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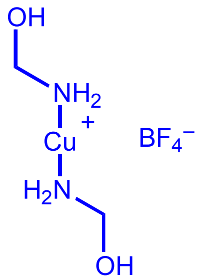

Polyoxometalate “Solutions” for Redox Flow Batteries

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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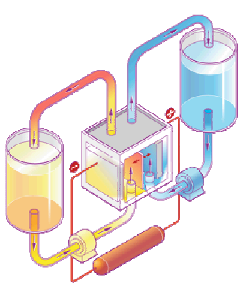
RFB Project Goals and Approach

Problem: Getting higher concentrations of redox active species as a vehicle for lowering cost and improving performance.

Approach: New multi-valent anode/cathode materials by judicious selection of ligands and anions for lower viscosity AND new SNL rapid prototyping with 3-D printing to quickly evaluate membranes, solutions, and cell designs.

Target Metrics

- 59 mV/n separation (n > 1)
- Viscosity < 500 cP
- Conductivity > 0.5 mS cm^{-1}
- Open Circuit Potential > 1.5 V

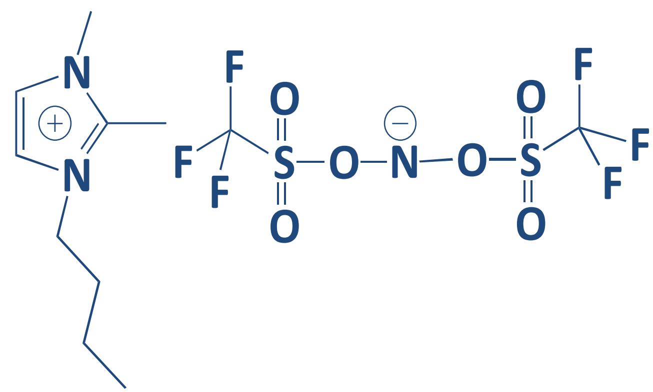


Aqueous versus non-aqueous, including ionic liquids

$$\text{Energy Density}_{RFB} \approx \tfrac{1}{2} n F V_{cell} c_{active}$$

$$ED_{AQ} = \tfrac{1}{2}\,\mathbf{1}\,F\,\mathbf{1.5}_{cell}\,\mathbf{2}_{active} = 1.5F$$

$$ED_{IL} = \tfrac{1}{2}\,\mathbf{2}\,F\,\mathbf{2}_{cell}\,\mathbf{3}_{active} = 6.0F$$

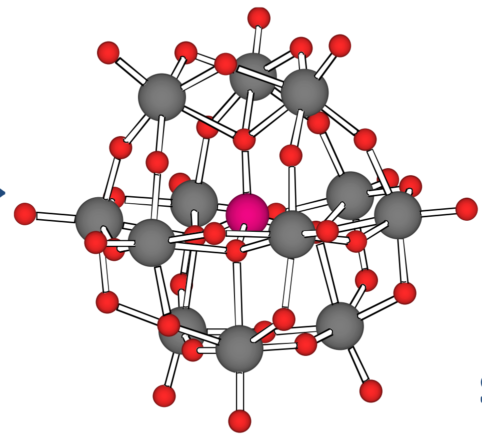


Polyoxometalates (POMs)

–Early transition metal-oxide clusters with diverse fundamental and applied interests

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Undergo multi-electron redox processes

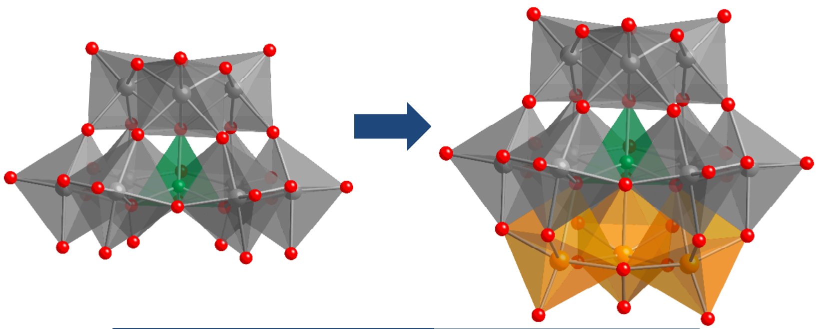
$12\ WO_4^{2-} + HPO_4^{2-} + 23\ H^+ \rightarrow$  $+ 12\ H_2O$

Keggin structure

$[PW_{12}O_{40}]^{3-}$

POMs are commonly formed by **acid condensation** reactions.

A-α-$K_6HSiV_3W_9O_{40}$



Metal Incorporation

Compound was synthesized in **high yield and high purity** using literature methods.

Fully Charged

$SiV^{V}_{3}W^{VI}_{9}O_{40}^{7-}$/

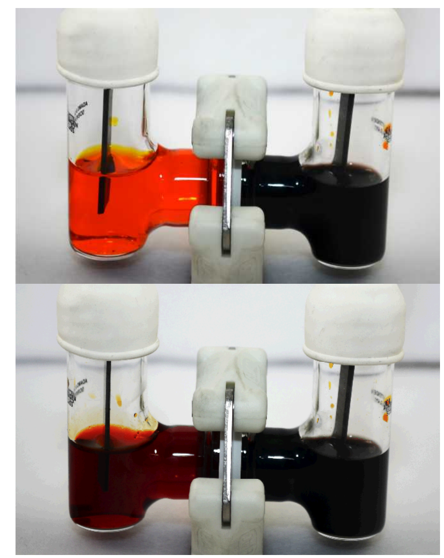
$SiV^{IV}_{3}W^{V}_{3}W^{VI}_{6}O_{40}^{13-}$

↓ 0.5 M H_2SO_4

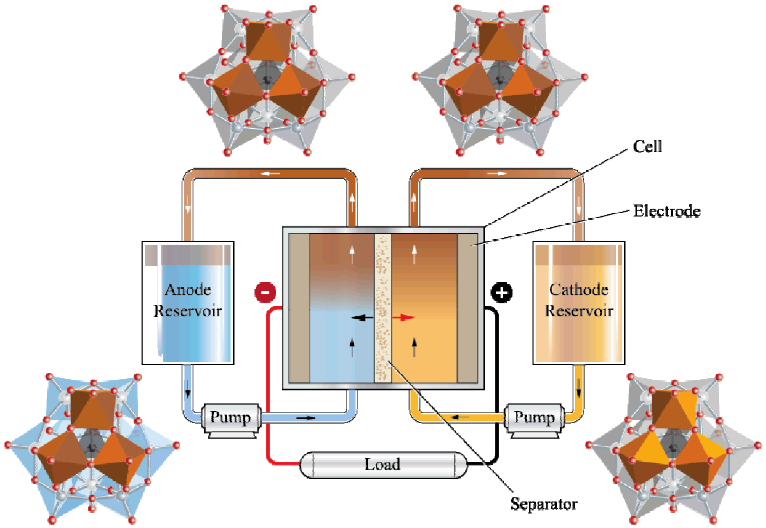
Fully Discharged

$SiV^{IV}_{3}W^{VI}_{9}O_{40}^{10-}$/

$SiV^{IV}_{3}W^{VI}_{9}O_{40}^{10-}$



Flow Cell Studies



Testing was performed in a cell with serpentine flow field, carbon felt electrodes, and a Nafion 117 membrane.

Electrochemical yield, observed capacity/theoretical, decreased from 90% to 80% after 100 cycles.

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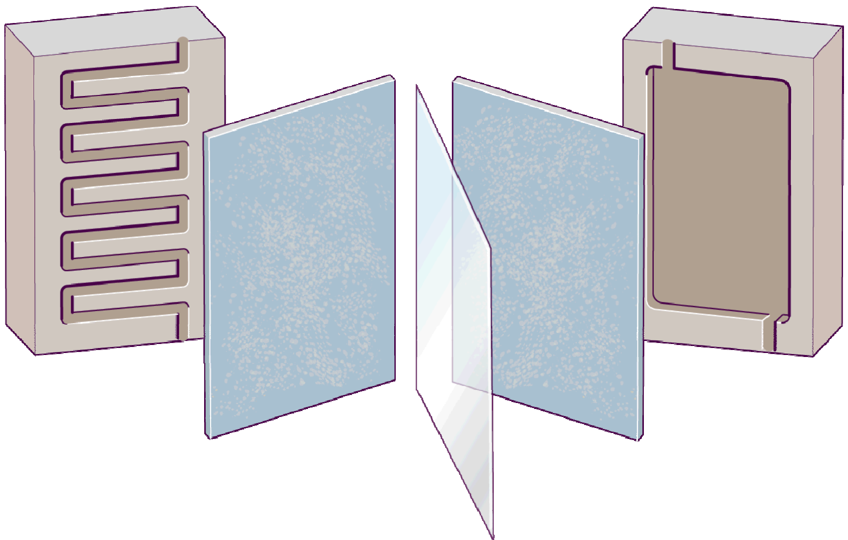
Cell Variations



Serpentine *versus* Well

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The non-aqueous analog had a cycling rate and electrochemical yield that were 65% and 15%, respectively, lower than the aqueous analogue. Reduced performance by a protonated analogue highlights the importance of the alkali cation.

POM Variations

– Iterations on A-α-$K_6HSiV_3W_9O_{40}$ were performed in order to determine what features lead to improved performance.

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A-α-$SiV_3W_9O_{40}^{7-}$

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A-α-$PV_3W_9O_{40}^{6-}$

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B-α-$PV_3W_9O_{40}^{6-}$

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α-$P_2V_3W_{15}O_{62}^{9-}$

Infrared Spectra

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^{31}P NMR Spectra

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– To achieve high yield and purity of the B-α-$PV_3W_9O_{40}^{6-}$, modifications to the synthesis were made. Specifically, the pH was increased from 1 to 5, and the compound was refluxed for 12 h.

Pratt and Anderson, *Dalton Trans.*, **2013**, 15650.

$PV_3W_9O_{40}^{9-}$ Studies

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A-isomer

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B-isomer

– The B-isomer displays less reversible vanadium chemistry and higher capacity fading than its A analogue.

Fully Charged		Fully Discharged
$PV^{V}_3W^{VI}_9O_{40}^{6-}$/ $PV^{IV}_3W^{V}_3W^{VI}_6O_{40}^{12-}$	→	$PV^{IV}_3W^{VI}_9O_{40}^{9-}$/ $PV^{IV}_3W^{VI}_9O_{40}^{9-}$

Overall Comparisons

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- ← **Wells-Dawson is a 1 e^- process**
- ← **Si-isomer is more efficient than P, reflects binding to $V_3W_9O_{40}^{3-}$ shell**
- ← **A-isomer is more efficient than B, corner *versus* edge sharing V**

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Both A-isomers show stable yields over cycling →

The B-isomer shows diminished yields over cycling →

POM Stability

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Infrared data of the A-α-$K_6HSiV_3W_9O_{40}$ indicate that the compound is stable over cycling and is consistent with NMR.

^{31}P data indicates compounds are relatively stable, cell dissection indicates that capacity fading is likely due to compound precipitation.

Summary/Conclusions

- POMs offer a new multivalent approach to RFBs.
- Silicon-centered and Keggin-based clusters appear to be the most promising, provided solubilities can be increased.
- Exchange of potassium for lithium can potentially lead to concentrations competitive with VRBs.
- Smaller molecular weight POMs also offer potential new routes to higher concentrations.

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