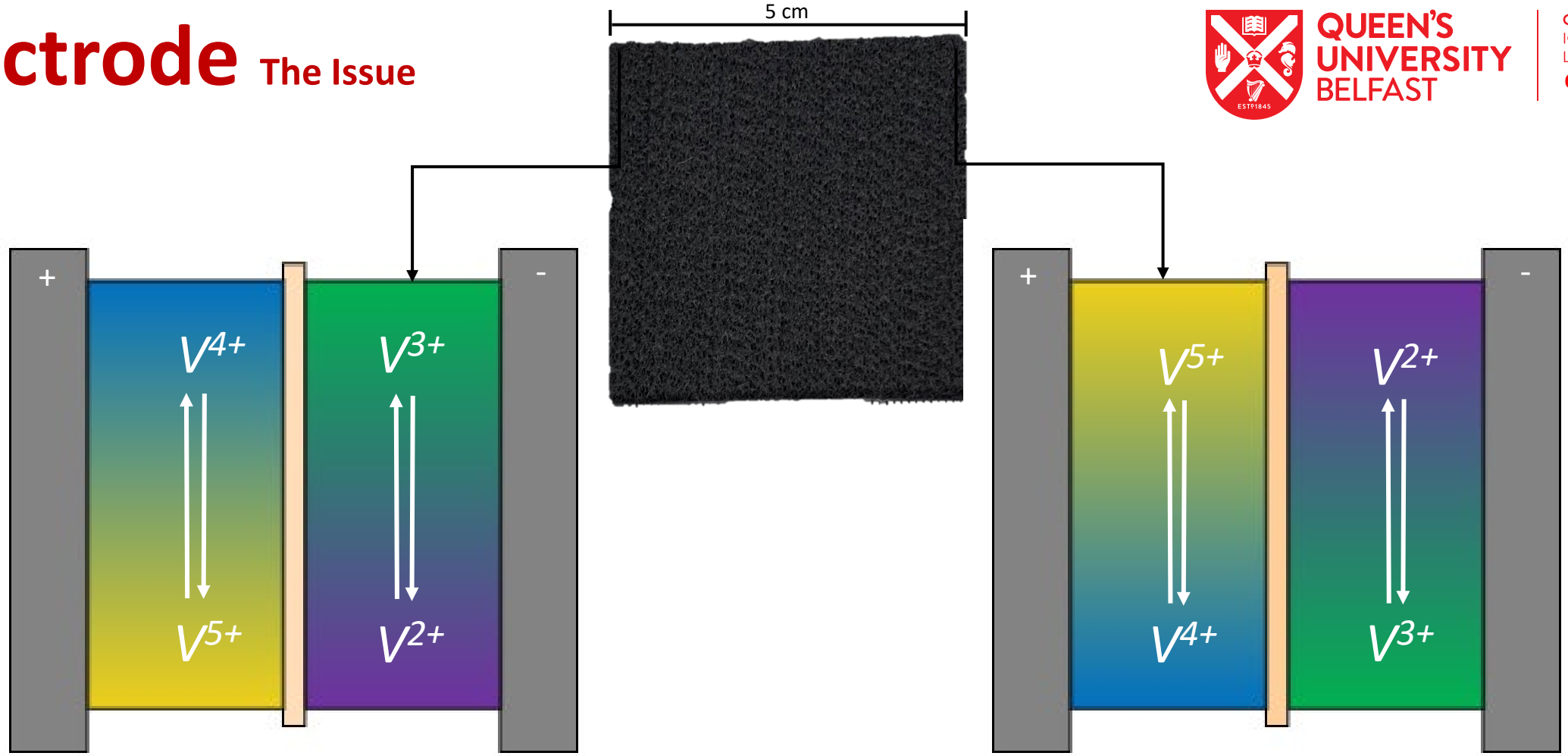


Electrode The Issue



The V^{2+}/V^{3+} and VO^{2+}/VO_2^{+} reactions on carbon felts suffer from:

- Poor electrochemical reversibility
- Slow kinetics

Aims and Objectives

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This project aims to:

- Improve the kinetics of electrolyte-electrode interaction.
- Using the novel approach of polyoxometalate-based catalysts.
- Subsequent work will focus on all-iron systems (FeRFB).
- Knowledge will be transferred from the vanadium system to the all-iron system.
- And potentially vice versa.

Electrode Treatment

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Intrinsic methods

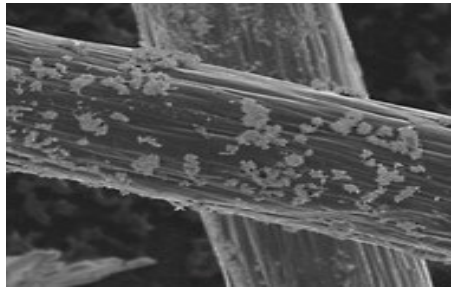
Heat

Plasma

Acid/Base

Metal-based catalysts

Metals: Sn, Bi, Ag



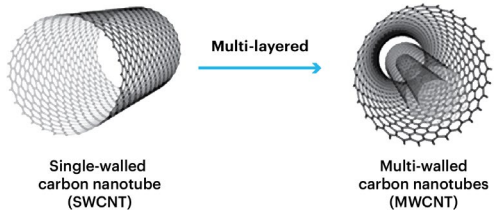
Metal oxides:
SnO_2, PbO_2, NiO

Carbon-based catalysts

Graphene

Composites

Carbon nanotubes



Carbon dots

Fullerene

Jiang Q, Ren Y, Yang Y, Wang L, Dai L, He Z. Recent advances in carbon-based electrocatalysts for vanadium redox flow battery: Mechanisms, properties, and perspectives. Composites Part B: Engineering. 2022;242:110094.
Marina Filchakova, Vladimir Saik Single-walled carbon nanotubes: structure, properties, applications, and health & safety, https://tuball.com/articles/single-walled-carbon-nanotubes
Lv Y, Han C, Zhu Y, Zhang T, Yao S, He Z, et al. Recent advances in metals and metal oxides as catalysts for vanadium redox flow battery: Properties, structures, and perspectives. Journal of Materials Science & Technology. 2021;75:96-109.
Pereira JFS, Rocha RG, Castro SVF, João AF, Borges PHS, Rocha DP, et al. Reactive oxygen plasma treatment of 3D-printed carbon electrodes towards high-performance electrochemical sensors. Sensors and Actuators B: Chemical. 2021;347:130651.

Polyoxometalates

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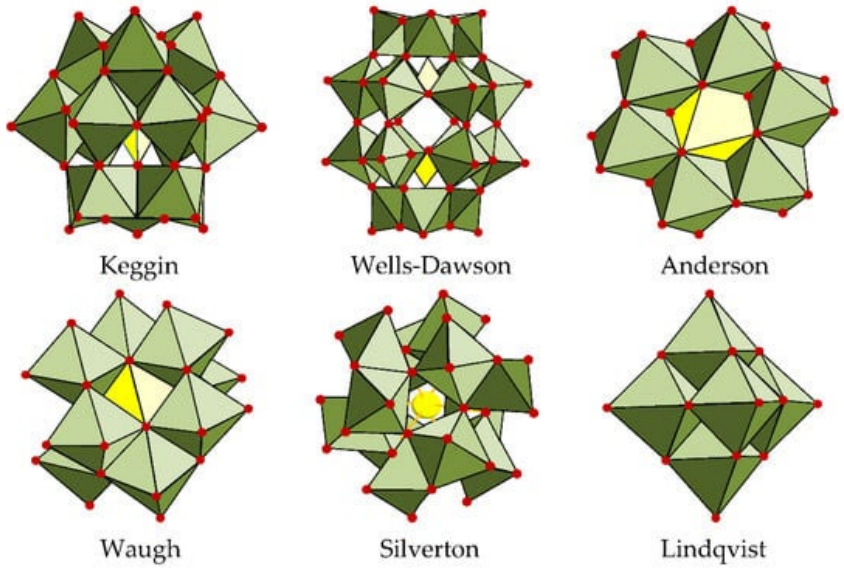
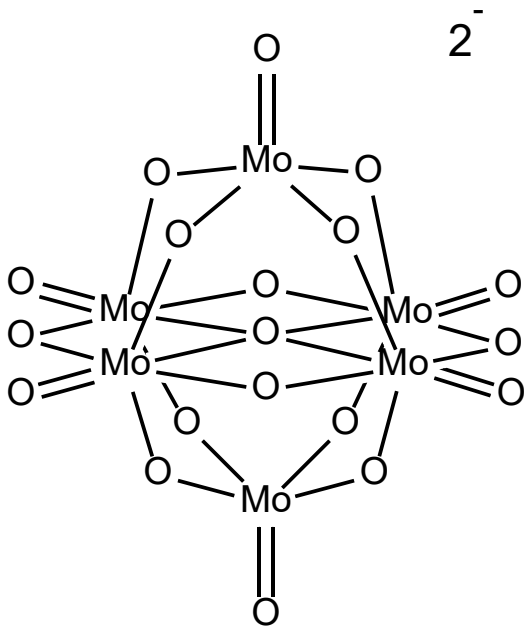


Current compound of interest is tetrabutylammonium hexamolybdate:

Hexamolybdate ion



$Mo_6O_{19}^{2-}$

These compounds contain many attractive features such as:

- High chemical stability.
- Unique redox characteristics.
- Chemical structure tunability.

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

Preliminary Results Synthesis of $(C_4H_9N_2)_2Mo_6O_{19}$

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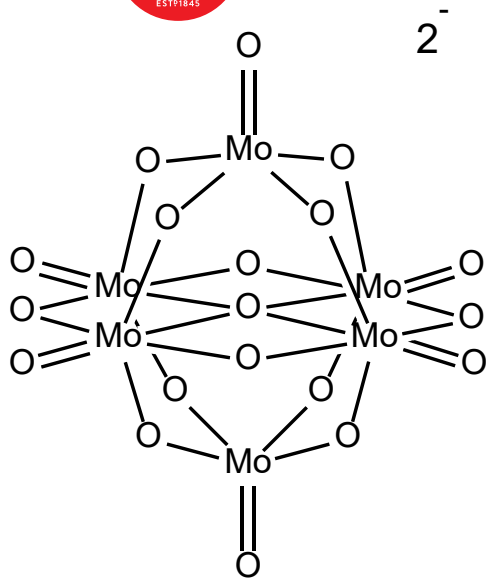

Na_2MoO_4 —(1. HCl, H_2O 2. TBABr, H_2O; Heat at 75°C, 45 min)→

←(Vacuum filter; Wash 3 x H_2O)—

—(Diss. C_3H_6O; Cool -20°C, 24 h)→

Klemperer WG. Tetrabutylammonium Isopolyoxometalates. Inorganic Syntheses. Inorganic Syntheses1990. p. 74-85.

Preliminary Results XRD

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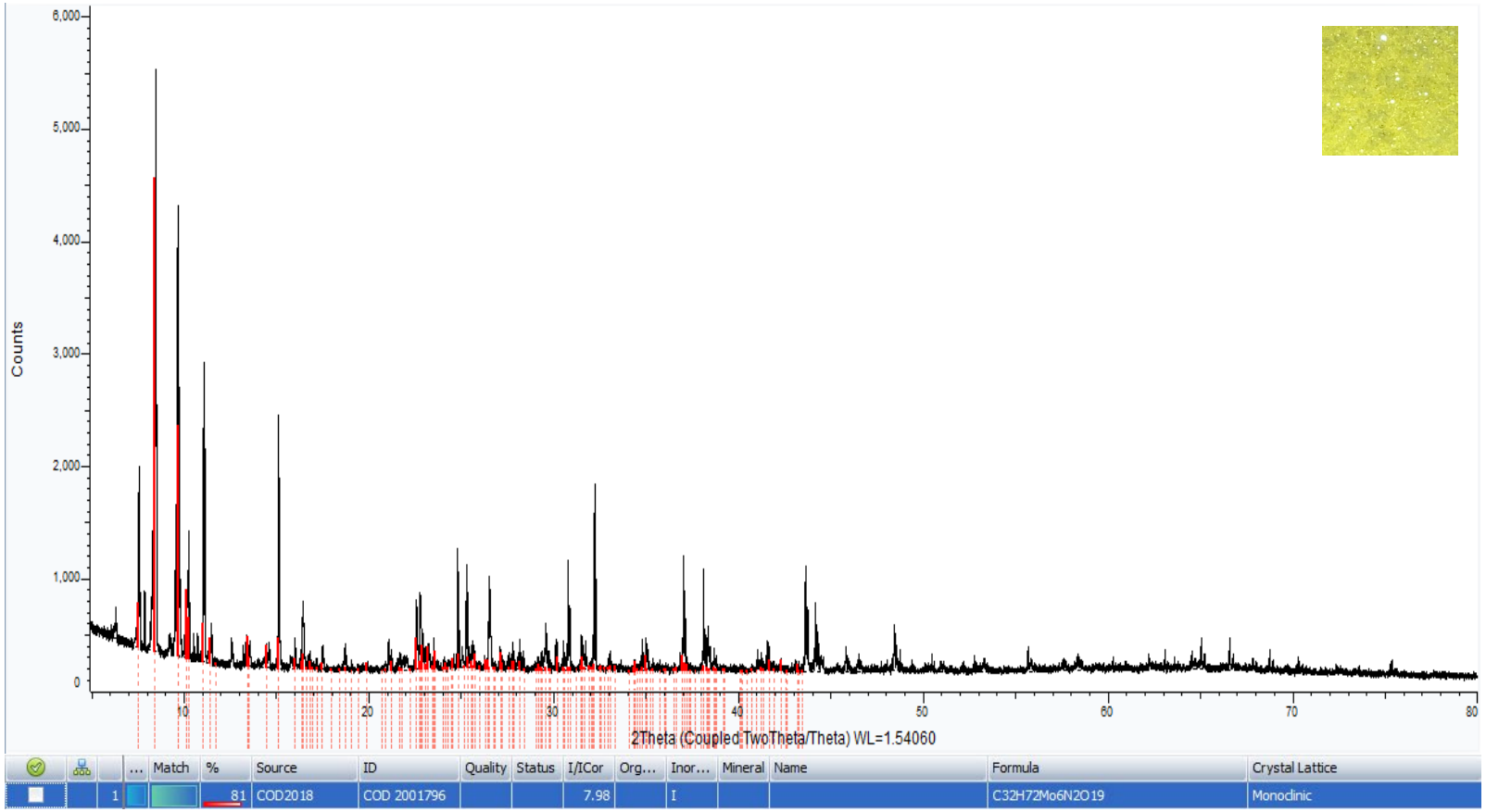
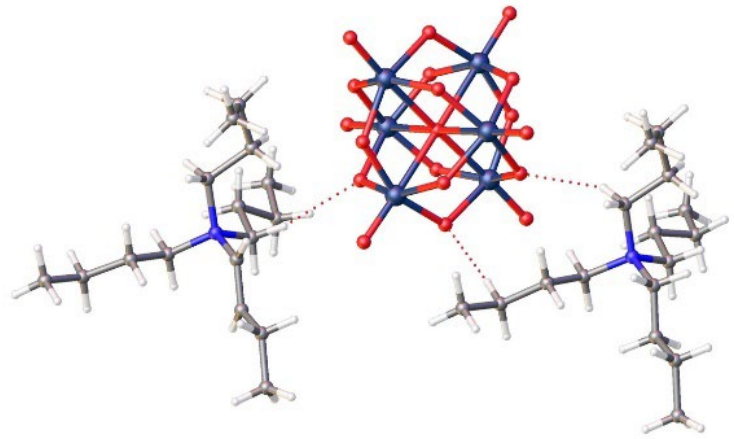


		Match	%	Source	ID	Quality	Status	I/ICor	Org...	Inor...	Mineral	Name	Formula	Crystal Lattice
1			81	COD2018	COD 2001796			7.98		I			C32H72Mo6N2O19	Monoclinic



- Single crystal XRD showing 6 MoO_6 octahedra.
- Each polyanion hydrogen bonded to two counter cations.
- Exhibits Lindqvist arrangement.
- PXRD diffraction pattern detailing formula present and crystal lattice structure.

Preliminary Results FTIR

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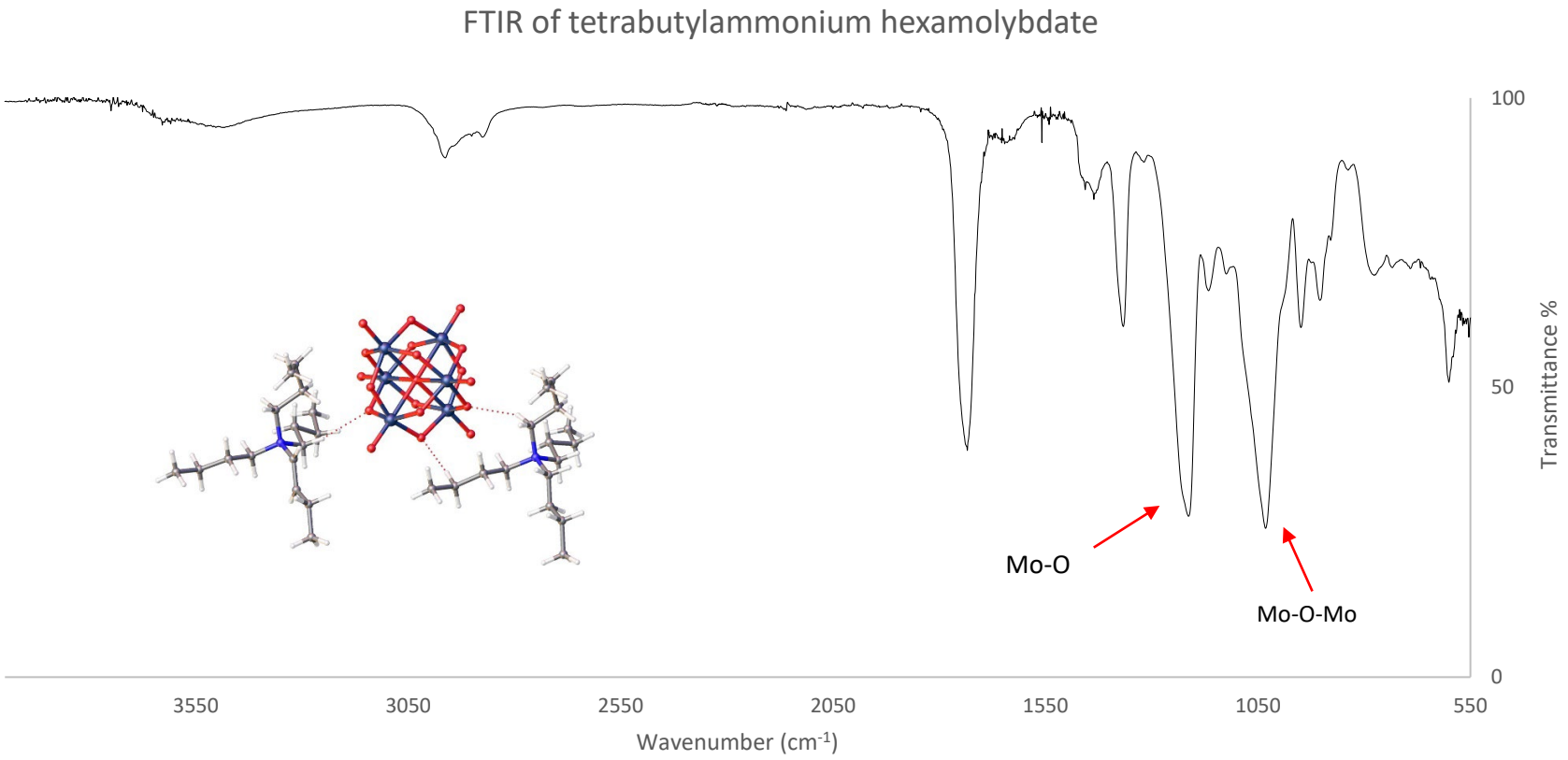

- FTIR spectrum for synthesised crystals.
- Two strong sharp stretches in the M-O range (M=Metal).
- Characteristic of bonds present in $[Mo_6O_{19}]^{2-}$.

Preliminary Results SEM

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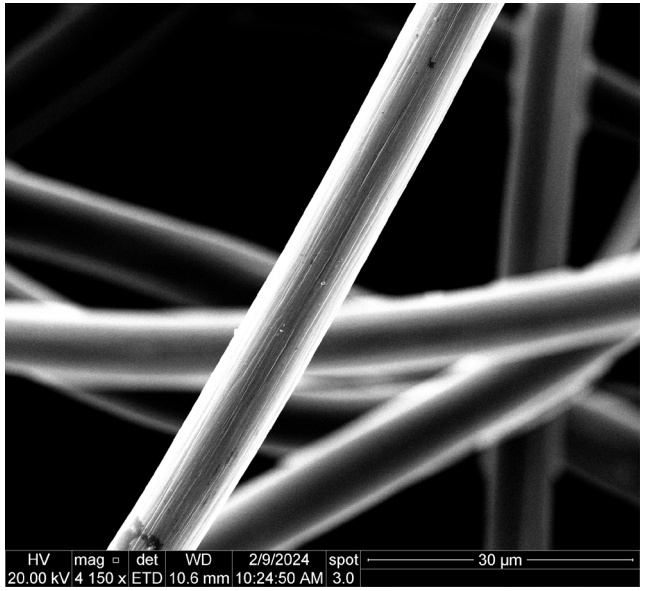
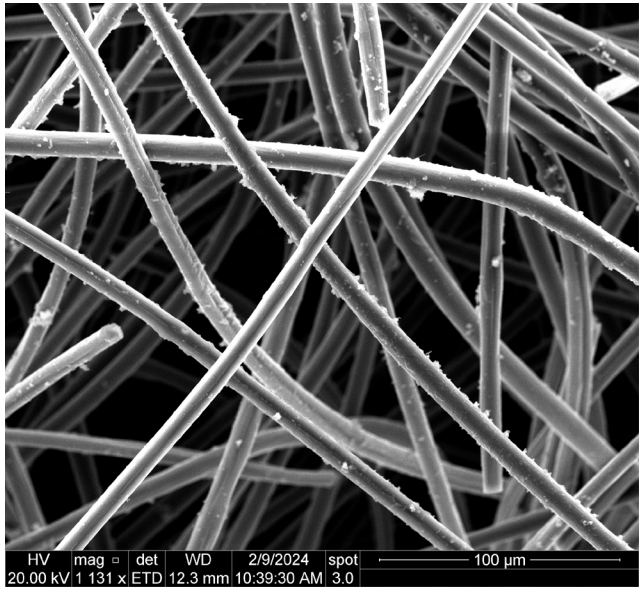
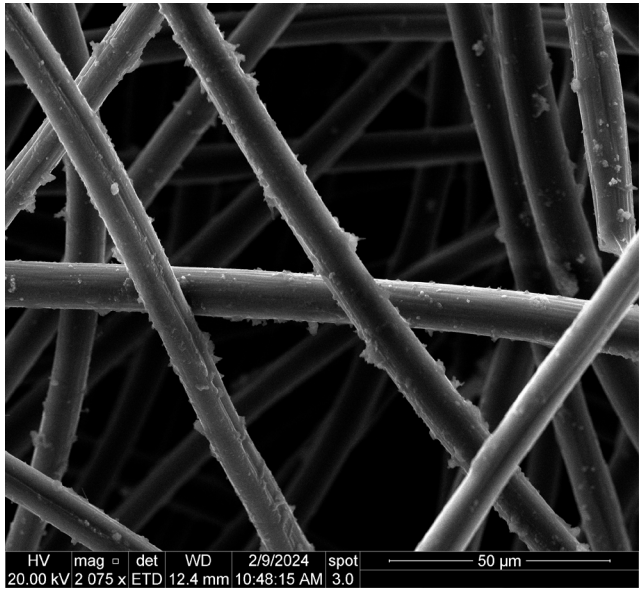
Pristine

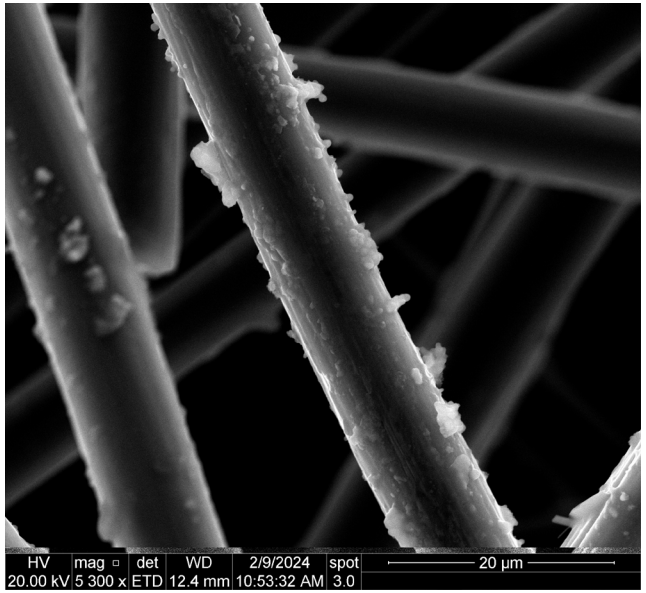
Immersed in $Mo_6O_{19}^{2-}$ solution

Heated at 200°C for 18h in stainless steel autoclave









- Deposition was successfully achieved.
- Random arrangement of particles observed.

Future Work

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Short Term Plan

- Investigate treated electrode electrochemically using CV and EIS.
- Construct a battery using treated electrode to test battery performance through charge-discharge analysis.

Long Term Plan

- Improve VRFB performance through electrode treatment.
- Turn attention to FeRFB.
- Improve FeRFB performance.

Acknowledgements

Peter N, Oana, Paul, Yoan, Peter K, Josh, Hugh and the rest of the team at QUILL.

Thank you for listening

Any questions?