Synthesis and characterization of a layered Fe(III)/Mn(III) sulfate material: Applications for lithium-ion battery cathodes and OER catalysis

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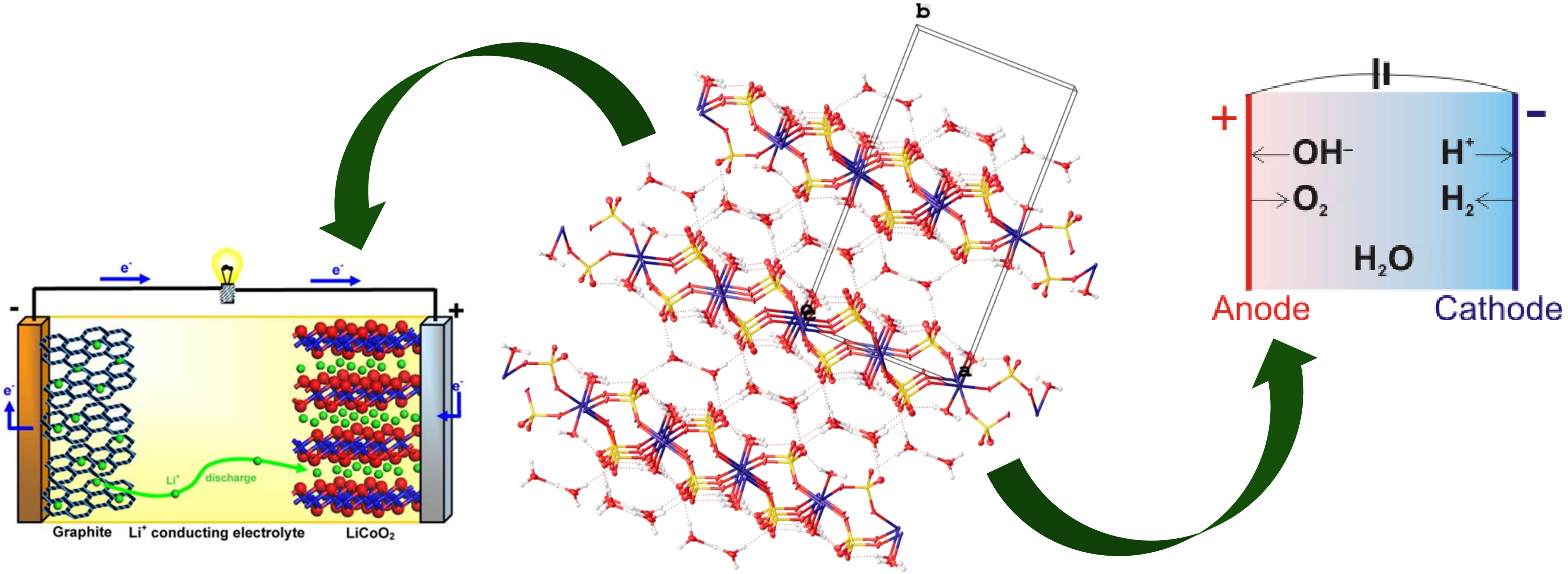
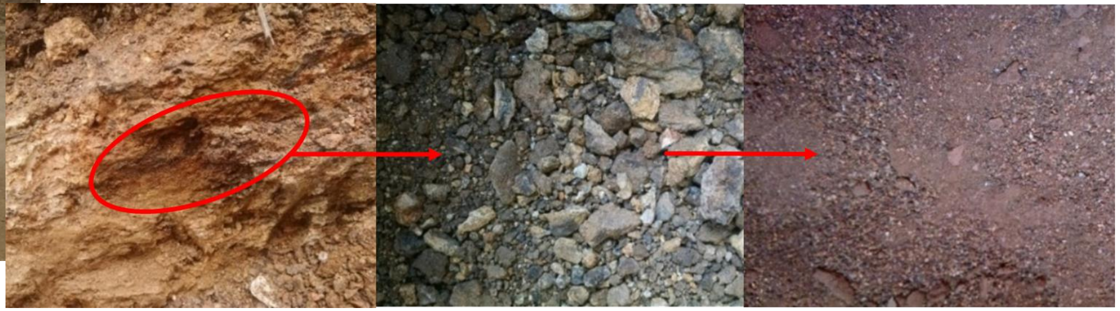


Motivation



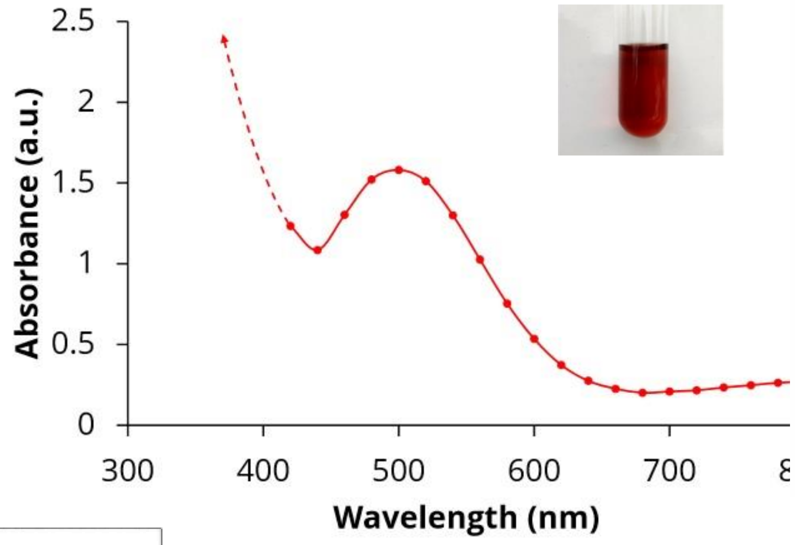
As [H_2SO_4] increases

Gradually turns purple

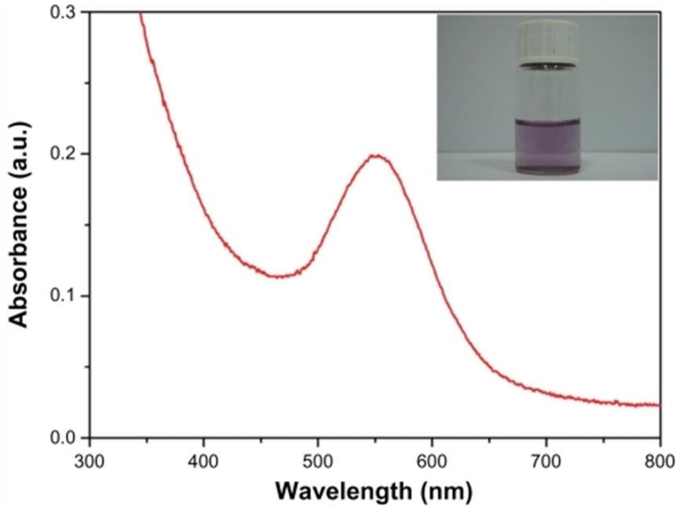
+ 5M H_2SO_4

Initial Hypothesis

Unknown material

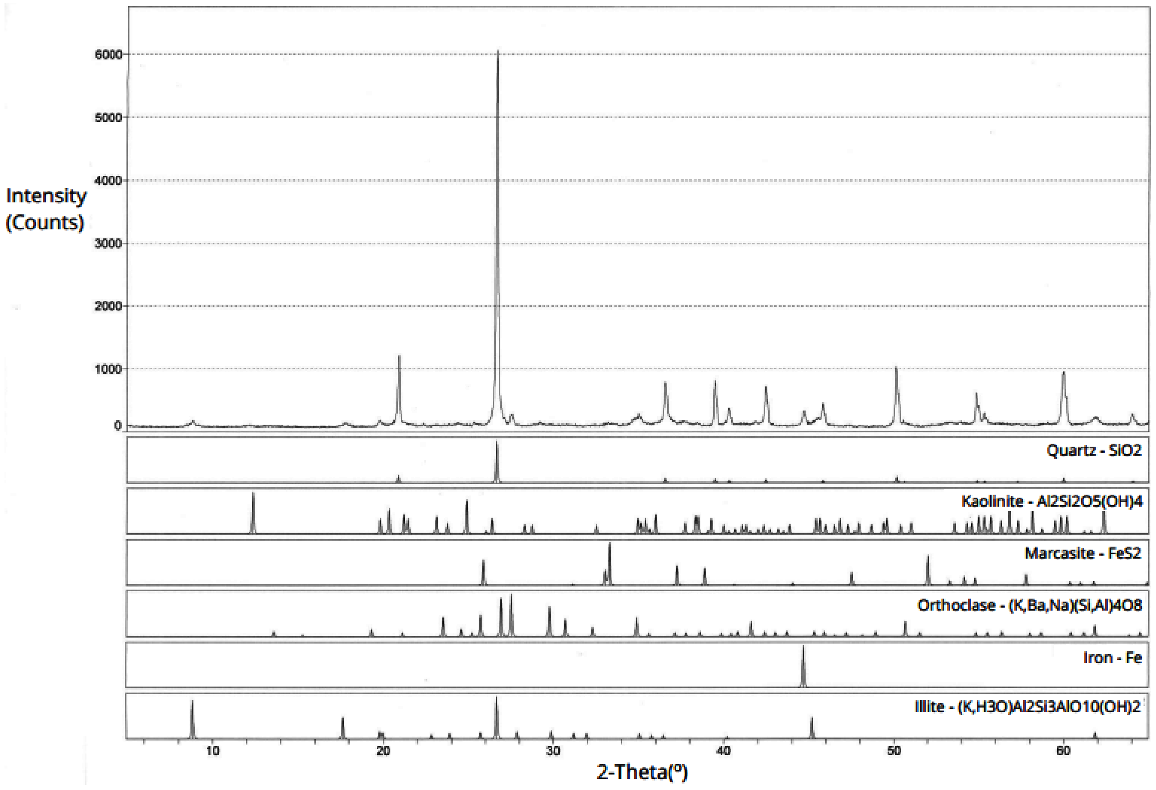


Colloidal gold nanoparticles



Zhang et al. 2011

Aggregation of colloidal gold nanoparticles produces a color shift from red to purple.

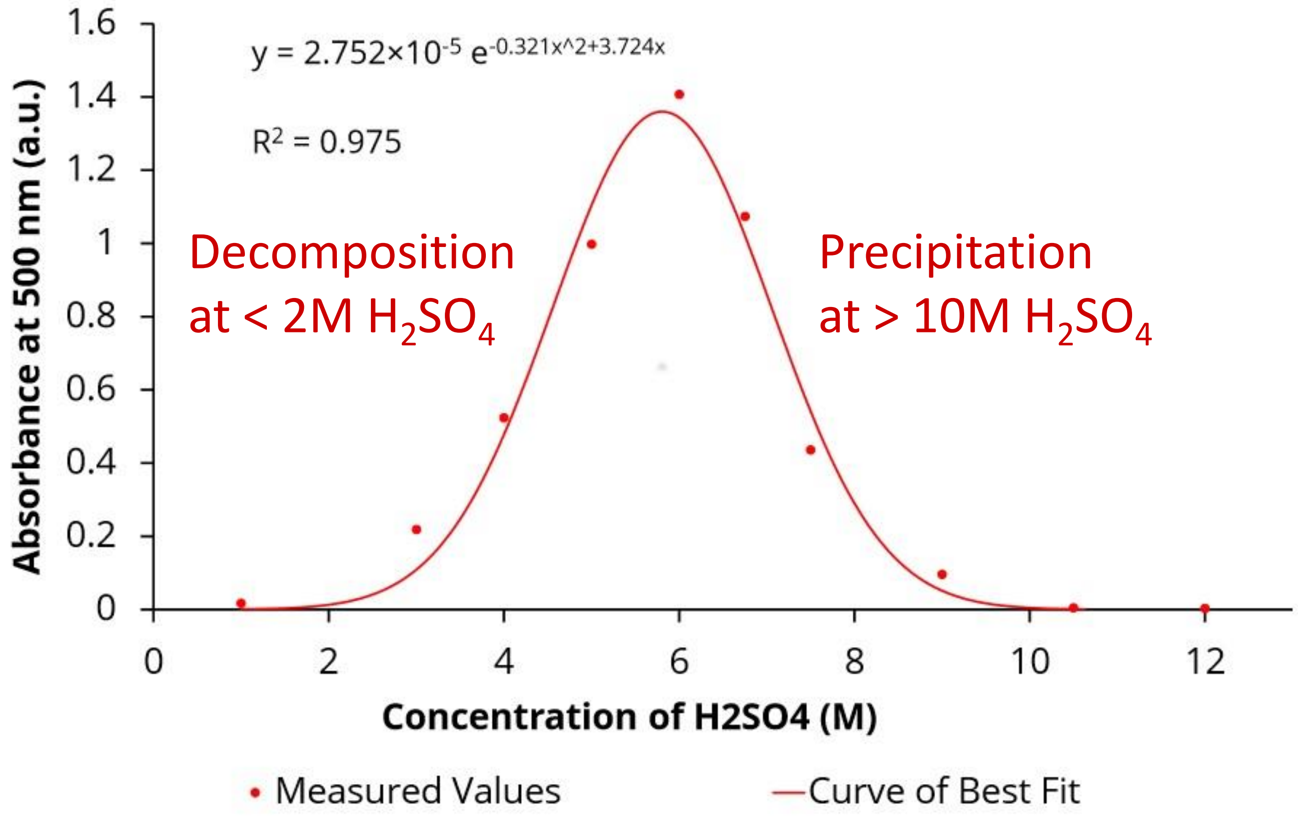


Y. X. Zhang, Y Zheng , G Gao , Y. F. Kong, X Zhi, K Wang, X. Q. Zhang, D. X. Cui. 2011. Biosynthesis of gold nanoparticles using chloroplasts. *International Journal of Nanomedicine*. 6: 2899-906.

Stability and reactivity

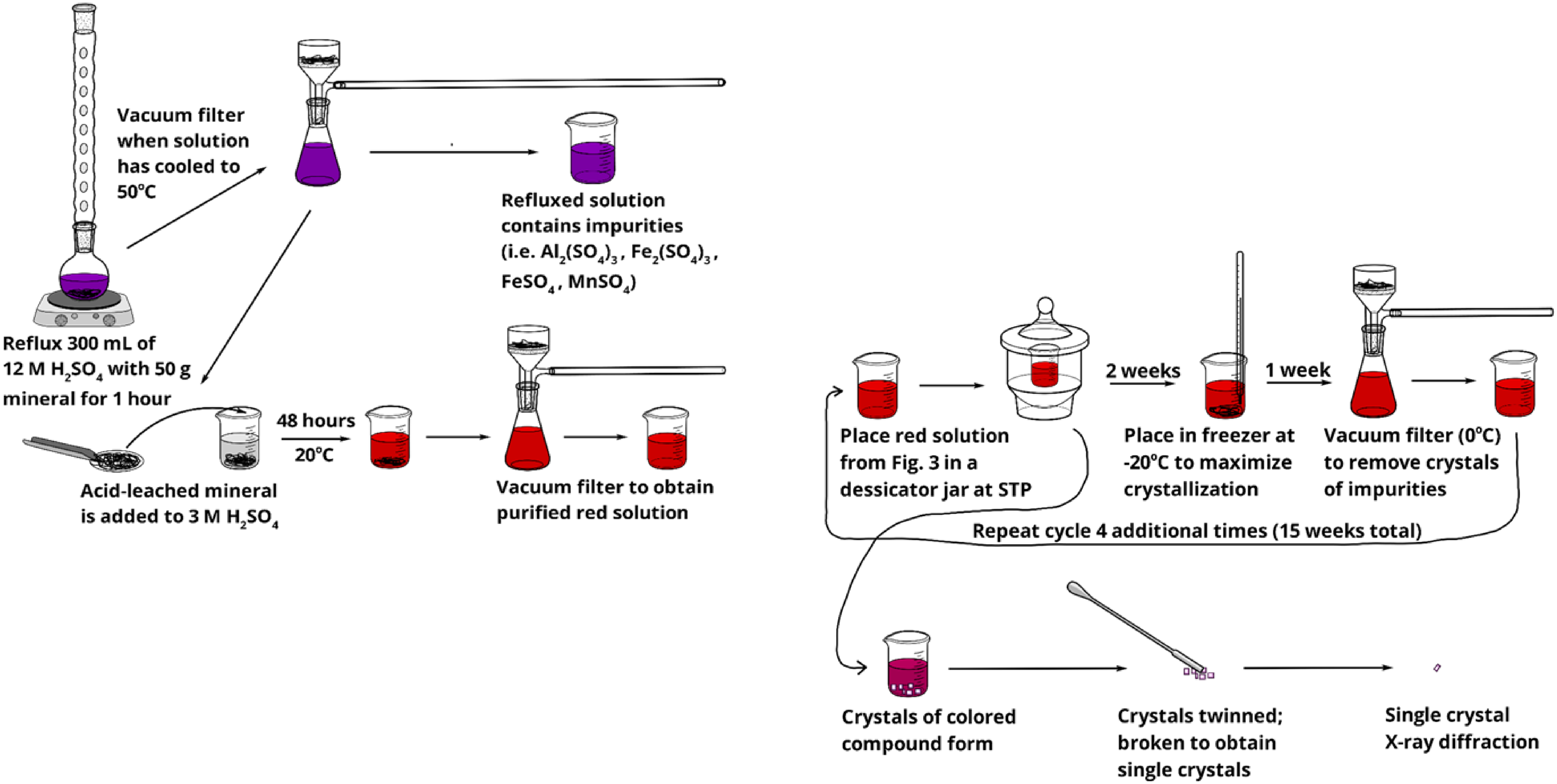
Standard reduction potentials for relevant half-reactions. Cu, Ag, and Cl^- are oxidized by solutions of the compound.

Half-reaction	Reduction potential
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	0.34 V
$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$	0.77 V
$Ag^{+}_{(aq)} + e^- \rightarrow Ag_{(s)}$	0.80 V
$Cl_{2\,(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$	1.36 V



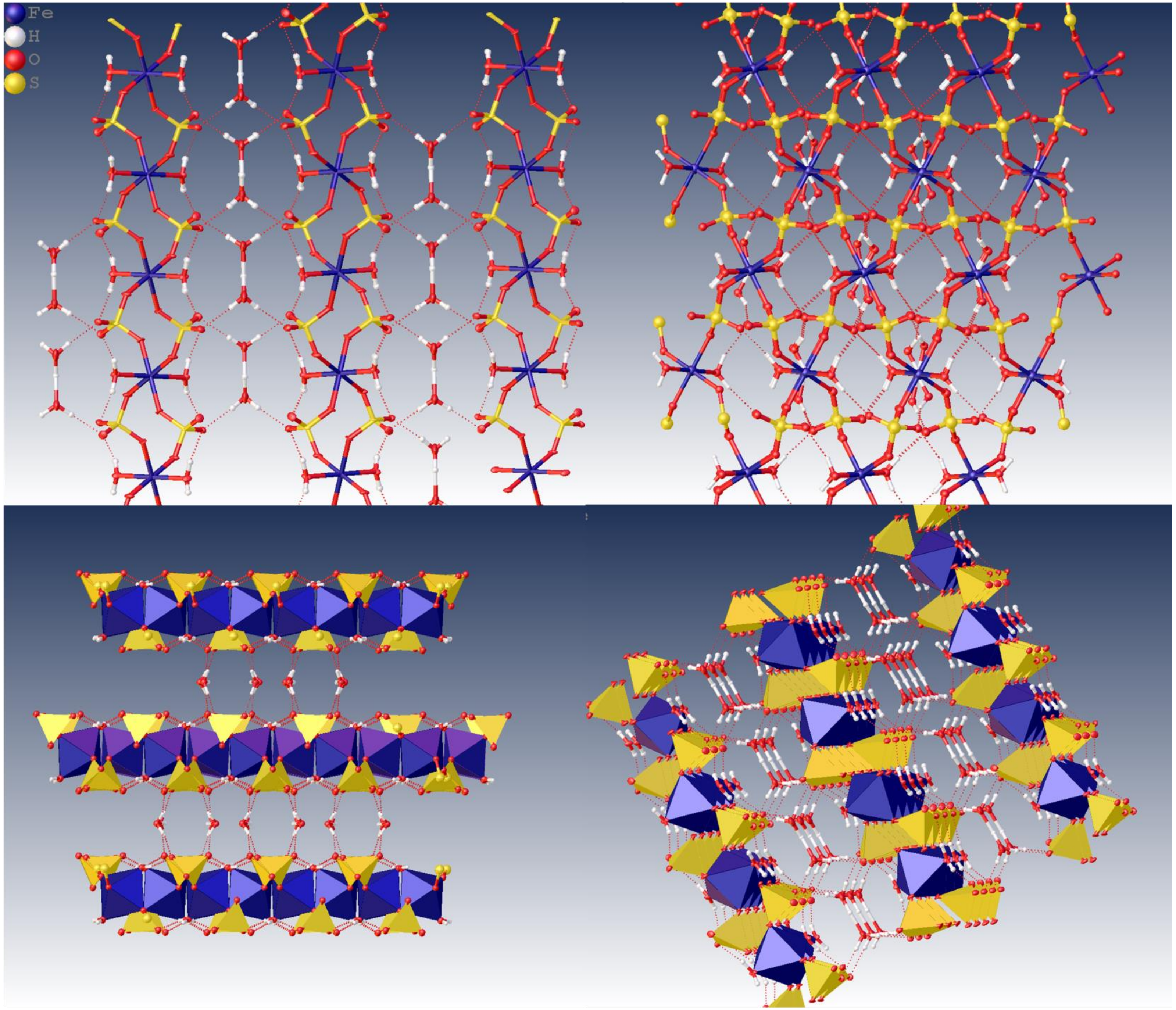
Long term stability of unknown compound at different acid concentrations. Absorbance at 500 nm (the wavelength of maximum absorbance in the visible spectrum) is directly dependent on concentration of target compound.

Purification and crystallization

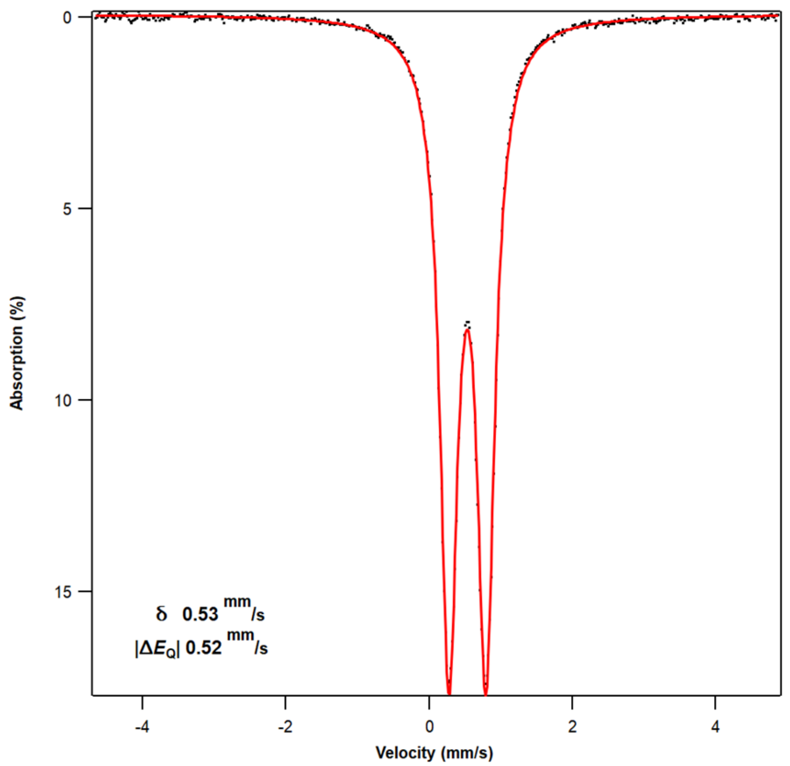


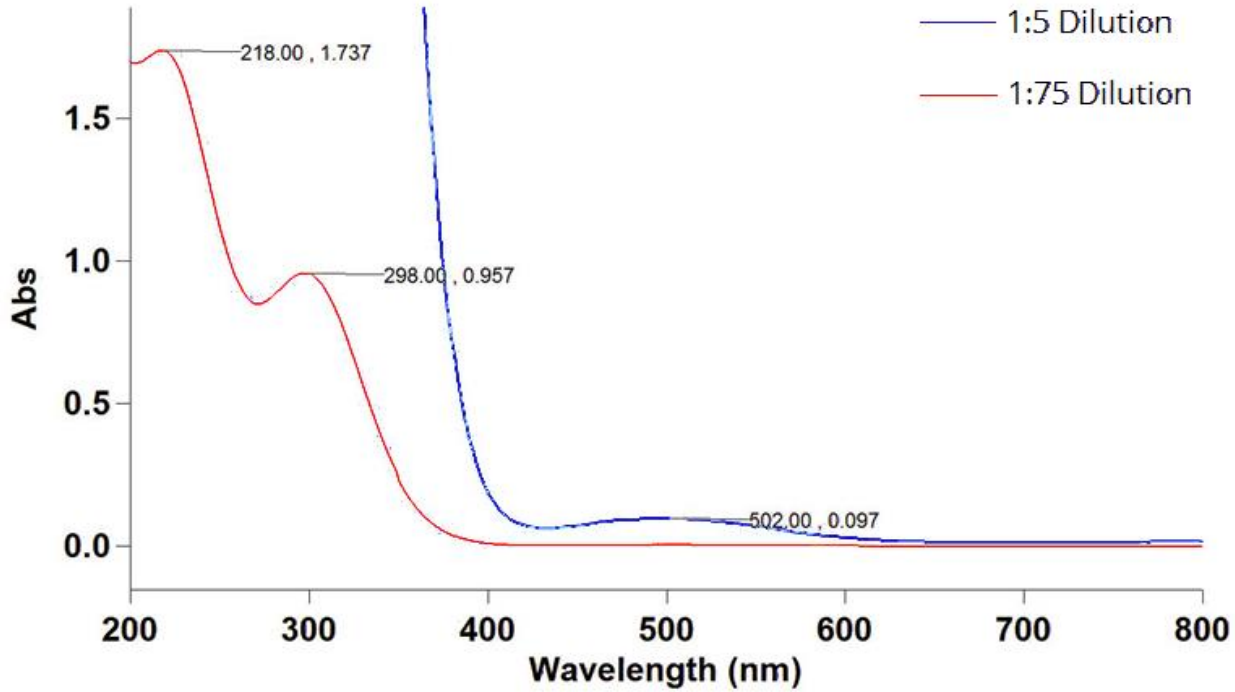
Crystal structure

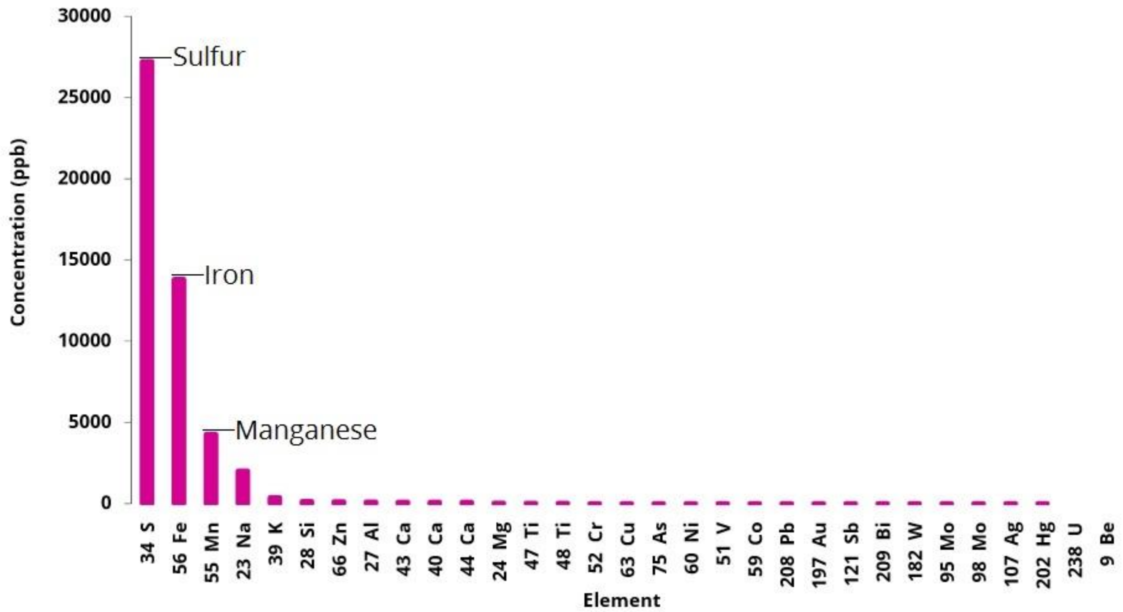
Formula: $H_5O_2Fe_{1-x}Mn_x(SO_4)_2(H_2O)_2$
Hydrogen ferric manganic sulfate (HFMS)
R1 = 3.20%
MM = 321.04 g/mol



Additional characterization







- Mossbauer spectrum confirms presence of Fe(III) in HFMS.
- UV-Vis spectrum confirms presence of Mn(III) in aqueous HFMS.
- Ratio of Fe to Mn is shown to be 3.1 to 1 by Inductively coupled plasma mass spectrometry.

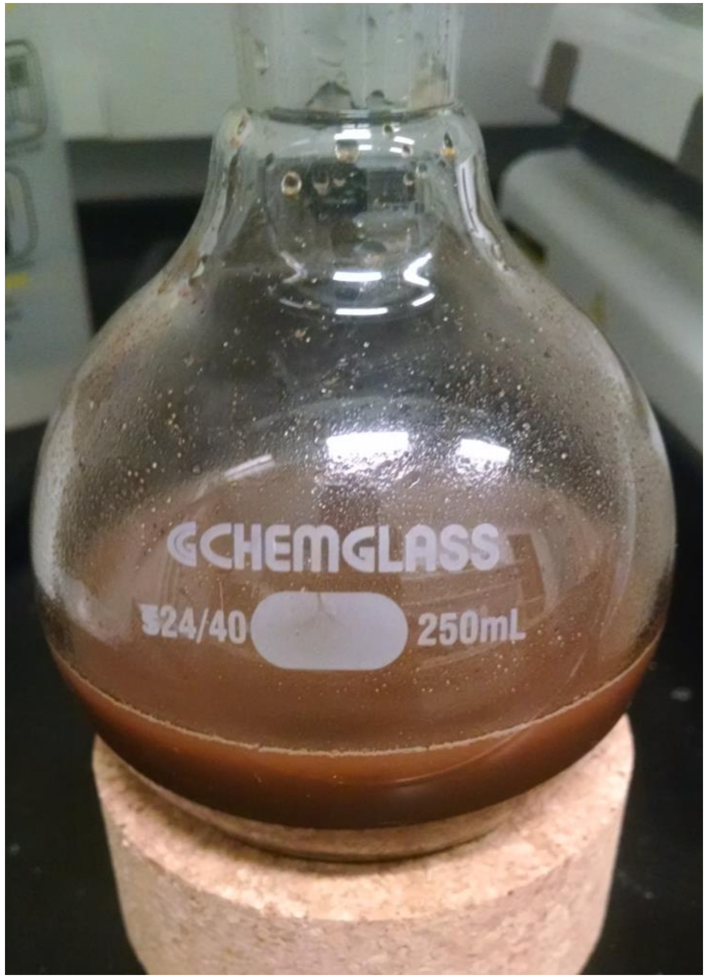
Development of HFMS Synthesis

HFMS synthesis based on natural system.

Hydrothermal vein hypothesis:

- The amorphous mineral precursor to HFMS is a Mn/Fe mixed metal oxide formed in a hydrothermal vein.
- MnO_2 deposited first and acted as a sponge for aqueous Fe(II)/(III) ions, allowing a mixed Mn/Fe oxide to form.

Hydrothermal vein conditions could not be easily replicated under laboratory conditions and timescale.



Unsuccessful HFMS synthesis attempt from Fe_2O_3 and MnO_2 ground together and mixed with aqueous H_2SO_4.

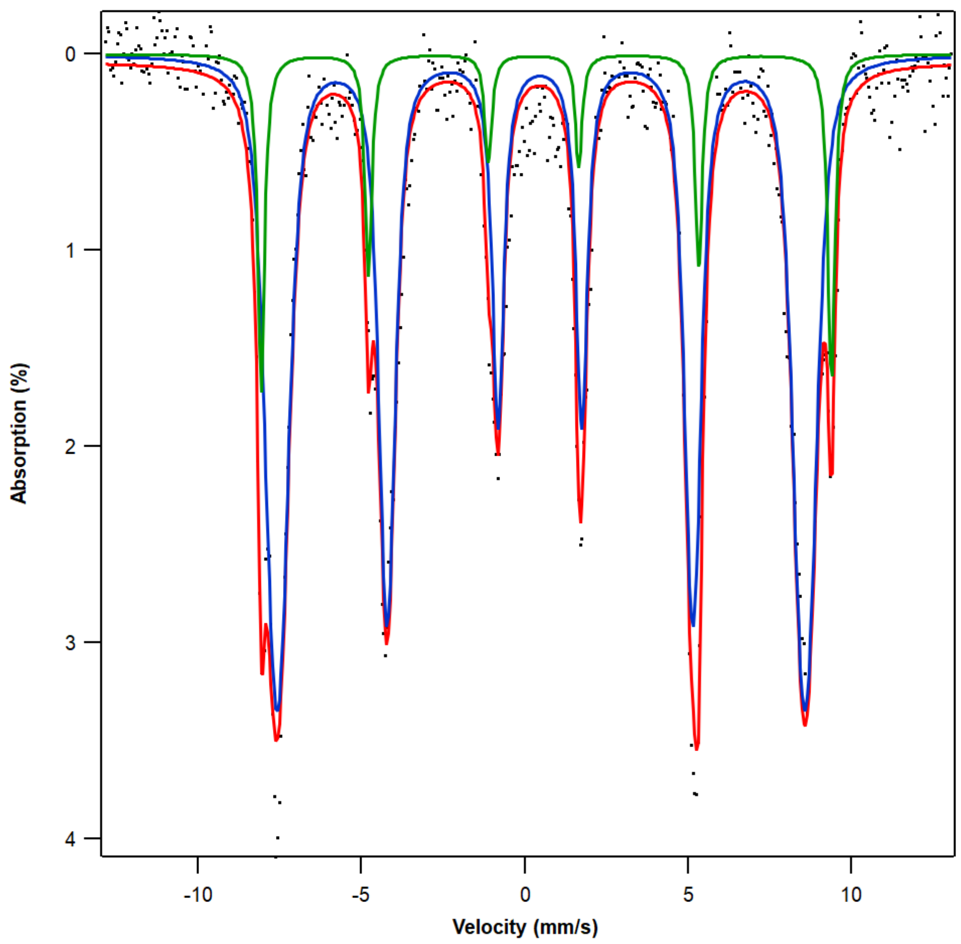
Mixed metal oxide HFMS precursor

Metal oxides were directly combined using a conventional 1000-watt microwave oven. Predicted reaction:

Overall: $Fe_2O_3 + 2MnO_2 \rightarrow 2FeMnO_3 + 0.5O_2$

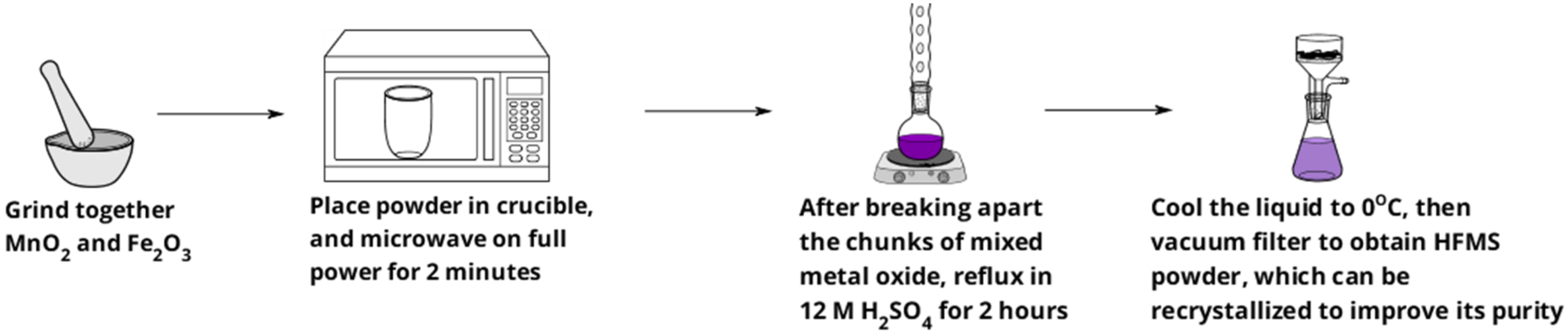
1: $2MnO_2 \rightarrow Mn_2O_3 + 0.5O_2$
2: $Mn_2O_3 + Fe_2O_3 \rightarrow 2MnFeO_3$

Mossbauer suggests actual reaction is not consistent with predicted reaction.

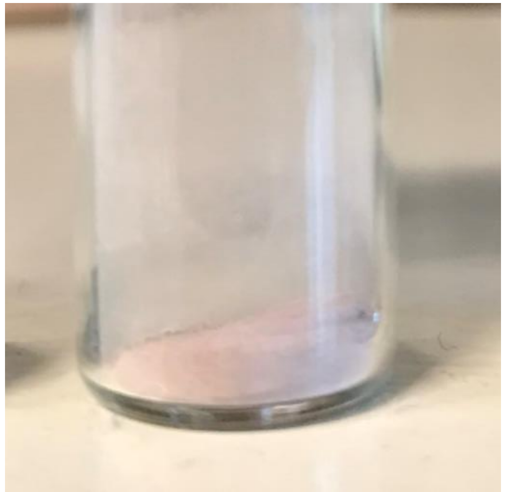


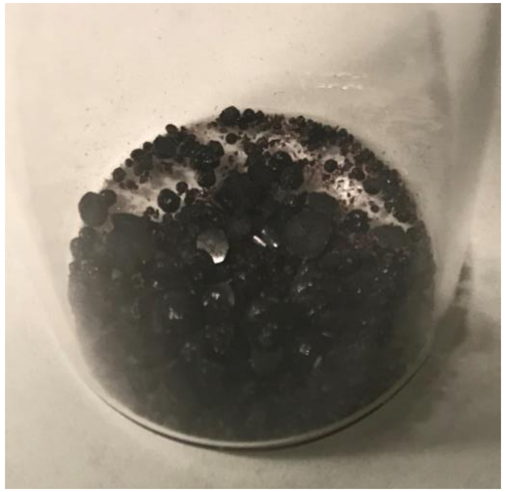
Mossbauer spectrum of mixed metal oxide. Notice the magnetic splitting in both phases of the material. Literature spectrums of bixbyite, $MnFeO_3$, only exhibit magnetic splitting at liquid helium temperatures.

Microwave-Assisted Synthesis of HFMS



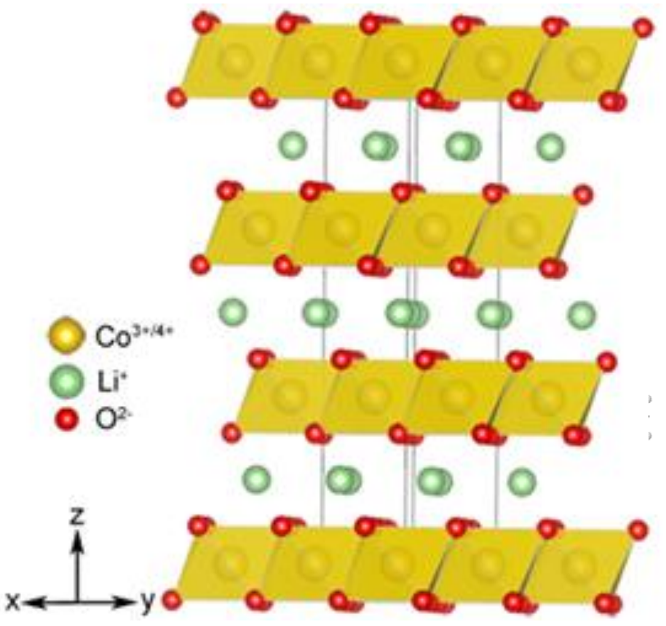
- Conventional 1000-watt microwave oven
- Yield is ~60%.

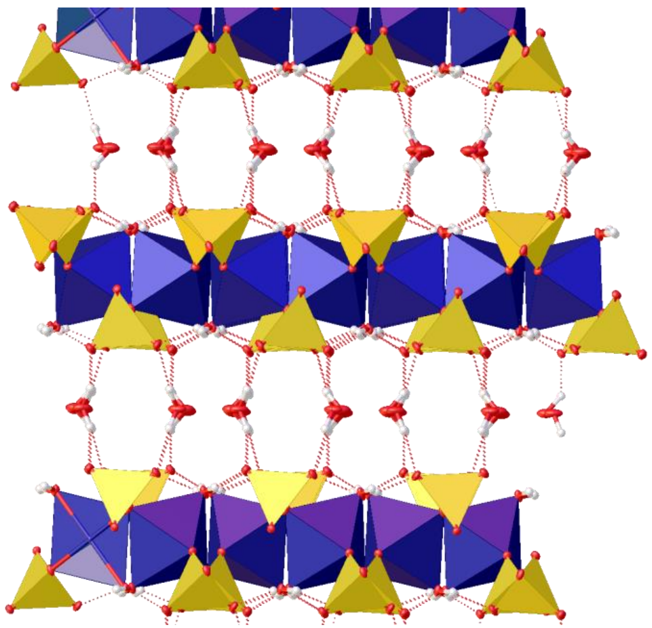




HFMS produced by microwave synthesis. HFMS powder is a light pink color, but the large crystals look black

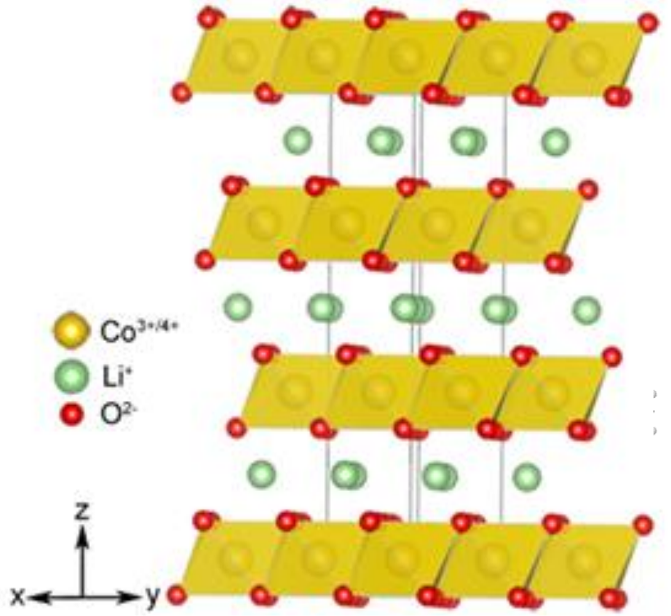
Potential applications of HFMS: Precursor to layered metal sulfate materials for rechargeable batteries

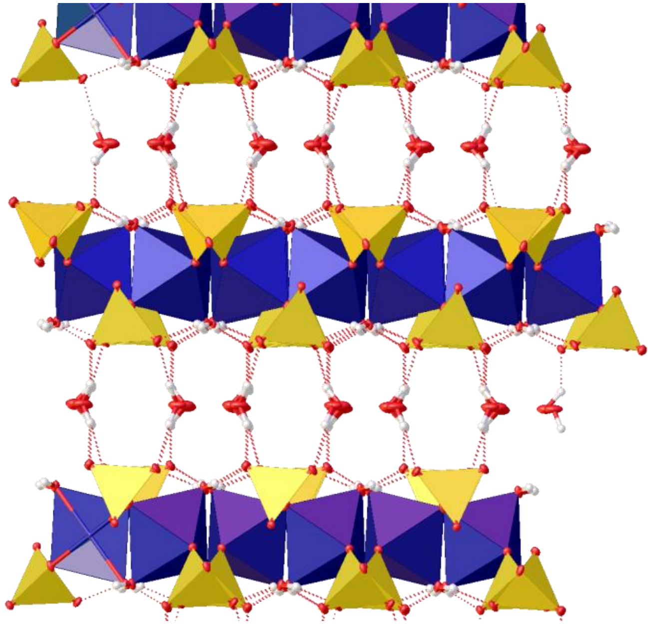




Notice similarities between layered structure of HFMS (left) and layered structure of lithium cobalt oxide (right), a high-performance cathode material for rechargeable Li-ion batteries.

Potential applications of HFMS: Precursor to layered metal sulfate materials for rechargeable batteries





- Reynaud et al. (2012) found that $Li_2Fe(SO_4)_2$ has a potential of 3.83 V vs Li^+/Li^0, which is one of the highest potentials ever discovered for the Fe^{3+}/Fe^{2+} redox couple.

- Layered structure is efficient for cation movement. Ex: $LiCoO_2$

- Mixed Fe/Mn system has been successful in other cathode materials.
    - $LiFe_{0.5}Mn_{0.5}PO_4$ has a better electrochemical performance in rechargeable Li-ion batteries than $LiFePO_4$ or $LiMnPO_4$ alone (Zhao et al. 2012).

M. Reynaud, M. Ati, B. C. Melot, M. T. Sougrati, G. Rousse, J. N. Chotard, J. M. Tarascon. Li2Fe(SO4)2 as a 3.83 V positive electrode material. *Electrochemistry Communications* 2012, 21, 77–80.

M. Zhao, G. Huang, B. Zhang, F. Wang, X. Song. Characteristics and electrochemical performance of LiFe0.5Mn0.5PO4/C used as cathode for aqueous rechargeable lithium battery. *Journal of Power Sources* 2012, 211, 202–207.

Challenges of using HFMS as a precursor to rechargeable battery cathode materials

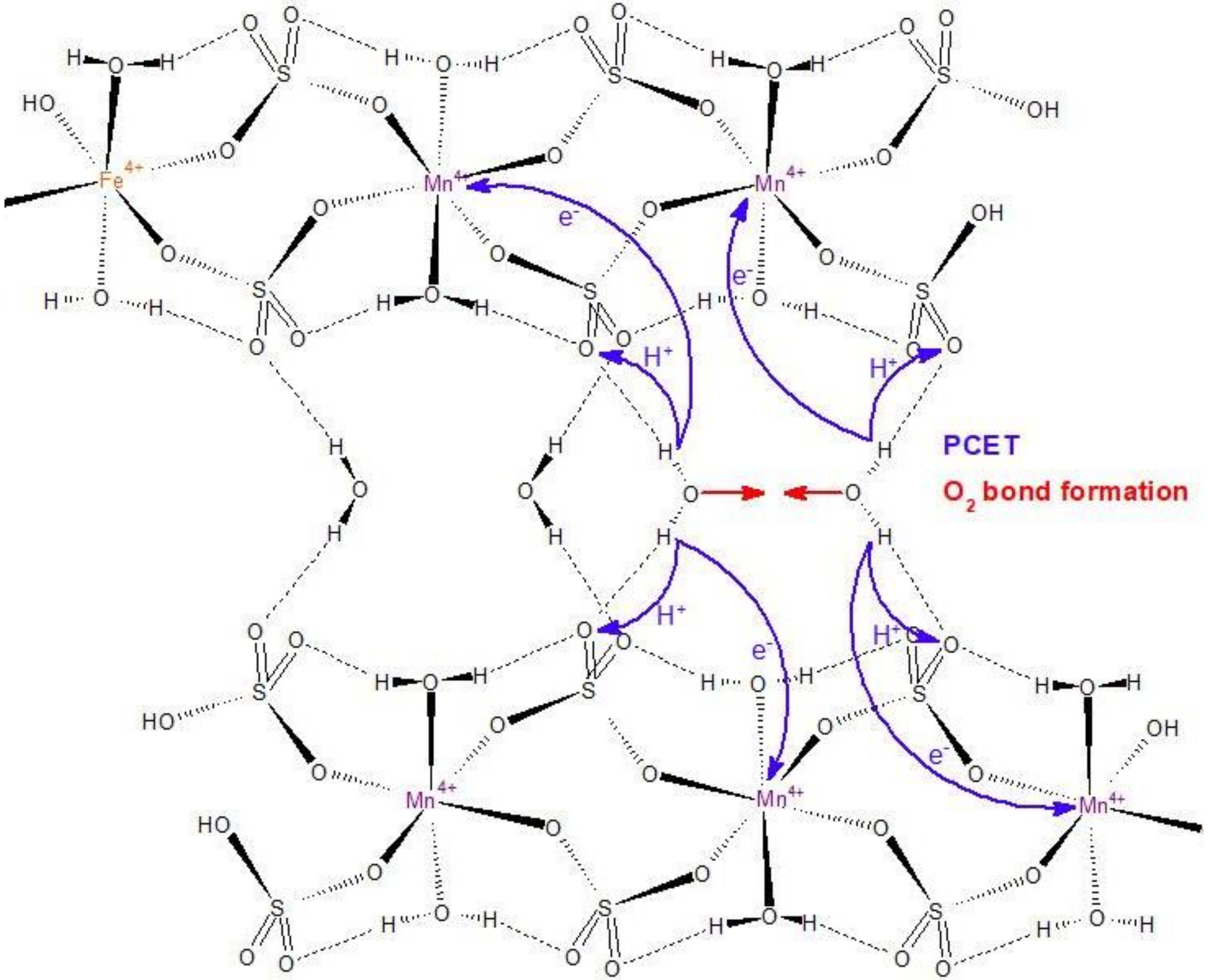
- Fe and Mn already in 3+ oxidation state.
  - Usually 2+ before electrochemical oxidation (Barpanda et al. 2015)

- Each metal has 2 water molecules coordinated to it.
  - Adds additional weight without increasing the charge.
  - If water desolvates, would cause problems in an anhydrous system.
  - Ability of water to fill octahedral metal sites stabilizes layered structure.

- Maintaining the layered structure.
  - Replacing dihydronium ions with metal ions could change packing.

P. Barpanda. Sulfate Chemistry for High-Voltage Insertion Materials: Synthetic, Structural and Electrochemical Insights. *Isr. J. Chem.* 2015, 55, 537–557.

Potential Applications of HFMS: Solid-State OER Catalysis in Acid



If HFMS is oxidized at the surface of an electrode, the following reaction is predicted to take place:

$$H_5O_2^+Fe_{1-x}^{3+}Mn_x^{3+}(SO_4)_2(H_2O)_2 + H_2O \rightarrow (H_2O)_2Fe_{1-x}^{3+}Mn_x^{4+}(SO_4)_2(H_2O)_2 + H_3O^+ + e^-$$

This would create Mn(IV)-rich environments between the layers where OER catalysis could occur (see cartoon).

Catalysis of water oxidation in a layered system could be interesting for mechanistic studies.

Typically, only Ir-based water oxidation catalysts can be used in acid solution.

Challenges of using HFMS as a material for OER catalysis

$Mn^{4+} + e^{-} \longrightarrow Mn^{3+}$ 1.30V
$2H_2O \longrightarrow 4e^{-} + 4H^{+} + O_2$ -1.23V

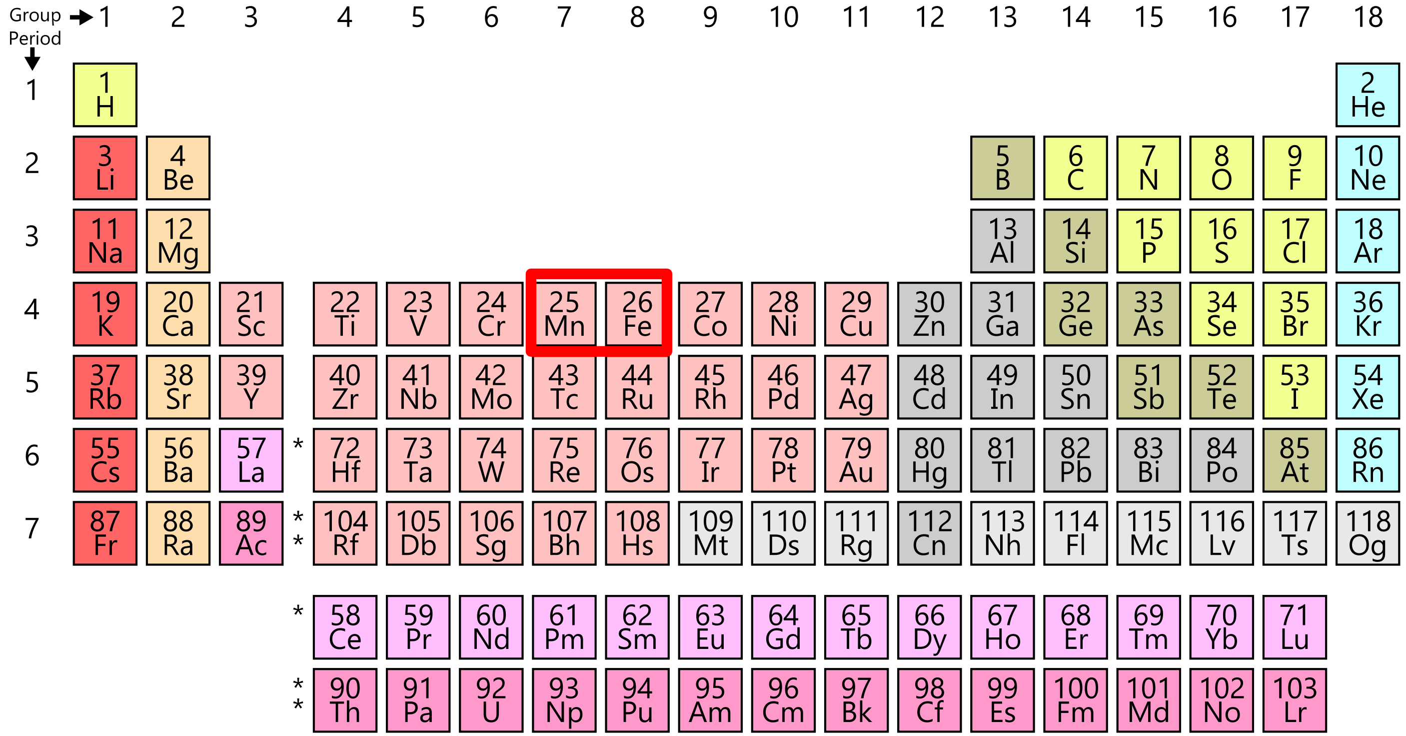
- Low conductivity.
- HFMS is soluble in dilute acid solution.

Possible solution:

- Use of an acid-stable, conductive binder to keep HFMS in contact with electrode.

Implications of HFMS for discovery of novel mixed metal systems

- The whole is not the sum of the parts.
- Exemplifies that interactions in mixed metal systems can be complex are difficult to predict.
- Mixed metal oxide materials could be a valuable starting point for discovery of new mixed metal systems.



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