POMs for Fuel Cell Catalysis:
Synthesis & Characterization

IDMinNYC Integrated Design of Materials in NYC

CREST IDEALS

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IMD Research Group

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Background and Introduction

What are Fuel Cells?

Electrochemical cells that convert chemical energy into electrical energy via redox reactions.

- Cost effective
- Secure and sustainable
- Reduce atmospheric pollution and fossil fuel dependence.

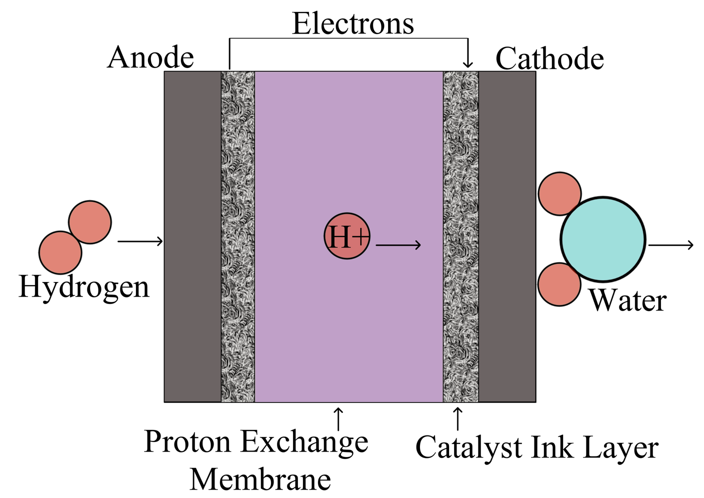


Figure 1. Schematic of a Fuel Cell

The Problems with the current Fuel cells:

- Use hydrogen gas as a fuel and this still a non-renewable resource
- Use a platinum (Pt) as a catalyst to facilitate the splitting of hydrogen to create the protons. This is expensive

AIM OF THIS WORK:
Use water as a proton source and explore the use of Co and Nb based POM complexes as potential catalysts for the splitting of water

What are polyoxometalates (POMs)?

Anionic polyatomic molecule comprised of XO_4 and MO_6 building blocks.

- "M": Principal metal, typically a transition metal from group 5 (V, Nb) or group 6 (Mo, W) in their highest oxidation state.
- "X": Heteroatom, most p and d block elements
- Environmentally friendly, reusable, versatile, tunable.
- Suitable for different application based on their structure & geometrical properties. Known to catalyze numerous chemical reactions

Ball & Stick Model **Polyhedral Model**

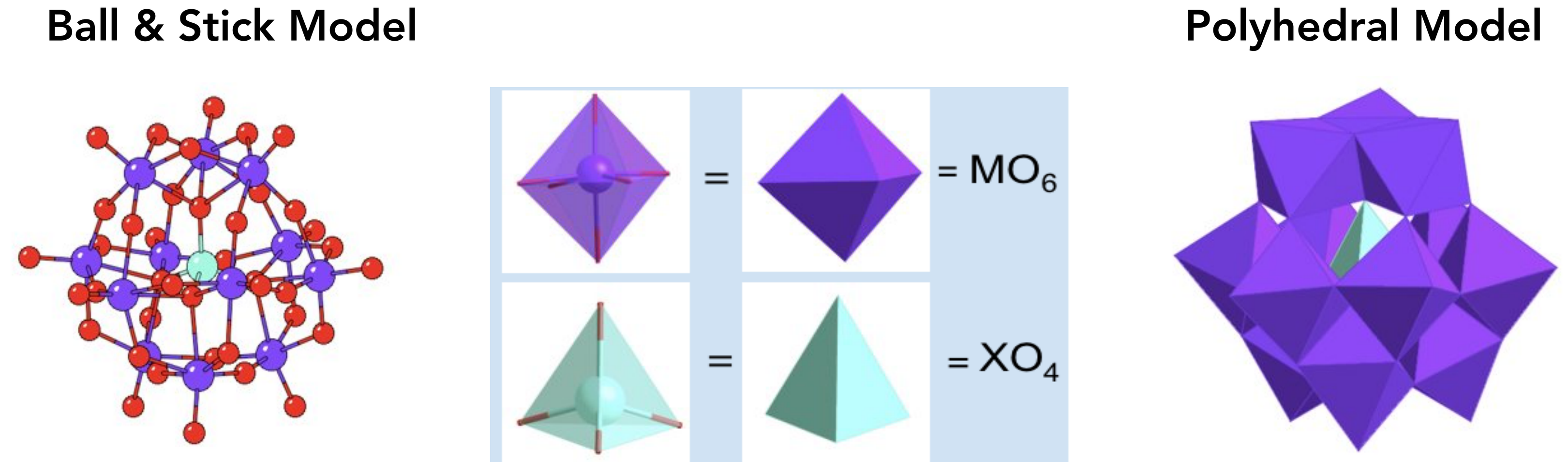
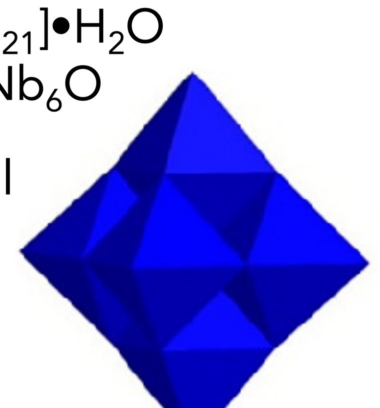


Figure 2. PW_{12} Keggin in the ball and stick and polyhedral representations

POMS of Interest to this work

Lindqvist:
$[M_6O_{19}]$, M= Nb
$KNa_2[Nb_{24}O_{72}H_{21}]\bullet H_2O$
Precursor: K_7HNb_6O

Nb is a principal metal in this structure



Finke:
$[M_4(H_2O)_2(W_9O_{34})_2]^{n-}]$
M=W
$Na_{10}Co_4(H_2O)_2(PW_9O_{34})_2$

Sandwich structure with 4 Co ions between two PW_9 units

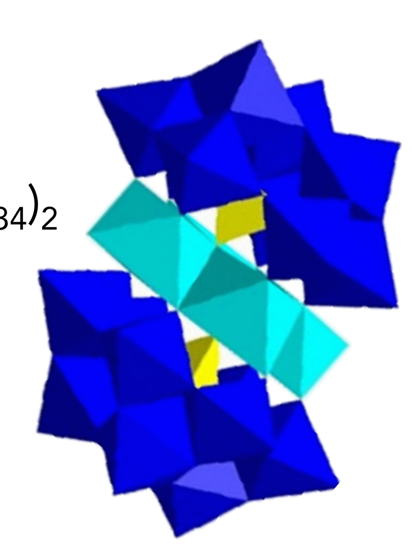


Figure 3. Polyhedral representations of Lindqvist (left) and Finke (right) POMS

Co_4PW_9 Synthesis and Characterization

$$Co(NO_3)_2\bullet 6H_2O + Na_2HPO_4\bullet 7H_2O + Na_2WO_4\bullet 2H_2O \xrightarrow[\text{2hr Reflux @100°C}]{\text{NaOH (pH = 7)}} Na_{10}Co_4(H_2O)_2(PW_9O_{34})$$

Figure 4. Starting materials for the Co_4PW_9 POM synthesis. Cobalt(II) nitrate hexahydrate (left), sodium phosphate dibasic heptahydrate (middle) and sodium tungstate dihydrate (right).

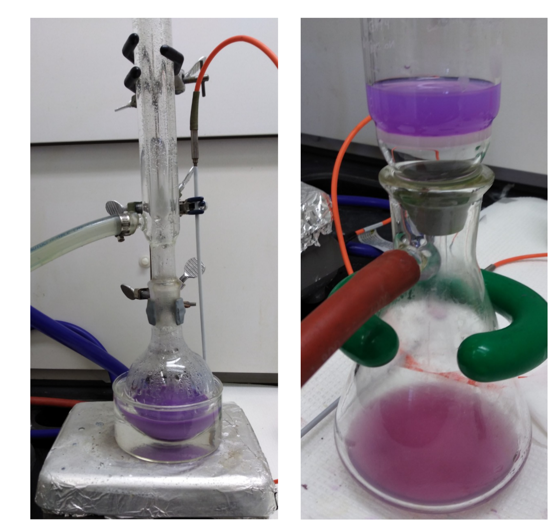
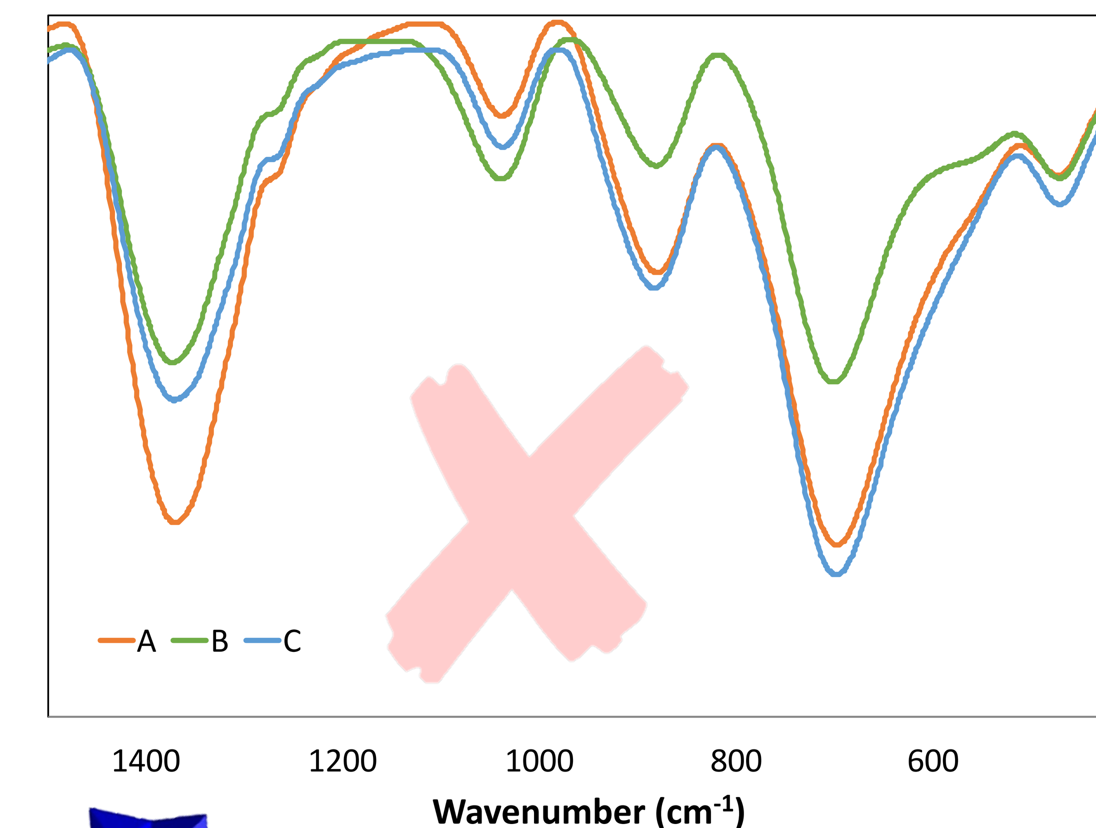


Figure 5. Reflux. Cool to room temp. Saturate with KCl and filter to obtain purple powder and filtrate



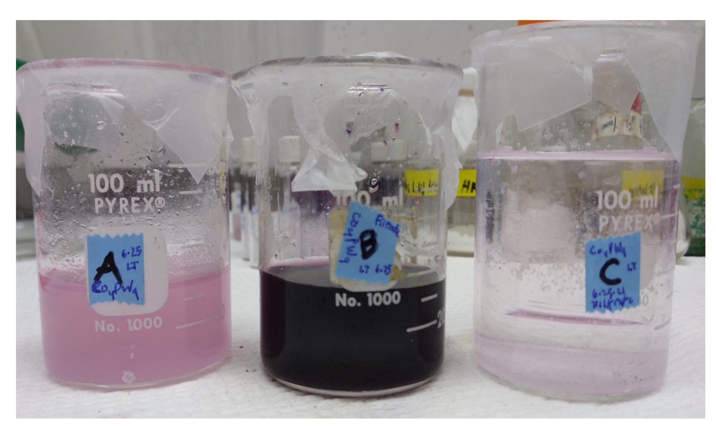


Figure 6. Attempts to drive the synthesis to completion.
Addition of PO_4 (A)
Addition of Co (B)
Addition of W (C)

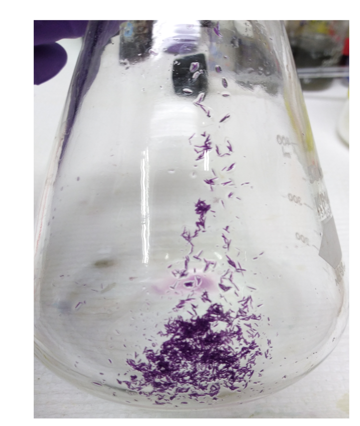
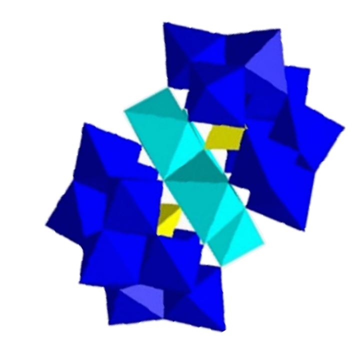


Figure 7. Allow the filtrate to evaporate slowly to obtain crystals. These may be PURE!



Expected FTIR, 4 Signals
P-O stretch: 1037 cm^{-1},
Terminal W-O stretch: 934 cm^{-1},
W-O-W bend: 882 cm^{-1}, 767 cm^{-1}

Precursor for $K_7Na_{21}[H_{21}Nb_{24}O_{72}]\bullet H_2O$(Polyoxoniobate) Synthesis and Characterization

$$6KOH(molten) + Nb_2O_5 \rightarrow 2K_3NbO_4 + 3H_2O \rightarrow HK_7Nb_6O_{19}$$

Figure 8. Starting materials for the Nb_6O_{19} POM synthesis. Molten potassium hydroxide (left) and niobium(V) oxide (right)

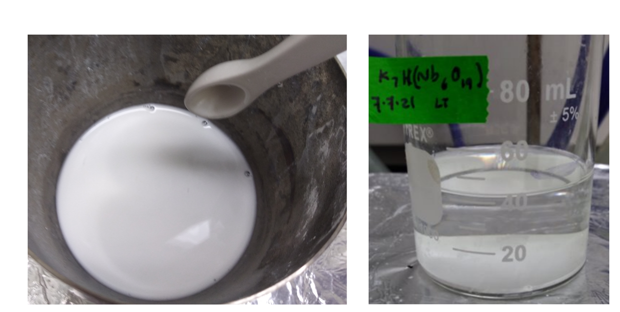
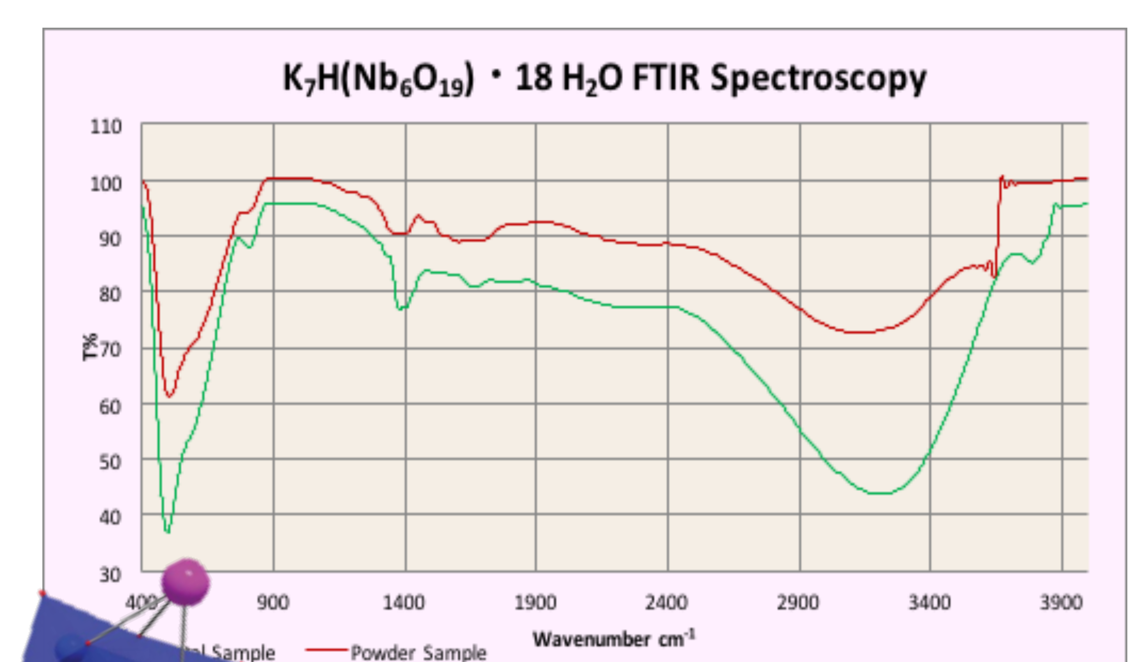
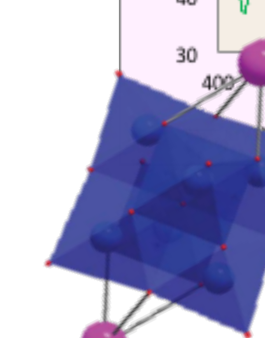


Figure 9. Heat KOH + Nb_2O5 mixture to reduce filtrate volume to ½ (left) Cool down & refrigerate for 8 Hrs in parafilm sealed beaker (right)

Figure 10. Colorless translucent crystals of product





Expected FTIR, 4 Signals
Nb Terminal O vibration: 856 cm-
Nb-O stretches: 704 cm^{-1}, 530 cm^{-1}, 422 cm^{-1}

Future plans, what's next?

- Synthesis adjustments for Finke type POM
- Synthesize a Lindqvist type POM: $KNa_2[Nb_{24}O_{72}H_{21}]\bullet H_2O$
- FTIR y & NMR Characterizations
- Test the POMS utility for the Splitting of water

Acknowledgments

Dr. Donna McGregor, Rachel Greenberg,
IDEALS: HRD-1547830
IDMinNYC: DMR-1950573