Synthesis and Characterization of Polyoxometalates For Energy Storage Applications

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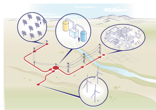
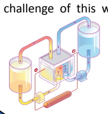
Introduction

Global energy consumption is projected to increase significantly by mid-century, and this increased need will be partially met, at least in part, through use of renewable energy sources. Due to the intermittent nature of these resources, large-scale energy storage sources must likewise be invented, developed, and deployed in this timeframe in order for these carbon neutral technologies to be fully utilized and to aid in controlling CO_2 emissions. The need for grid storage is also being driven by the evolving nature of the grid (smart grid, green grid, and the distributed nature of the grid) as well as by other technological developments, such as vehicle electrification.



Flow Batteries

Concentrating on promising flow battery technologies, we are working specifically to create new cathode and anode solutions to increase energy density. Flow batteries are rechargeable systems where the storage medium (electrolyte and dissolved charge storage species) flows through an electrochemical cell that converts chemical energy into electricity. The primary challenge of this work is to produce a new dissolved charge storage species that will yield a higher energy density than the current vanadium- and zinc-bromine-based flow battery systems without an increase in cost or toxicity.



Polyoxometalates

We investigated a series of polyoxometalates (POMs), as a new dissolved charge storage material. POMs are nanometer-size analogues of metal-oxide lattice with an array of attractive attributes including solubility in non-aqueous solvents, which is of interest for new battery materials.

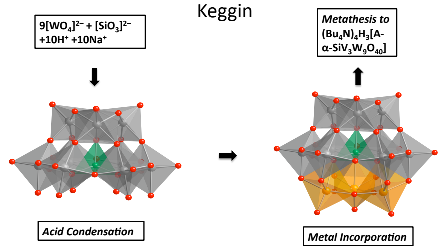
POMs

- Highly alterable sizes, shapes, and charge densities
- Stable in a wide range of battery electrolytes
- Ability to undergo simultaneous multi-electron reactions

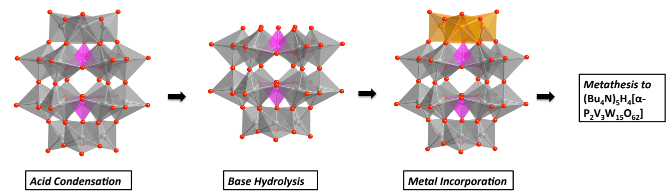
Non-Aqueous Systems

- Wider voltage window
- Higher charge cycle efficiency
- Decreased temperature sensitivity
- Increased cycle life
- Favorable cost projections

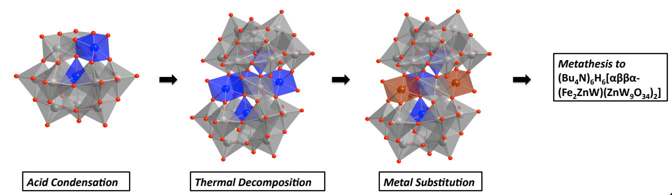
Keggin



Wells-Dawson

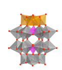


Fe-Zn Sandwich

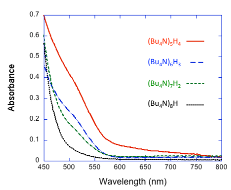


UV-vis

Wells Dawson



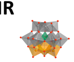
Synthesis of the various protonation states of the Wells Dawson POM can be monitored with UV-vis spectroscopy.



Various protonation states of Wells Dawson POM
10 mM Wells Dawson
5 mL 0.1 M $Li(OTf)_2$ in propylene carbonate

NMR

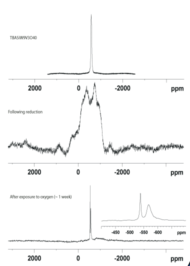
Keggin



^{51}V NMR was used to monitor stability of the compound before and after charge/discharge cycling. Pre-discharge NMR displays one V peak for three symmetry/ equivalent V atoms.

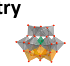
Significant peak broadening is displayed due to paramagnetic centers

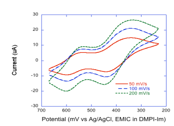
Two peaks observed after re-oxidation due to cap rotation with no impact on cell performance



Electrochemistry

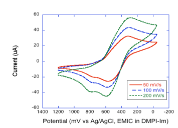
Keggin





K_6H[A-α-$SiV_3W_9O_{40}$]•$3H_2O$

10 mM Keggin
5 mL 0.1 M H_2SO_4 solution



$(Bu_4N)_4H_3$[A-α-$SiV_3W_9O_{40}$]

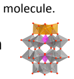
10 mM Keggin
5 mL 0.1 M $Li(OTf)_2$ in propylene carbonate

Cyclic voltammetry (CV) of the water soluble Keggin displays 2 redox pairs. The first redox pair is reversible (59 mV) with the second redox pair being quasi-reversible (~100 mV).

CV of the organic soluble Keggin displays some noticeable differences from the aqueous Keggin. The 2 reduction peaks have merged into a single peak. Also the oxidation peaks have shifted.

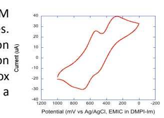
Upon undergoing controlled potential electrolysis at -50 mV, we calculate that each Keggin releases two electrons per molecule.

Wells Dawson



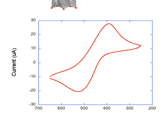
Synthesis of the Wells Dawson POM allows for a variety of protonation states. There are two distinct CV results based on protonation state. At the higher protonation state (four protons), we observe 2 redox pairs. After partial deprotonation, only a single redox pair occurs.

CV of the fully metathesized Wells Dawson POM in a solution of propylene carbonate and $Li(OTf)_2$ displays not only the redox pair associated with the vanadium atoms, but also the tungsten electrochemistry. Controlled potential electrolysis at 0 mV, reveals that each molecule releases one electron per molecule.



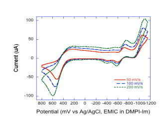
$(Bu_4N)_5H_4$[α-$P_2V_3W_{15}O_{62}$]

10 mM Wells Dawson
5 mL 0.1 M $Li(OTf)_2$ in propylene carbonate



$(Bu_4N)_7H_2$[α-$P_2V_3W_{15}O_{62}$]

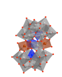
10 mM Wells Dawson
5 mL 0.1 M $Li(OTf)_2$ in propylene carbonate

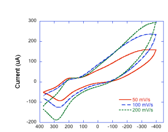


$(Bu_4N)_9$[α-$P_2V_3W_{15}O_{62}$]

10 mM Wells Dawson
5 mL 0.1 M $Li(OTf)_2$ in propylene carbonate

Fe-Zn Sandwich





40 mM Sandwich
5 mL 0.1 M $(Bu_4N)Cl$ in acetonitrile

CV of the sandwich was unobtainable in a $Li(OTf)_2$ and propylene carbonate solution. A $(Bu_4N)Cl$ and acetonitrile solution was required to obtain CV of the compound. Due to the lower currents of the redox pair, the concentration had to be increased to 40 mM. Based on the CV, controlled potential electrolysis was performed at 150 mV, resulting in the release of less than one electron per molecule.

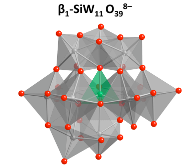
Conclusions

We have synthesized a family of organic soluble POMs and discovered a new flow battery cathode material with the Keggin POM. This two electron species offers the potential for higher energy density, lower cost, and lower toxicity over existing technology.

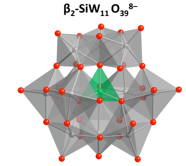
Future Work

A variety of Keggin isomers exists that allow us to investigate how both location and number of vanadium atoms can affect the electrochemistry of the Keggin POM, the compound displaying the best performance to date.

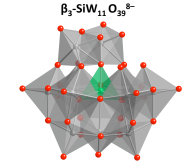
$β_1$-$SiW_{11}O_{39}^{8-}$



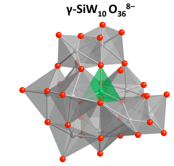
$β_2$-$SiW_{11}O_{39}^{8-}$



$β_3$-$SiW_{11}O_{39}^{8-}$



γ-$SiW_{10}O_{36}^{8-}$



Acknowledgements

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