Uranium and Europium Molten Salt Spectroelectrochemistry

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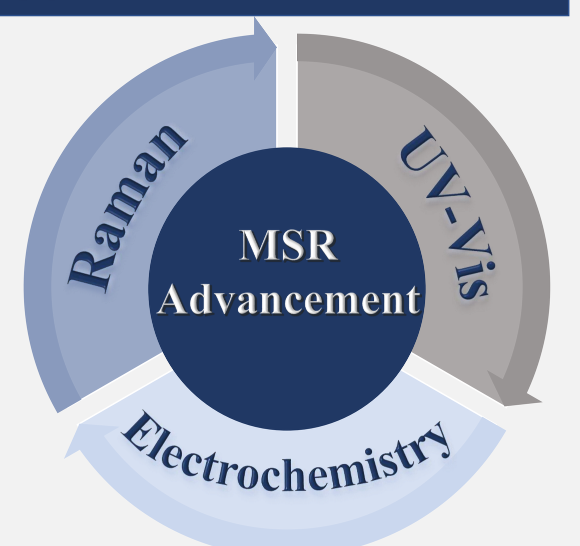
Introduction

- Advancing MSR technology requires an understanding of the chemistry of the components in the eutectics in real-time
- Call to develop hybrid technologies for **real-time quantification** of chemical species and to achieve control of **redox potentials** in molten salt systems



Online Monitoring

- Provides **electronic** and **vibrational** signatures to characterize and monitor in real-time chemical species in the molten salt
- Key benefits are nondestructive data collection and **proliferation risk minimization**

Questions

- What chemistry is taking place that can contribute to **reduction and oxidation effects**?
- How does the concentration of the analyte affect the **speciation** of the metal in the melt?

Objective

To inform MSR pyroprocessing redox systems through online monitoring by obtaining fundamental data on uranium and selected lanthanides coupling **electrochemistry** with optical spectroscopy (**UV-Vis**) and vibrational spectroscopy (**NIR**).

- **Step 1**: Verify all systems work within the high temperature furnace
- **Step 2**: Test electrochemistry systems at high temperature in molten salts
- **Step 3**: Electrochemically determine the concentration where aggregation starts to form at a larger scale
- **Step 4**: Test electrochemistry system at a small scale with UV-Vis measurements to determine species at the electrode

Acknowledgments and References

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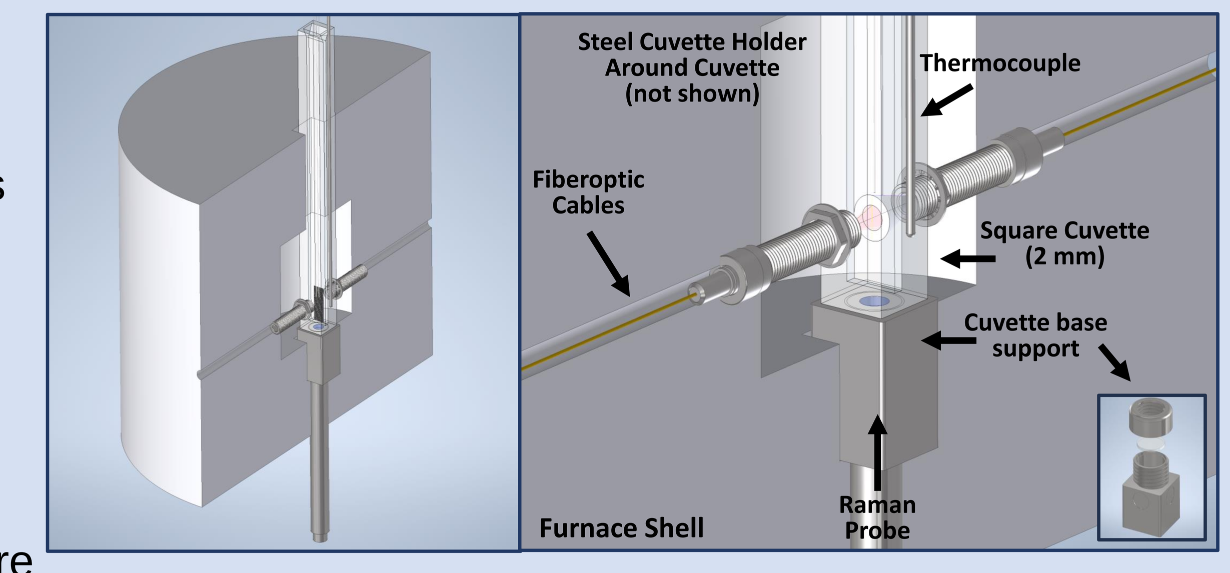
Hege, N.; et al. *J. Electrochem. Soc.* **2023**, 170, 016503.
Schroll, C. A.; et al. *Electroanalysis*. **2016,** 28, 2158 – 2165.

Methods and Validation

Accomplishments

- Fiberoptic cables are optically aligned
- Raman laser focal point is within the 2 mm cuvette pathlength
- Electrochemical cable calibration successful
- NIR, UV-Vis, and Raman Instruments have been validated at room temperature



Diffusion Equations

Spectroelectrochemistry

$$\mathcal{A} = \frac{2\varepsilon_R C D^{1/2} t^{1/2}}{\pi^{1/2}}$$

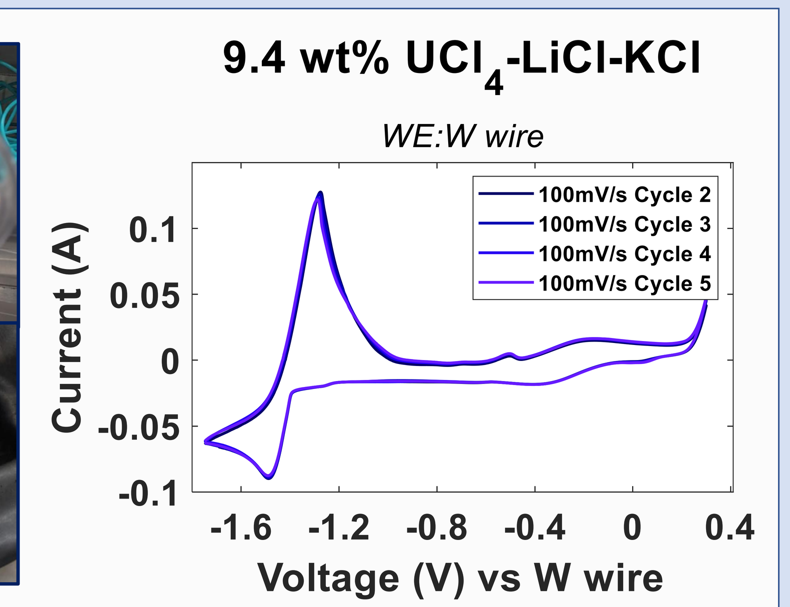
Cyclic Voltammetry

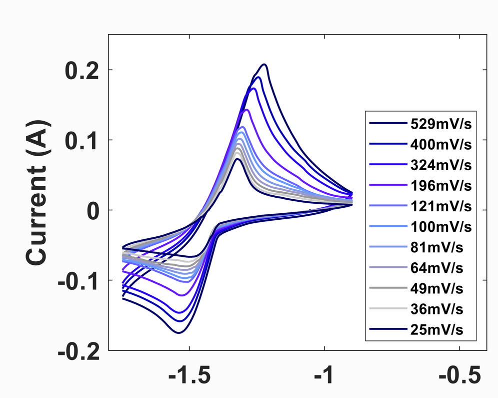
$$i_p = 0.4463 nFAC \left(\frac{n\nu F D}{RT}\right)^{1/2}$$

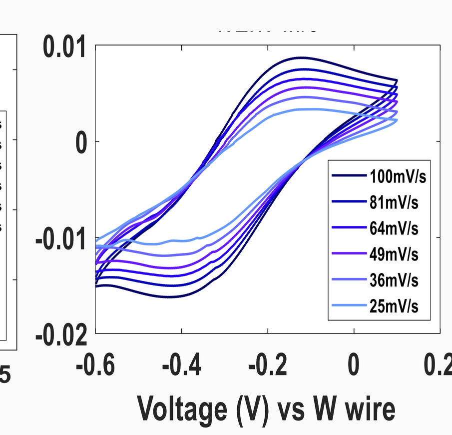
Molten Salt Large Scale System

Experiment details

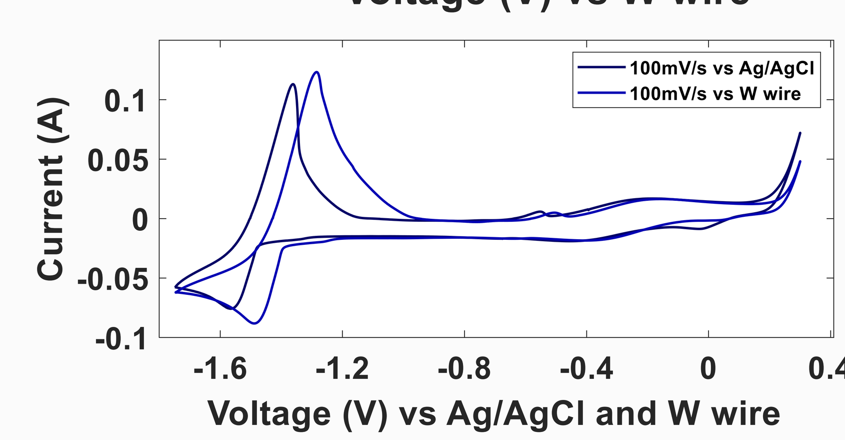
- 50g total of UCl_4-LiCl-KCl
- 9.4 wt% UCl_4
- Alumina crucible
- Internal temperature of 650°C
- Aligns well with literature data
- $U^{3/0}$ $E_{1/2}$ = -1.416 V vs ref.
- $U^{3/4}$ $E_{1/2}$ = -0.272 V vs ref.







Cyclic voltammograms of 1.5 mol% UCl_4-LiCl-KCl with varying scan rates for $U^{3/0}$ and $U^{3/4}$ redox couples.

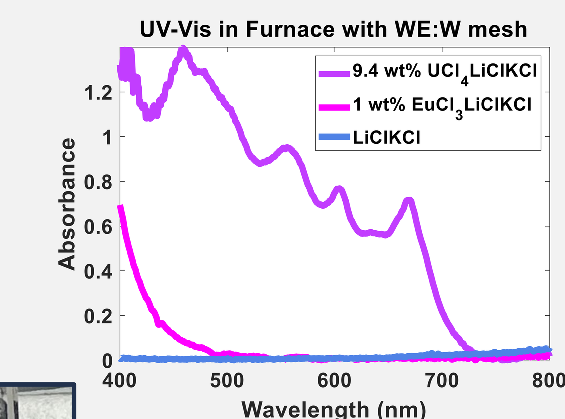


Reference electrode effects on the half wave potentials of the $U^{3/0}$ redox couple, which has a difference of 6 mV.

Molten Salt Small Scale System

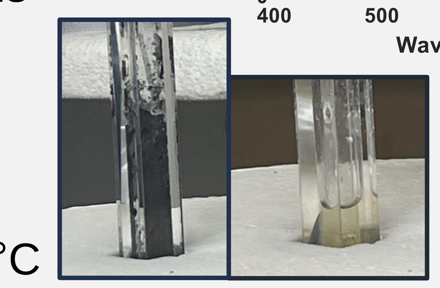
Molten salt electrochemistry melt successes

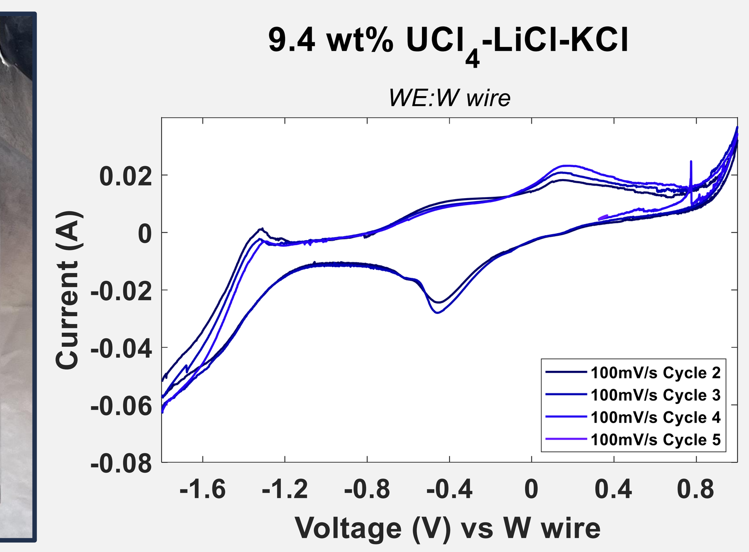
- Proper heat/cool ramps to 650°C
- Electrodes assembled with no short circuits
- Featureless background
- No corrosion of cell materials
- UV-Vis signatures



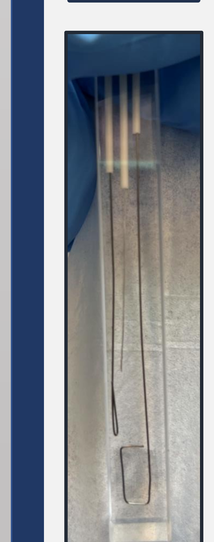
Experiment details

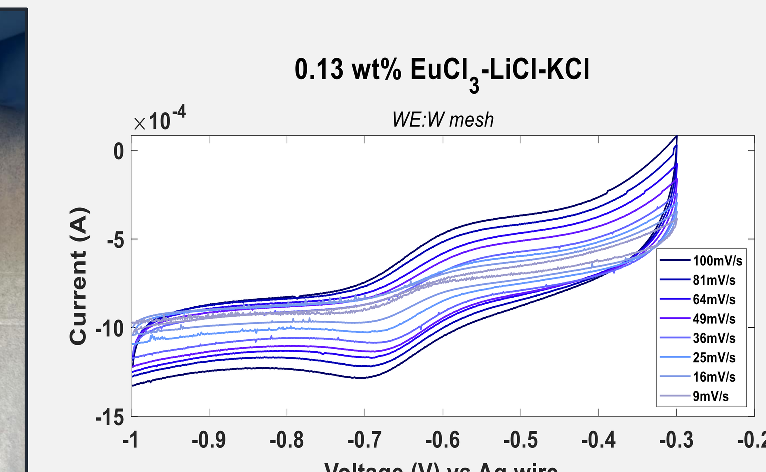
- 1.5g total of mixture
- 2 mm pathlength quartz cell
- Internal temperature of 650°C





Cyclic voltammogram of 9.4 wt% UCl_4-LiCl-KCl with consequent cycles.





Cyclic voltammogram of 0.13 wt% $EuCl_3$-LiCl-KCl with varying scan rates.

Future Work

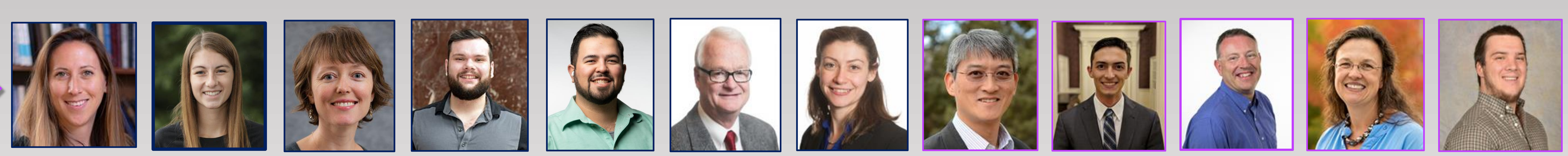
High Metal Loading Measurements

- Determine possible redox potential changes with increasing Eu(III) and U(III) concentrations in LiCl-KCl
- Determine diffusion differences at higher analyte concentrations

Diffusion Coefficients

- Determine the diffusion coefficient for Eu(III) in the LiCl-KCl eutectic melt
- Determine the diffusion coefficient for U(III) and U(IV) in molten salt mixtures with spectroscopy

Project Team



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