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Effects of Temperature, Concentration, and Uranium Content on Zirconium Electrochemistry in LiCl-KCl Eutectic Molten Salt

Robert O. Hoover[a] and Supathorn Phongikaroon[b]
University of Idaho, Idaho Falls
Currently at: a) Idaho National Laboratory and
b) Virginia Commonwealth University
2014 IPRC
October 19-23, 2014

Outline

- Introduction
- Purpose
- Literature Survey
- Experimental Equipment
  - $ZrCl_4$ Salt Preparation
- Data Collection Methods
- Electrochemistry Results
  - Zirconium Electrochemistry
    - Diffusivity
    - Apparent Standard Reduction Potential
  - Uranium-Zirconium Electrochemistry
- Summary & Future Work

Purpose

- Study the effect of temperature, concentration, and uranium content on the electrochemical behavior of zirconium.
  - 723 – 823 K: 0.5 – 5 wt% $ZrCl_4$ in LiCl-KCl eutectic
  - 773 K: $ZrCl_4$ (0.5 & 5 wt%) in LiCl-KCl-UCl_3 (~10 wt% UCl_3)

- Determine, describe and report thermodynamic and electrochemical properties to help explain their influence on the electrochemical separation process
  - Apparent standard reduction potential, E^{0*}
  - Diffusion coefficient, D

Purpose

Metallic U-Zr Fuel

- U and Zr constitute a large amount of the metallic fuel.
- Zr *should* remain unoxidized in the anode baskets.
- Extents of U and Zr oxidation are directly related.
  - Zr is building up in the ER and should be recovered.

LWR Fuel

- Zr is the primary constituent of zircaloy cladding used for commercial LWR fuel.
- Pure Zr recovery could reduce the volume of HLW.

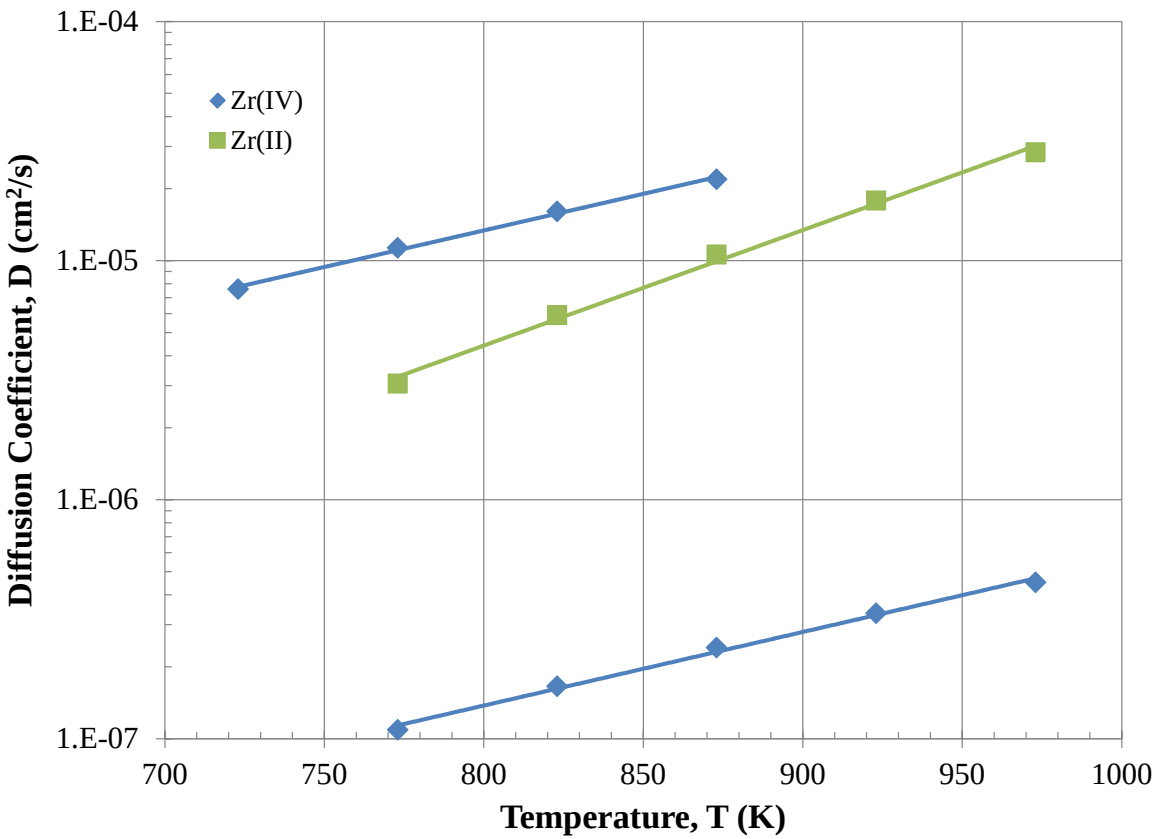
Used Metallic Fuel Composition			
Element	**Weight % in used fuel[1]**	**E^0 (V vs. Ag/AgCl)[2]**	**Post-processing location**
Mo	0.771	0.119	Anode baskets
Zr	10.805	-1.088	
U	80.596	-1.496	Collected at solid cathode
Nd	0.930	-2.097	Salt
Na	2.160	-2.50	

To collect a pure Zr product, the behaviors of U and Zr must be known

1. Li & Simpson, *Min. Metall. Proc.*, **22(4)**, (2005).
2. Bard, *Encyclopedia of Electrochemistry of the Elements, Vol. X, Fused Salt Systems*, Marcel Dekker, Inc., (1976).

Diffusion Coefficient, D

- Ahluwalia, et al., *Nucl. Tech.*, **126** (1999).
- Baboian, et al., *J. Electrochem. Soc.*, **112(12)** (1965).
- Bard, "Encyclopedia of Electrochemistry of the Elements, Vol. X, Fused Salt Systems, Marcel Dekker, Inc. (1976).
- Bychkov, et al., Proceedings of the Workshop on Pyrochemical Separations, Avignon, France, March 14-16, 2000.
- Chen et al., *J. Alloys Comp.*, **509** (2011).
- Fabian, et al., *J. Electrochem. Soc.*, **160(2)** (2013).
- Murakami and Kato, *J. Electrochem. Soc.*, **155(7)**, (2008).
- Plambeck, *J. Chem. Eng. Data*, **12(1)**, (1967).
- Yamada, et al., *J. Alloys Comp.*, **444-445** (2007).



Standard Reduction Potential, E^0

- Ahluwalia, et al., *Nucl. Tech.*, **126** (1999).
- Baboian, et al., *J. Electrochem. Soc.*, **112(12)** (1965).
- Bard, "Encyclopedia of Electrochemistry of the Elements, Vol. X, Fused Salt Systems, Marcel Dekker, Inc. (1976).
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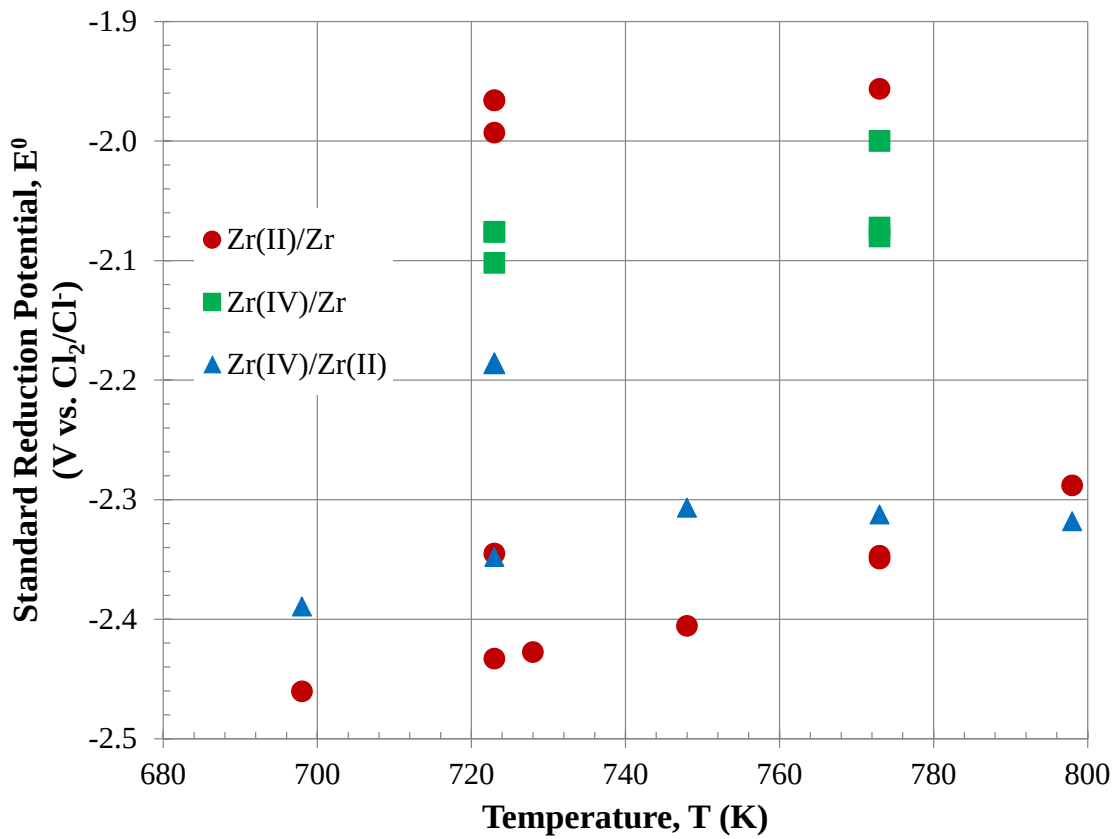
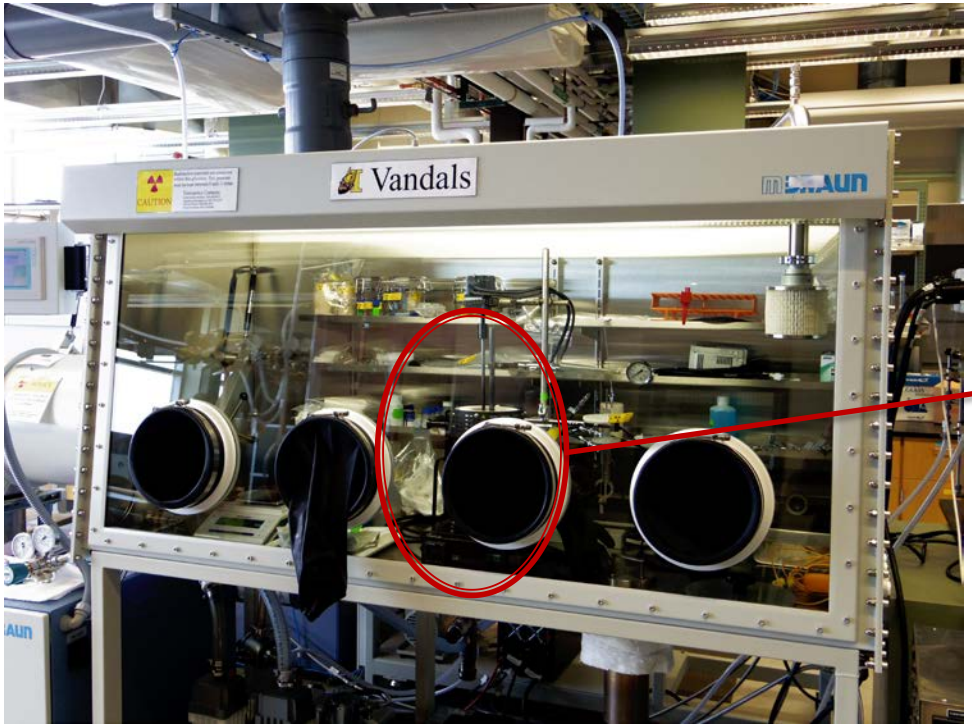
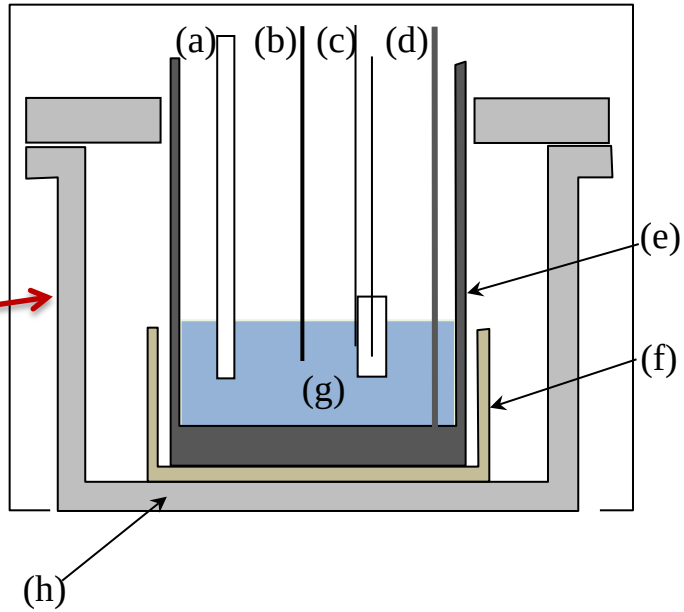


Experimental Equipment

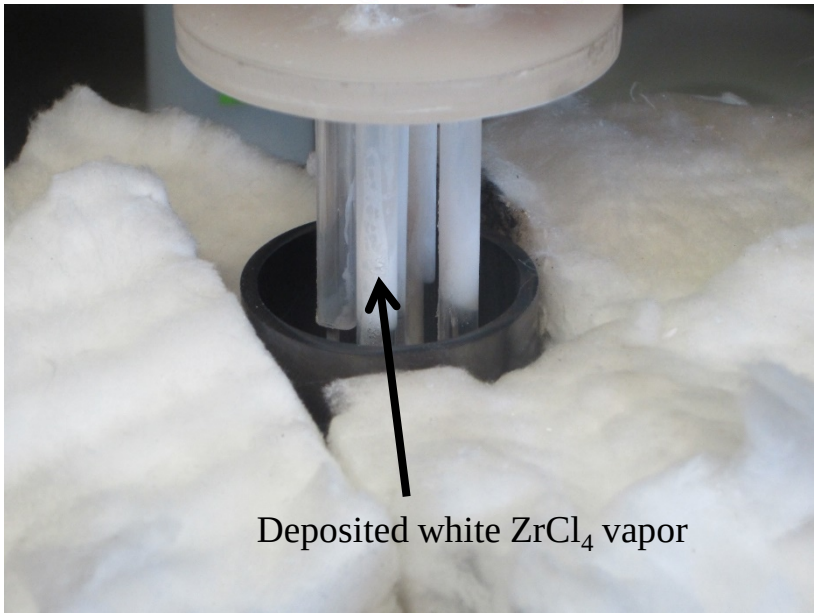


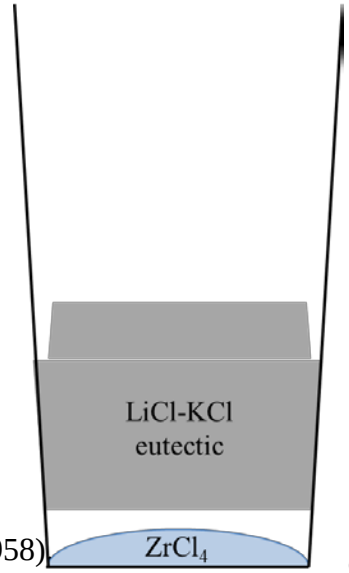


a) Al_2O_3 sheathed thermocouple
b) Tungsten (99.95%) working electrode
c) Ag/AgCl (99.997%) reference electrode (5 mol%)
d) Glassy carbon counter electrode lead
e) Glassy carbon crucible/counter electrode
f) MgO secondary crucible
g) Eutectic LiCl-KCl (99.99%) containing $ZrCl_4$ (99.95+%) and $dUCl_3$ (75 wt%)
h) Kerrlab furnace

$ZrCl_4$ Salt Preparation

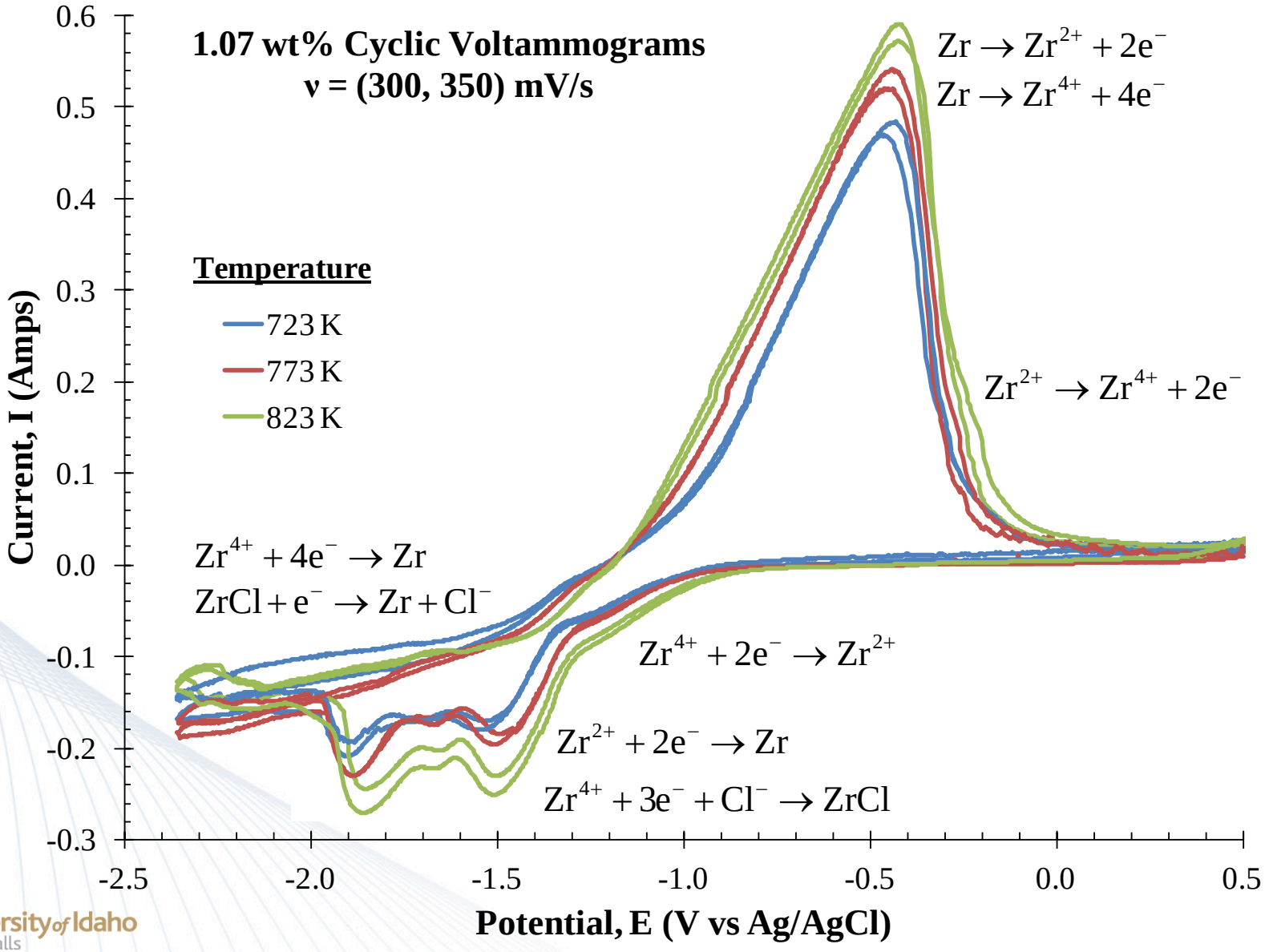
- Pure $ZrCl_4$ sublimes at 604 K[1], which is lower than the melting point of the LiCl-KCl eutectic at 621 K to 634 K[2], which creates issues with adding $ZrCl_4$ directly to the LiCl-KCl and heating.
- A process was developed to trap $ZrCl_4$ beneath the LiCl-KCl until the salt melts and all $ZrCl_4$ can be dissolved into the eutectic:
  - Pre-cast a LiCl-KCl ingot in the tapered crucible.
  - Cut the bottom off of the ingot.
  - Weigh the $ZrCl_4$ into the crucible.
  - Place the ingot in above the $ZrCl_4$.
  - Due to the taper, the ingot sits tightly against the walls, trapping the powder in the crucible.
- For UCl_3-$ZrCl_4$-LiCl-KCl experiments, 25 wt% $ZrCl_4$ mixtures were prepared and added to the UCl_3 mixture.





[1] Blumenthal, *The Chemical Behavior of Zirconium*, Van Nostrand Company, Inc. (1958).
[2] Sangster and Pelton, *J. Phys. Chem. Ref. Data*, **16(3)** (1987).

Results: 1.07 wt% $ZrCl_4$ CVs (723, 773, & 823 K)



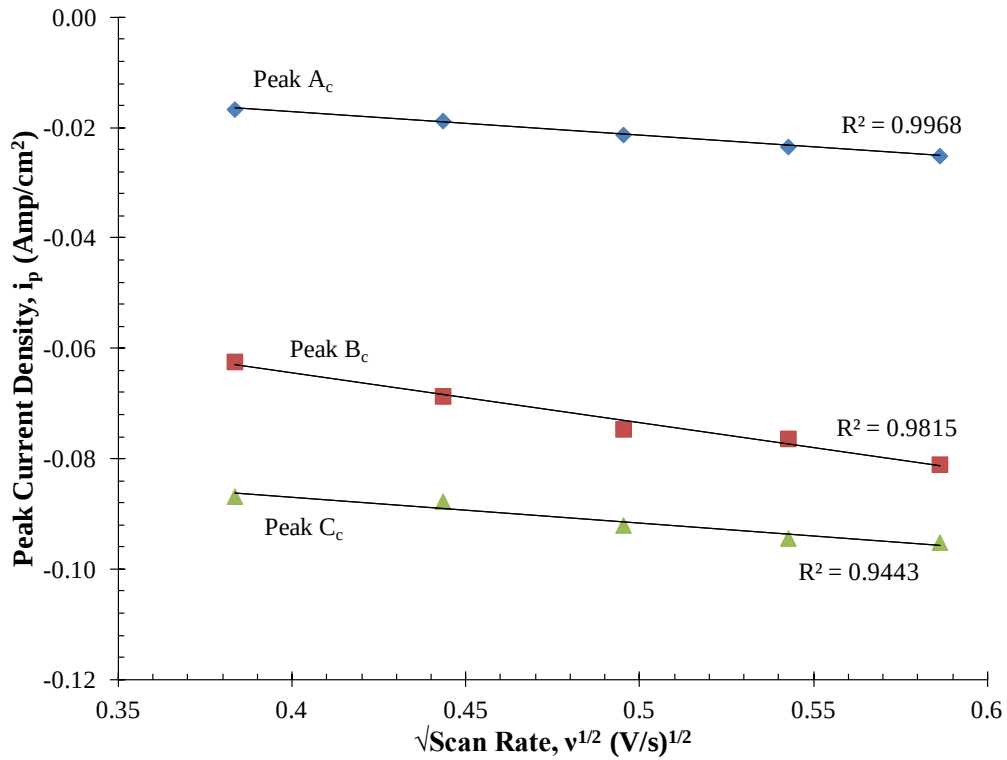
Zr CV Analysis: Diffusivity

- Product of the number of electrons transferred and the transfer coefficient, nα

$$\left|E_{pc} - E_{p/2}\right| = 1.857\frac{RT}{n\alpha F}$$

- Diffusivity can be calculated from CV data.

$$\frac{I_{pc}}{\sqrt{\nu}} = 0.4958nFAC\sqrt{\frac{n\alpha FD_{ox}}{RT}}$$

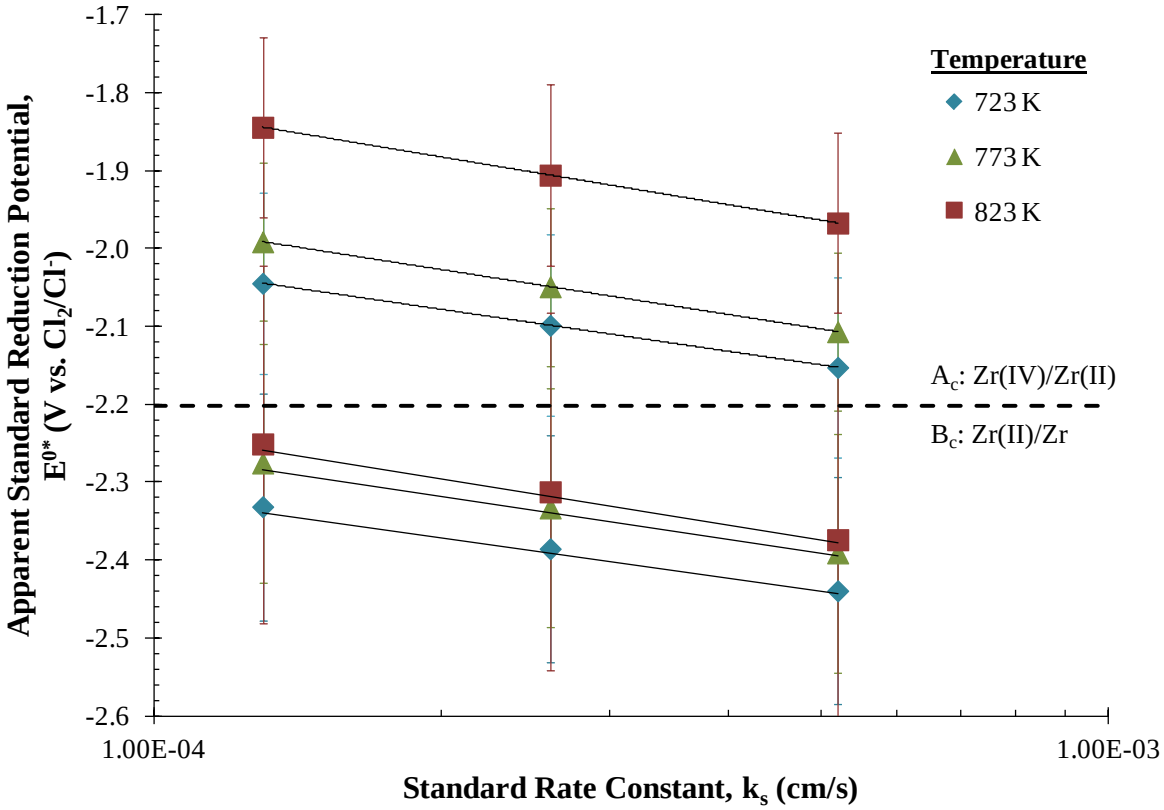


Peak: Species	Product of electrons transferred and transfer coefficient, nα			Diffusion Coefficient, D (cm^2/s)		
	723 K	773 K	823 K	723 K	773 K	823 K
A_c: Zr(IV)	0.85	0.825	0.93	3.06×10^{-6}	2.86×10^{-6}	5.82×10^{-6}
B_c: Zr(II)	0.75	0.65	0.875	1.27×10^{-5}	1.47×10^{-5}	3.33×10^{-5}

Zr CV Analysis: Apparent Standard Reduction Potential

$$E_{pc} = E^{0*} - \frac{RT}{n\alpha F}\left[0.78 - \ln k_s + \ln\sqrt{\frac{n\alpha F\nu D_{ox}}{RT}}\right]$$

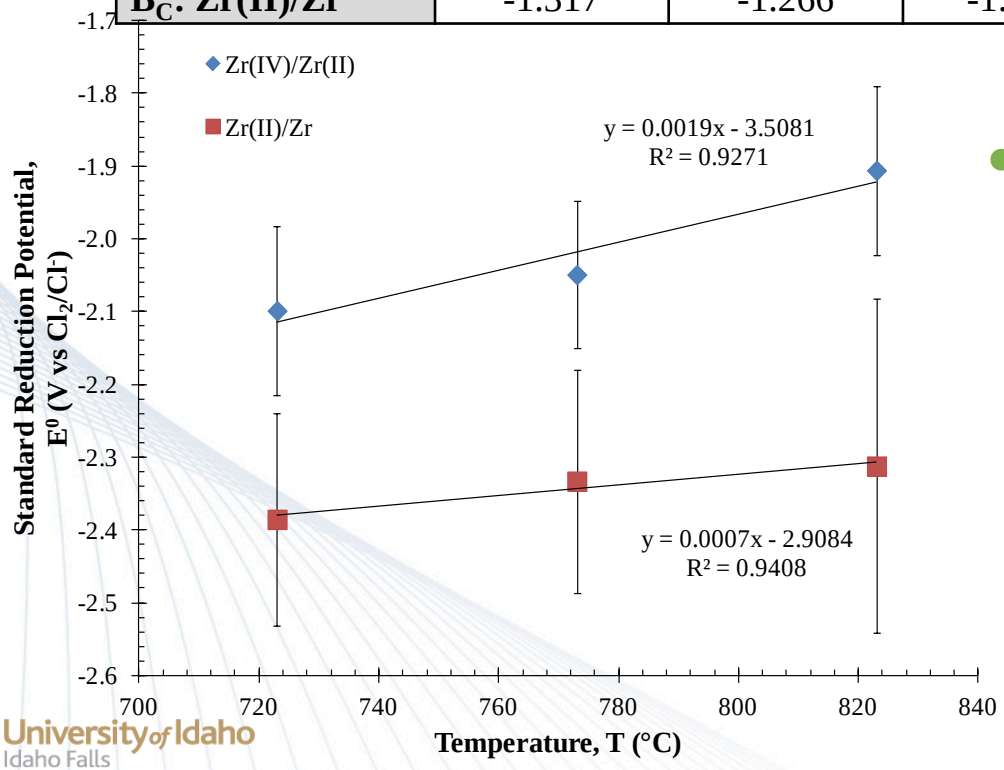
- The standard rate constant is not known for the Zr reactions.
- Values ranging from one half to twice the value for U are analyzed, with an average of ~5% variation in E^{0*}.



Zr Apparent Standard Reduction Potential Temperature Dependence

- Apparent standard reduction potential has a linear dependence with temperature.
- Assumed $k_s = 2.6 \times 10^{-4}$ cm/s

Peak	Apparent Standard Reduction Potential, E^{0*} (V vs Ag/AgCl)			Apparent Standard Reduction Potential, E^{0*} (V vs Cl_2/Cl^-)		
	723 K	773 K	823 K	723 K	773 K	823 K
A_C: Zr(IV)/Zr(II)	-1.031	-0.982	-0.841	-2.099	-2.049	-1.906
B_C: Zr(II)/Zr	-1.317	-1.266	-1.247	-2.385	-2.333	-2.312

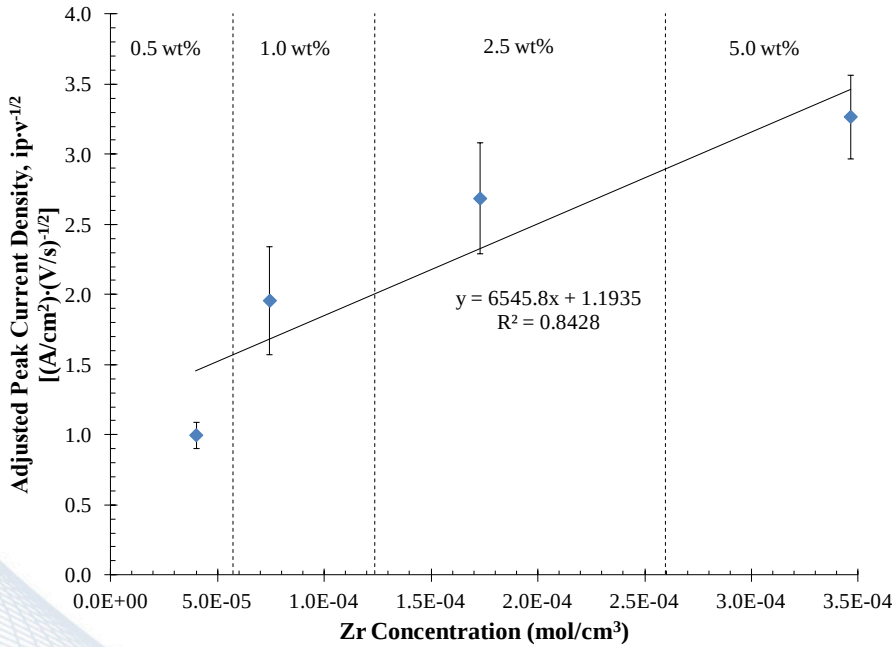


- Apparent standard reduction potential (vs. Cl_2/Cl^-)
  - Zr(IV)/Zr(II)
    - $E^{0*} = 0.002T - 3.508$
  - Zr(II)/Zr
    - $E^{0*} = 0.0007T - 2.908$

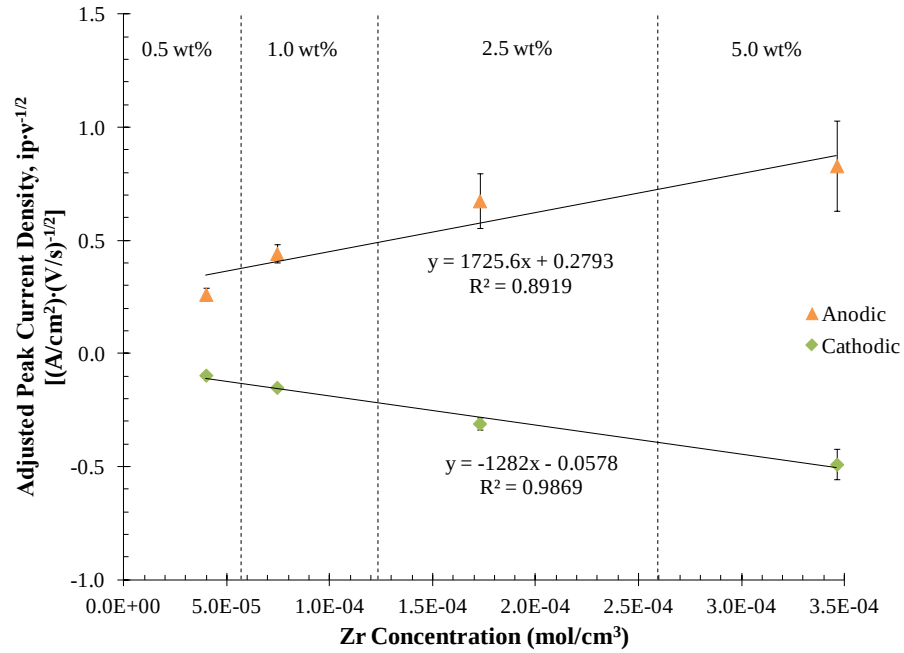
$ZrCl_4$ Concentration Detection (773 K)

- Three methods to determine concentration of analyte in solution:

ASV Peak Height



CV Peak Heights (Anodic and Cathodic)

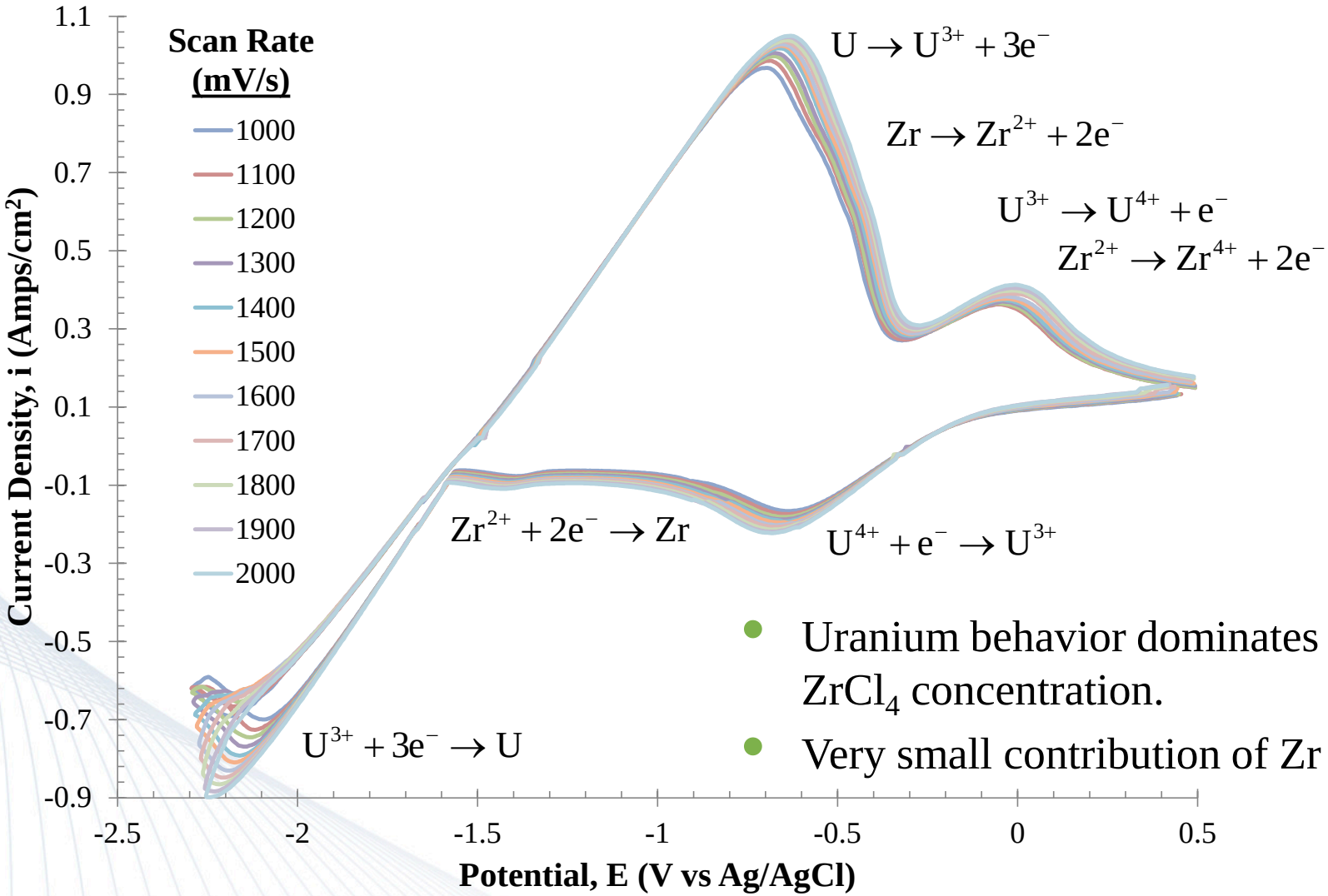


$$\frac{I_p}{\sqrt{\nu}} = 0.4958nFAC\sqrt{\frac{n\alpha FD}{RT}}$$

- Calibration curve is best fitted using the **CV cathodic peak** height divided by the square root of scan rate.

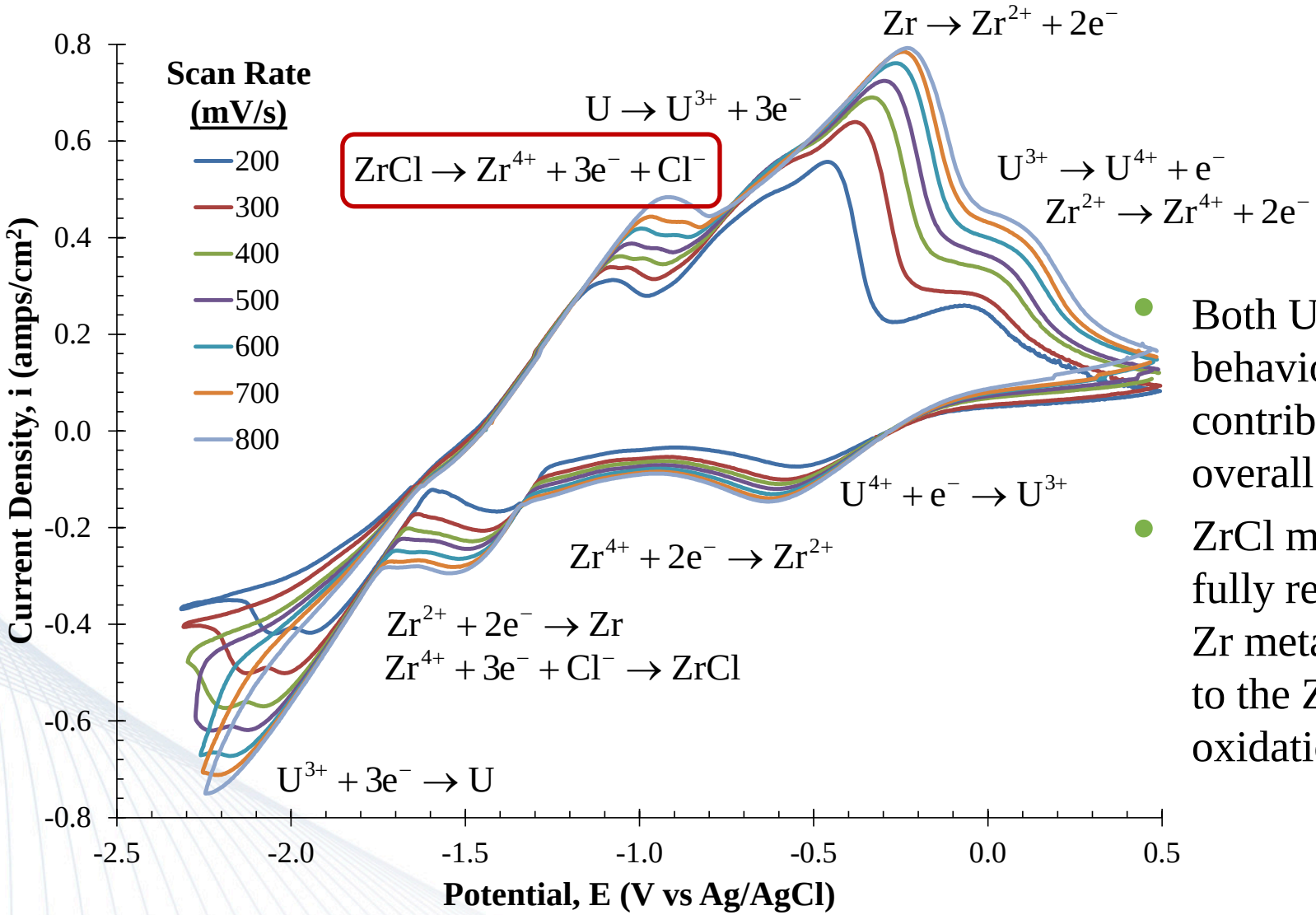
UCl_3-$ZrCl_4$-LiCl-KCl Electrochemistry

0.497 wt% $ZrCl_4$ and 9.80 wt% UCl_3 CVs



- Uranium behavior dominates with low $ZrCl_4$ concentration.
- Very small contribution of Zr reactions.

4.17 wt% $ZrCl_4$ and 8.34 wt% UCl_3 CVs



- Both U and Zr behaviors contribute to the overall CVs.
- ZrCl may not be fully reduced to Zr metal, leading to the ZrCl oxidation peak.

Summary

- The importance of Zr behavior in LiCl-KCl-UCl_3 to the electrochemical processing of used nuclear fuel has been discussed.
- A thorough and comprehensive literature review was performed.
  - Two important electrochemical and thermodynamic parameters were introduced along with previous studies.
    - Standard reduction potential, E^0
    - Diffusion coefficient, D
  - Three electrochemical techniques were identified as promising methods of determining these parameters.
    - Cyclic Voltammetry (CV)
    - Chronopotentiometry (CP)
    - Anodic Stripping Voltammetry (ASV)
- An experimental program was developed and performed using the identified methods to analyze the behavior of U and Zr in the molten LiCl-KCl eutectic.

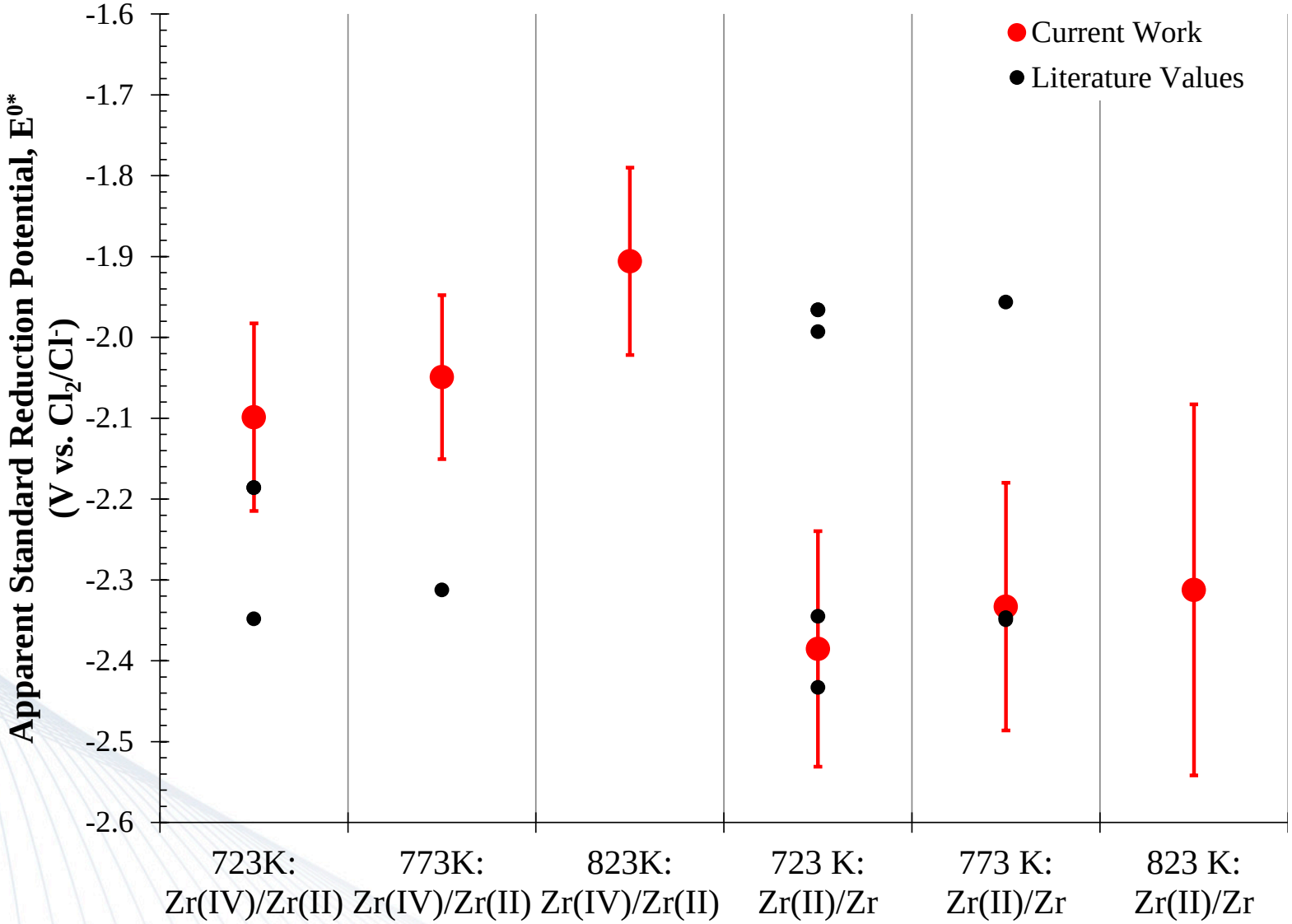
Summary – U & Zr Electrochemistry

- CV cathodic and anodic peaks were identified.

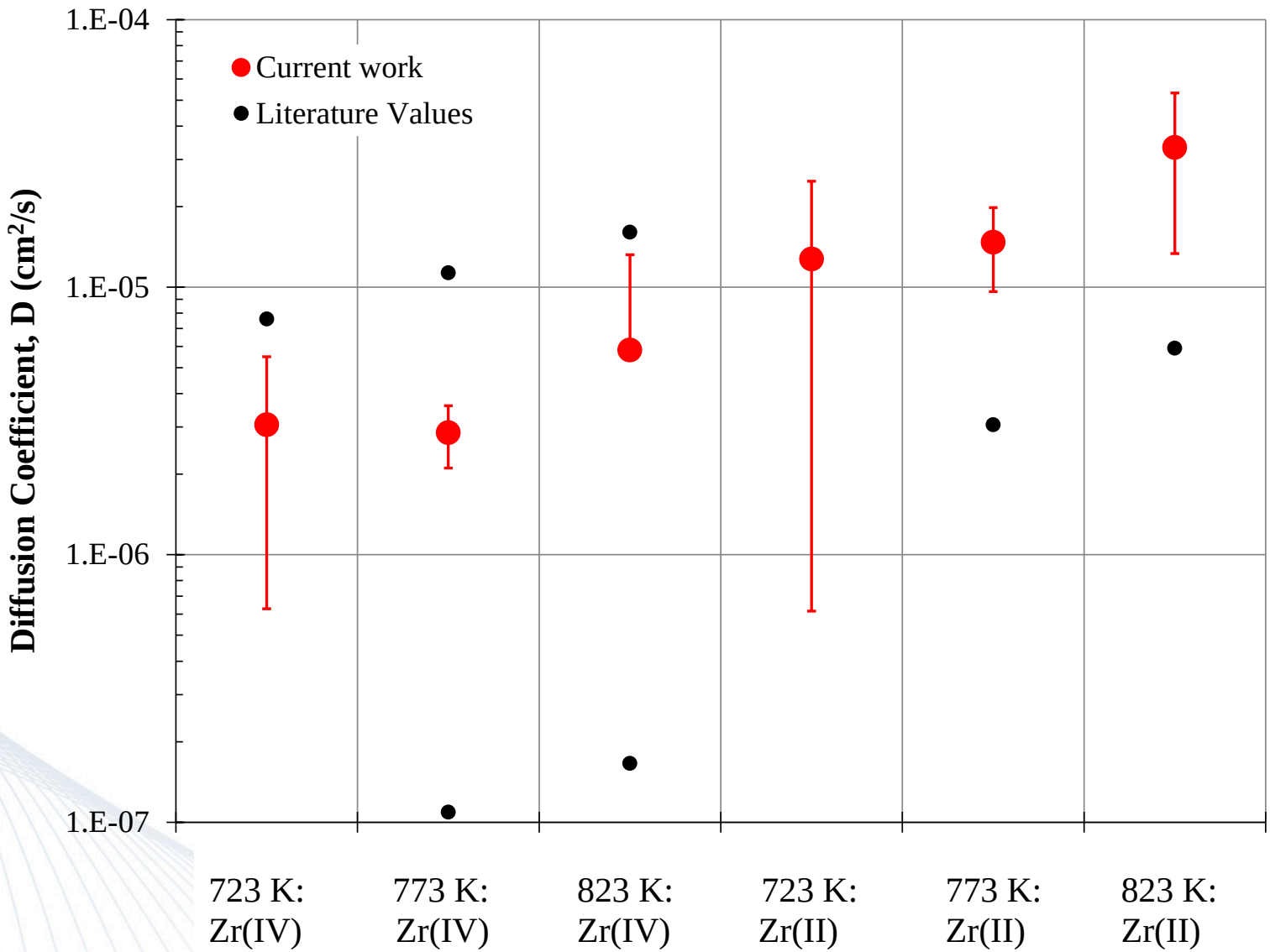
	Peak	Cathodic Reaction, Location	Anodic Reaction, Location	Reversibility
Zr	A	$Zr^{4+} + 2e^- \rightarrow Zr^{2+}$, –1.06 V	$Zr^{2+} \rightarrow Zr^{4+} + 2e^-$, shoulder near B_a	Irreversible
	B	$Zr^{2+} + 2e^- \rightarrow Zr$ and $Zr^{4+} + 3e^- + Cl^- \rightarrow ZrCl$, –1.5 V	$Zr \rightarrow Zr^{4+} + 4e^-$ and $Zr \rightarrow Zr^{2+} + 2e^-$, –0.5 V	Irreversible
	C	$ZrCl + e^- \rightarrow Zr + Cl^-$ and $Zr^{4+} + 4e^- \rightarrow Zr$, –1.85 V	NONE	Irreversible

- ASV was compared with CV as a potential in-situ concentration measurement technique.
  - CV cathode peak data shows the most promise.
- Diffusion coefficients, D, apparent standard reduction potentials, E^{0*}, and activity coefficients, γ, were calculated at 723-823 K.
- Due to the large variation in theoretical data, from which γ is calculated, it is recommended that the experimentally determined E^{0*} be used in place of E^0 and γ.

Summary – Apparent Standard Reduction Potential



Summary – Diffusion Coefficient



Recommended Future Work

- There are several recommendations for future work based on this study:
  - The standard rate constants, k_s, for the Zr reactions are necessary to improve the accuracy of the calculated apparent standard reduction potentials.
    - These values could be determined from experimental potentiostatic electrochemical impedance spectroscopy (P-EIS) data.
    - This data was collected for the zirconium experiments and detailed analysis of these data sets is recommended.
  - The exchange current density, i_0, is an additional electrochemical parameter that is required for accurate modeling work. It is directly related to the standard rate constant

Acknowledgements

- This work was performed by University of Idaho as part of an International Nuclear Energy Research Initiative project (I-NERI 2010-001-K) with Idaho National Laboratory (INL), Seoul National University (SNU), and Korea Atomic Energy Research Institute (KAERI).

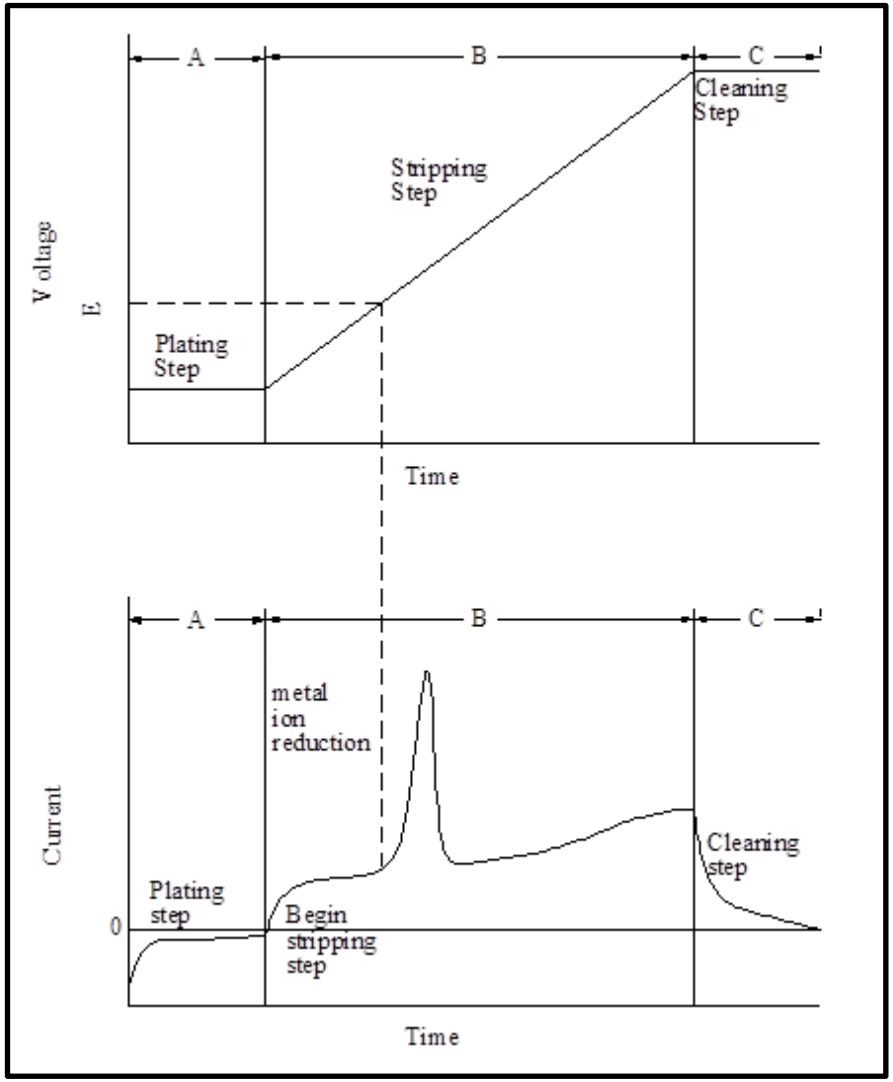
- Thanks to all who have helped out with this work including, but not limited to:
  - INL: Dr. Michael Simpson and Dr. Tae-Sic Yoo
  - SNU: Prof. Il-Soon Hwang, Jaeyeong Park, Sungjune Sohn
  - KAERI: Dr. Kwang-Rag Kim
  - UI: Michael Shaltry, Ammon Williams, Josh Versey, Debbie Lacroix, Joanna Taylor, and Sean Martin (U. Wisc.)

Supplementary Slides

Anodic Stripping Voltammetry (ASV)

- ASV is an electrochemical method that can be used to take advantage of the relationship between concentration and peak current in linear sweep voltammetry.
- The analyte is plated onto the working electrode for a known period of time.
- Potential is linearly ramped, causing the analyte to oxidize, resulting in a current peak.
- Without plating time, Delahay equation provides the relationship.

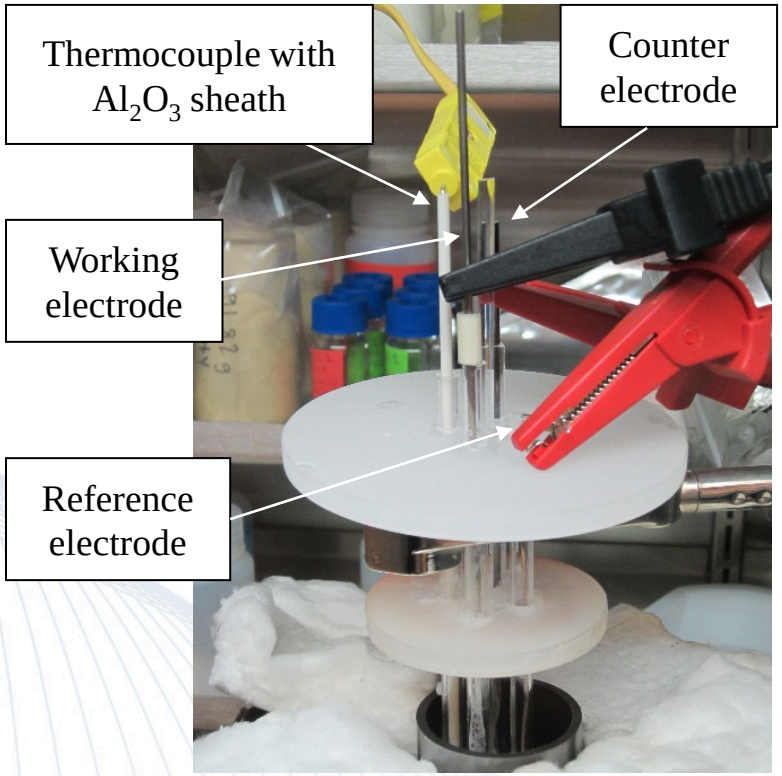
$$\frac{I_p}{\sqrt{\nu}} = 0.4958nFAC\sqrt{\frac{n\alpha FD}{RT}}$$

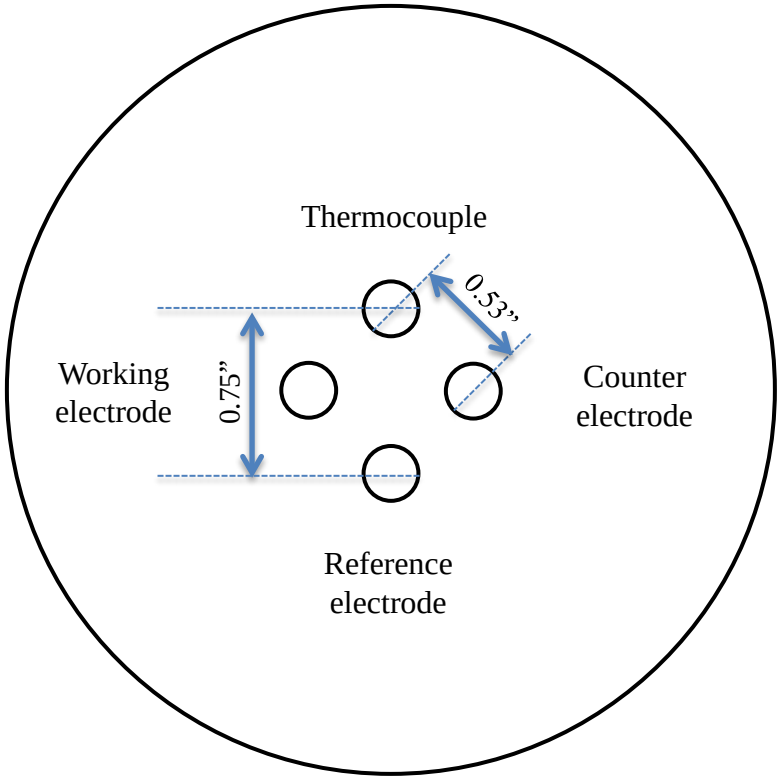


Sridharan, et al., "Thermal Properties of LiCl-KCl Molten Salt for Nuclear Waste Separation," US DOE, NEUP Final Report Project No. 09-780 (2012).

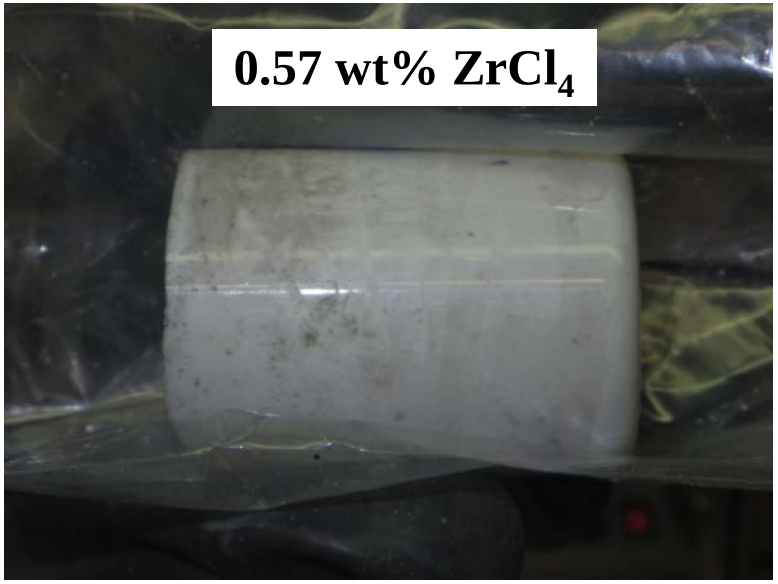
Experimental Equipment

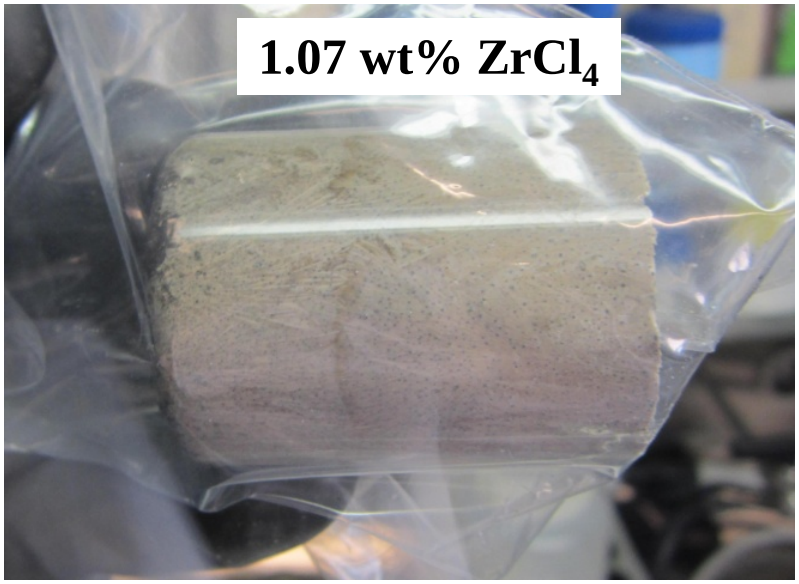
- A quartz electrode assembly was used to position the electrodes and thermocouples at reproducible locations.

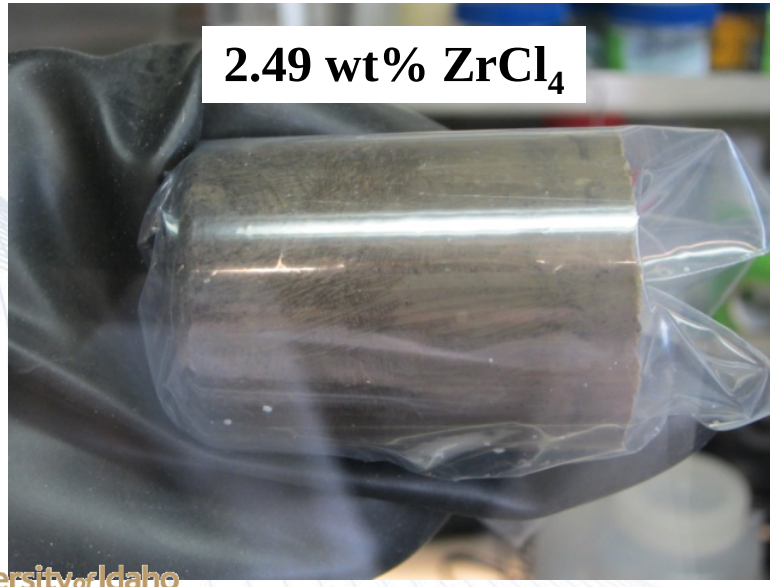


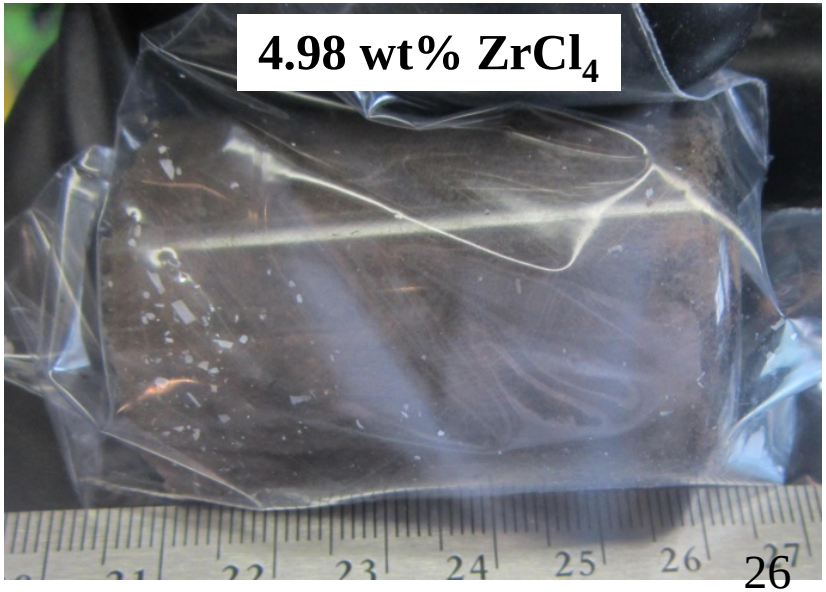


$ZrCl_4$-LiCl-KCl Salt Ingots

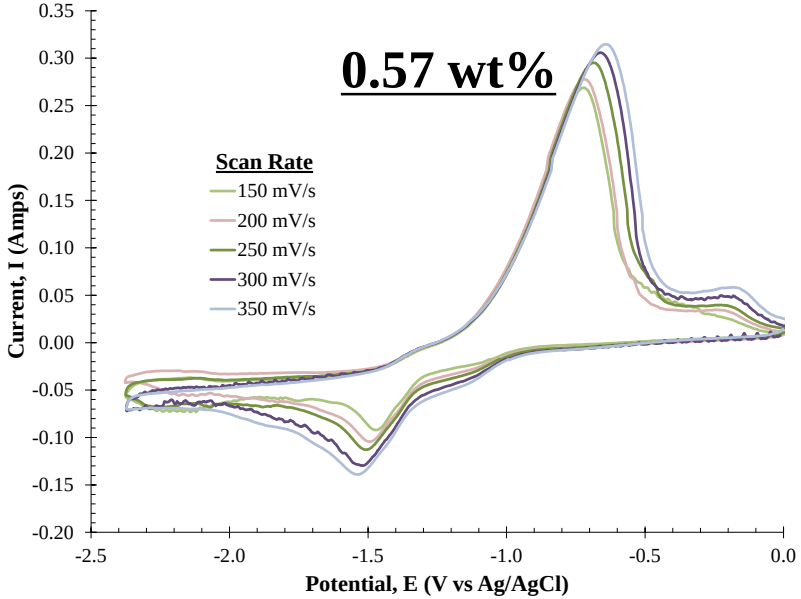


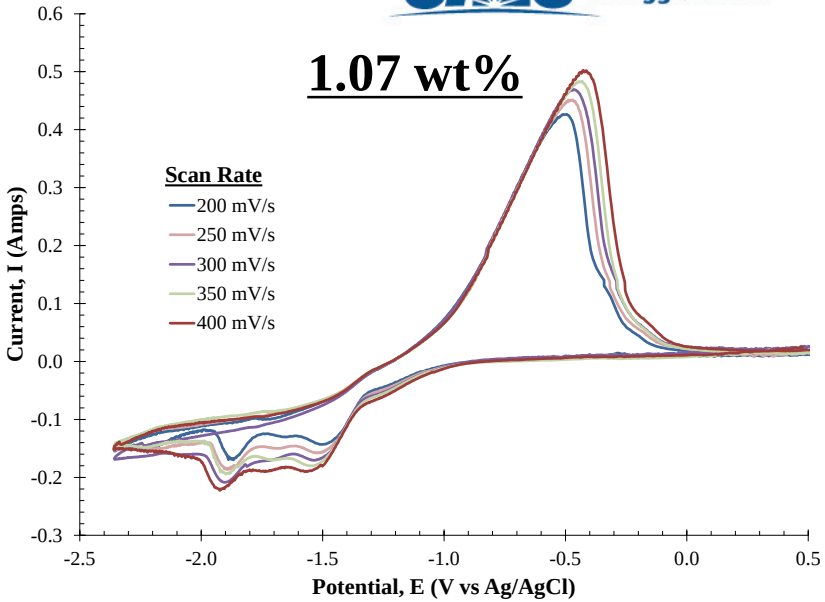


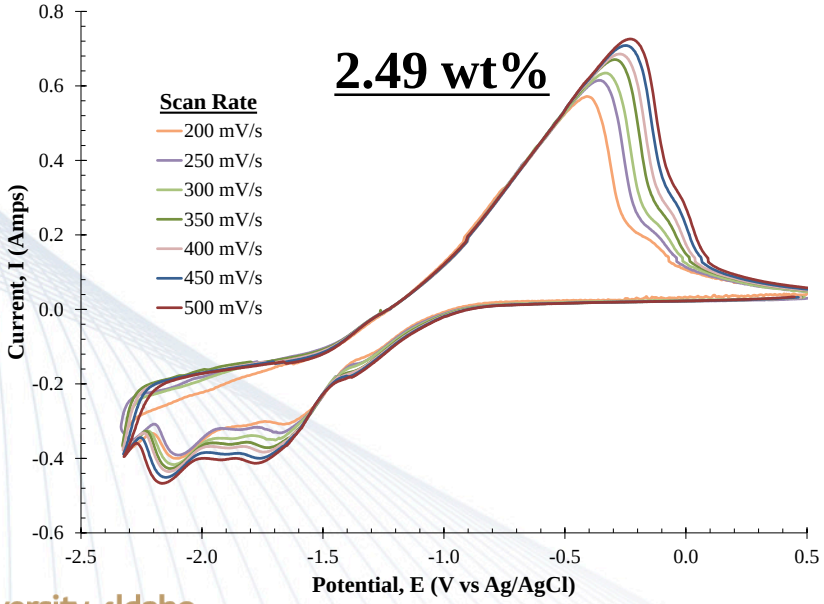


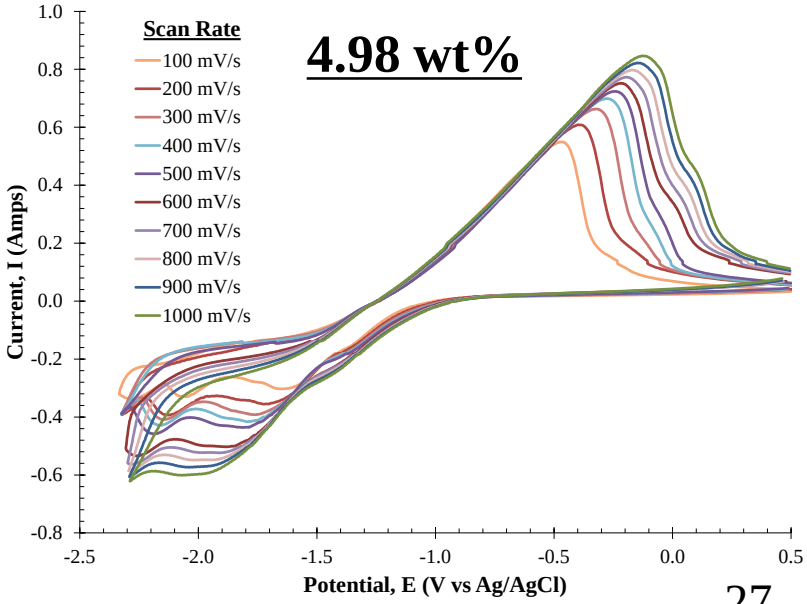


Results: $ZrCl_4$ CVs (723 K)









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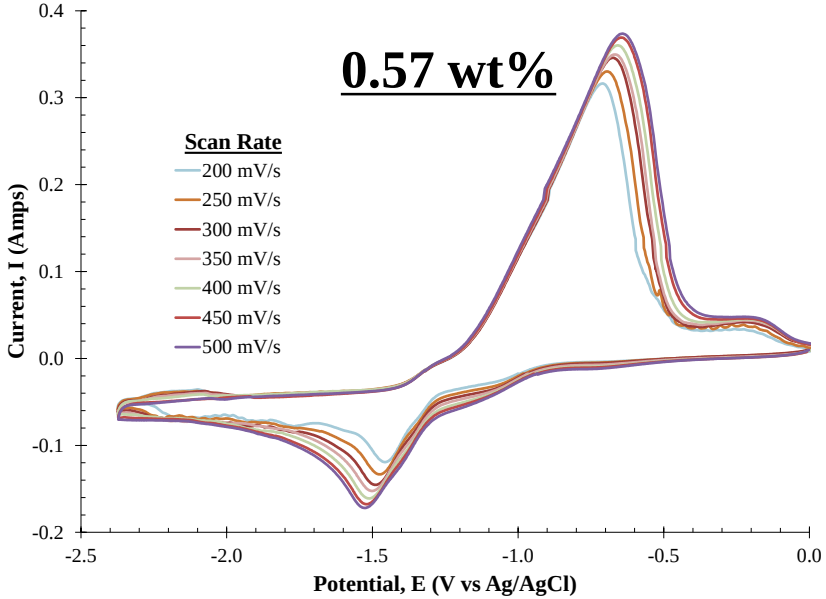
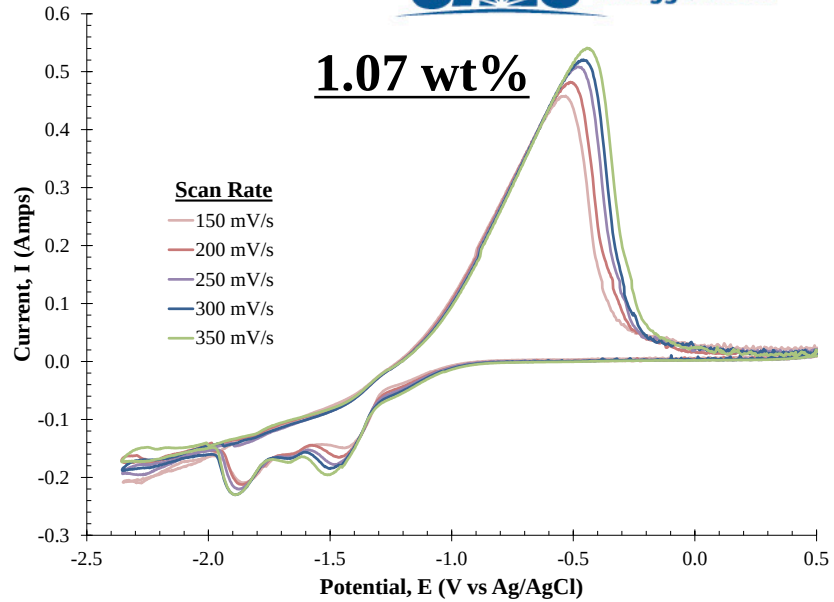
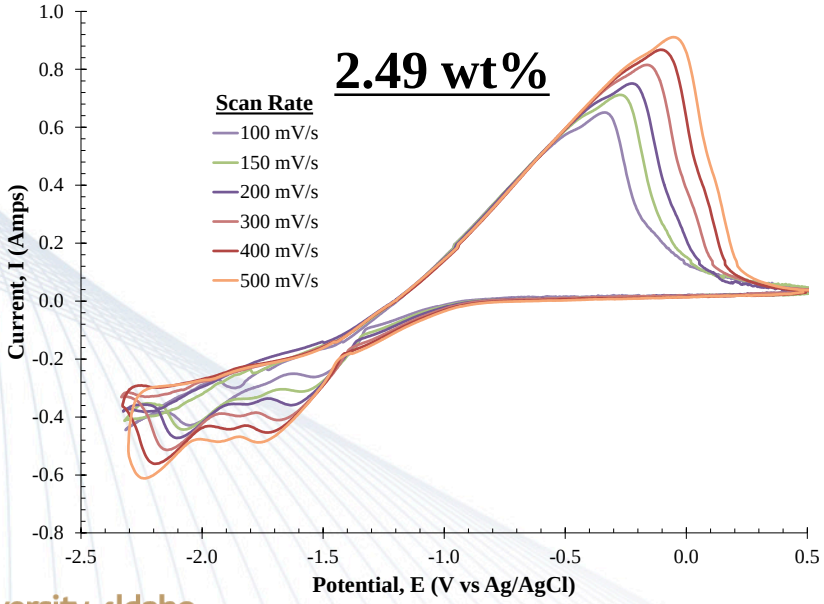
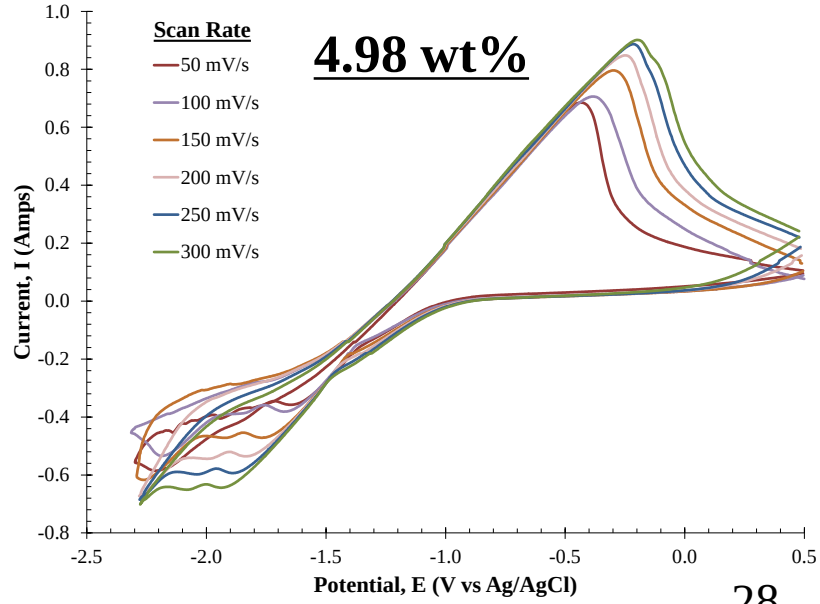
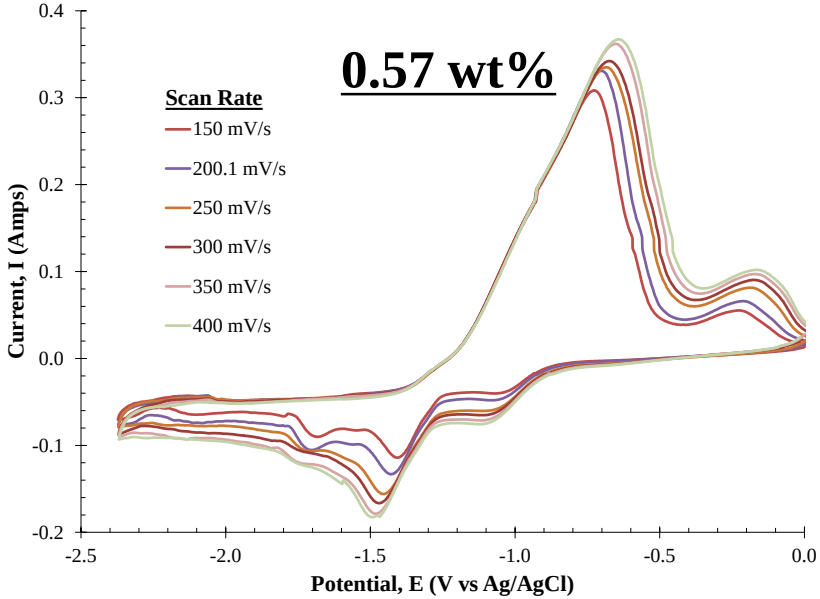


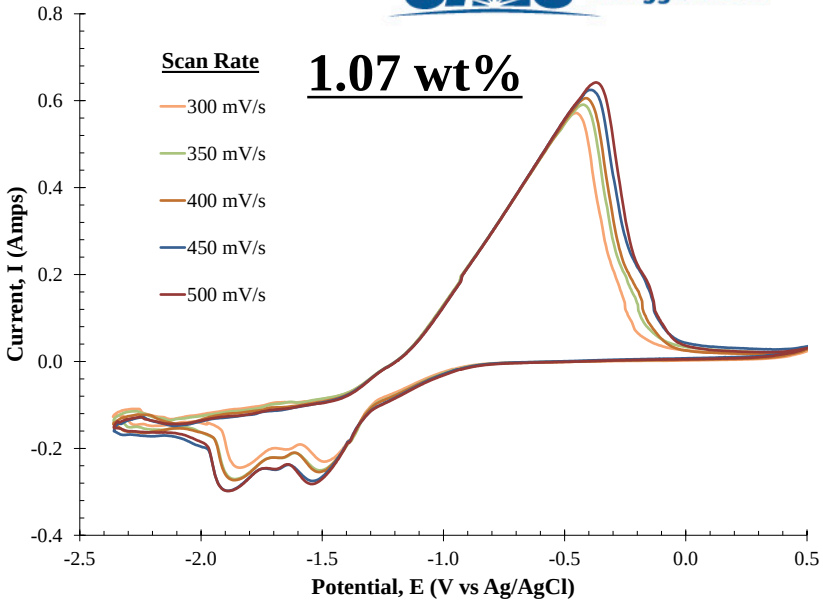


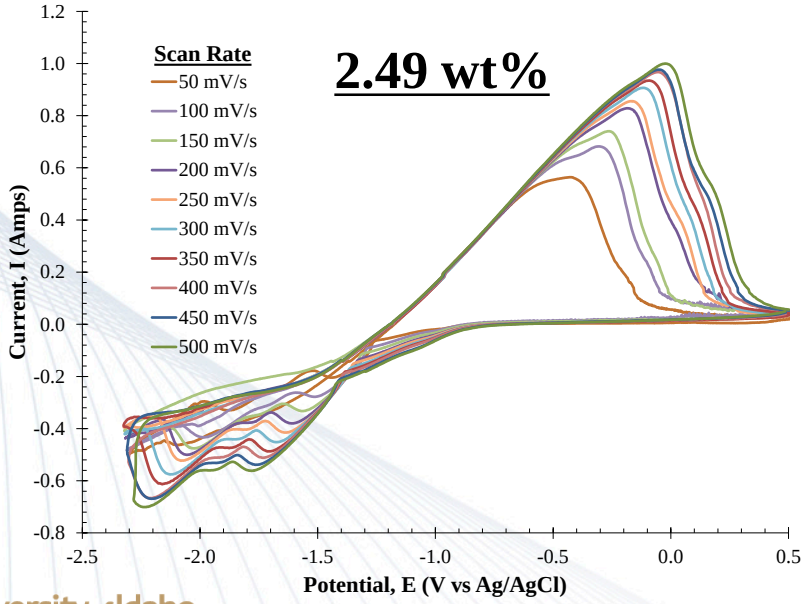


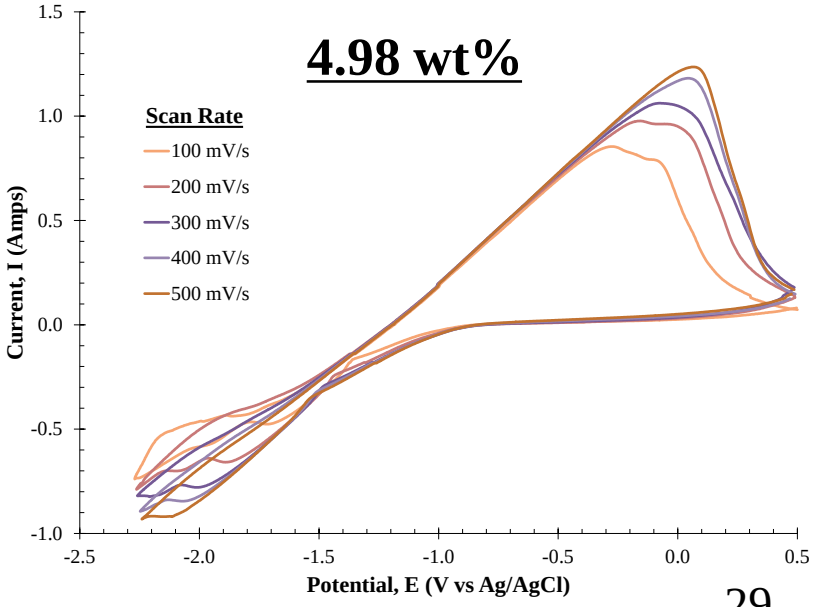


Results: $ZrCl_4$ CVs (823 K)

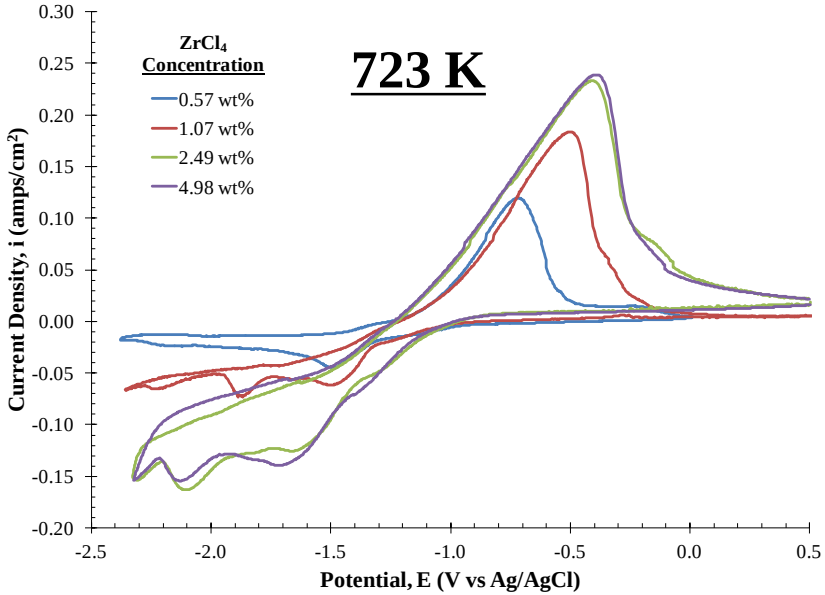


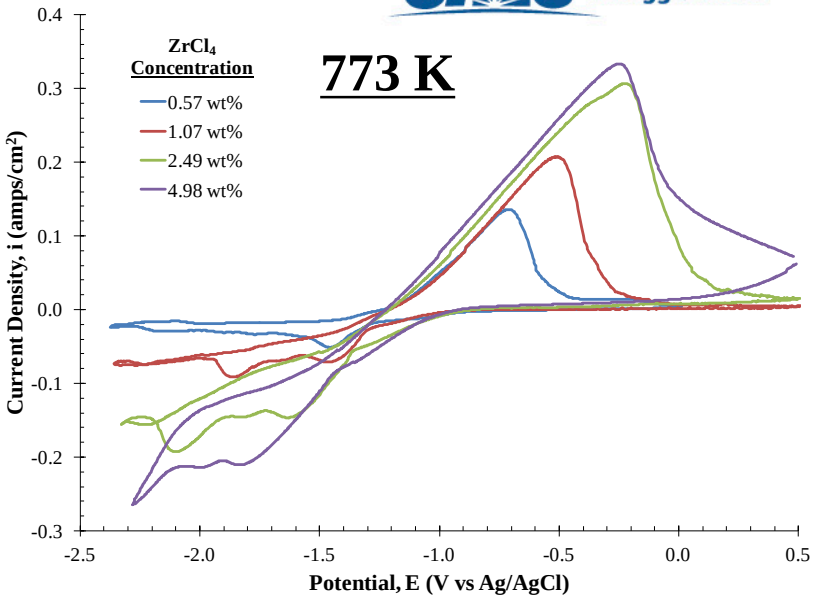


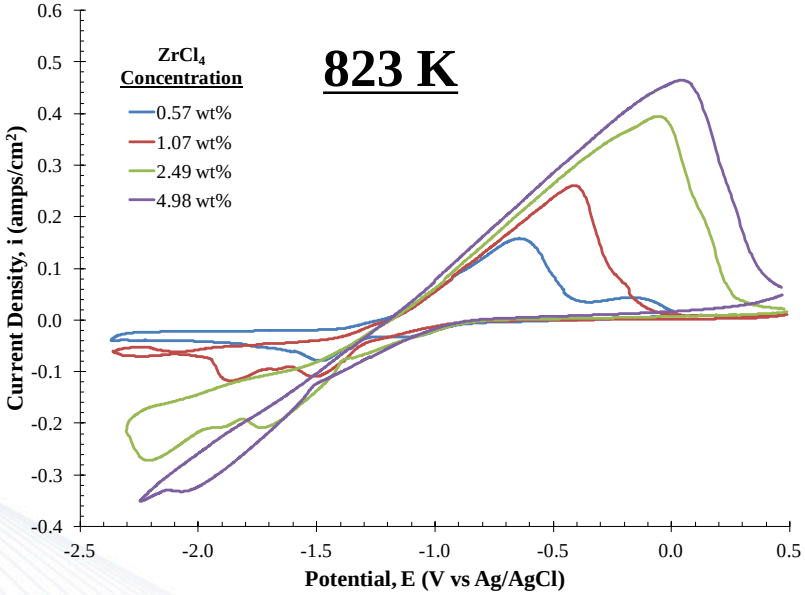
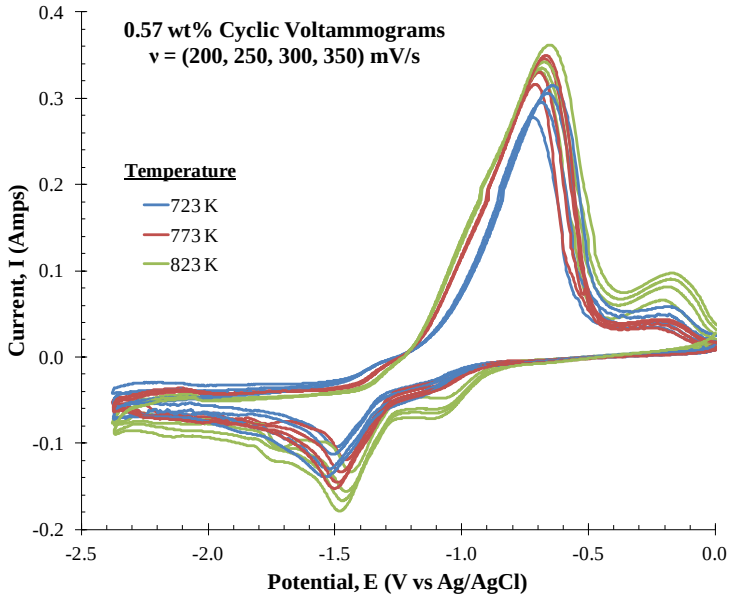
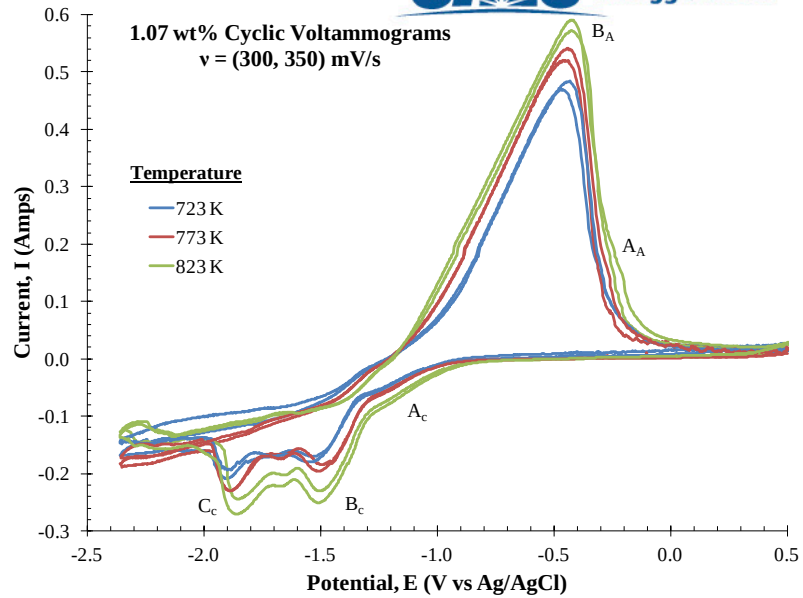
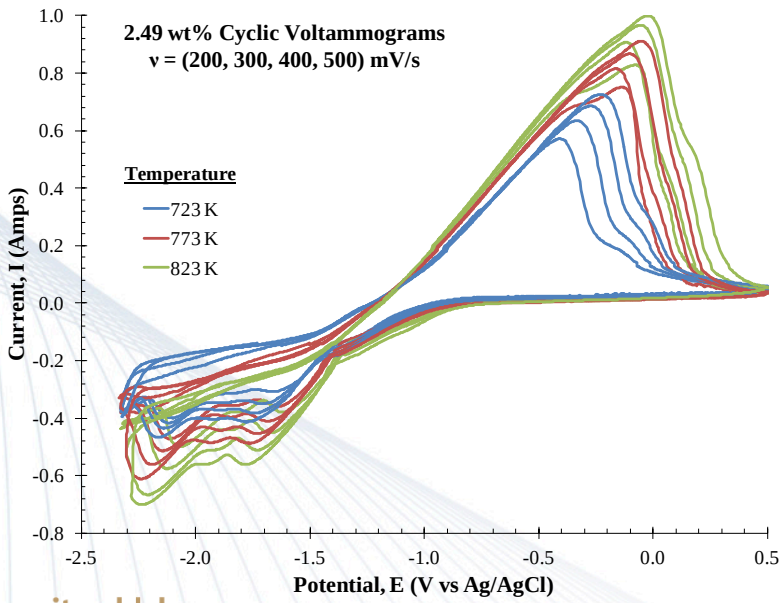
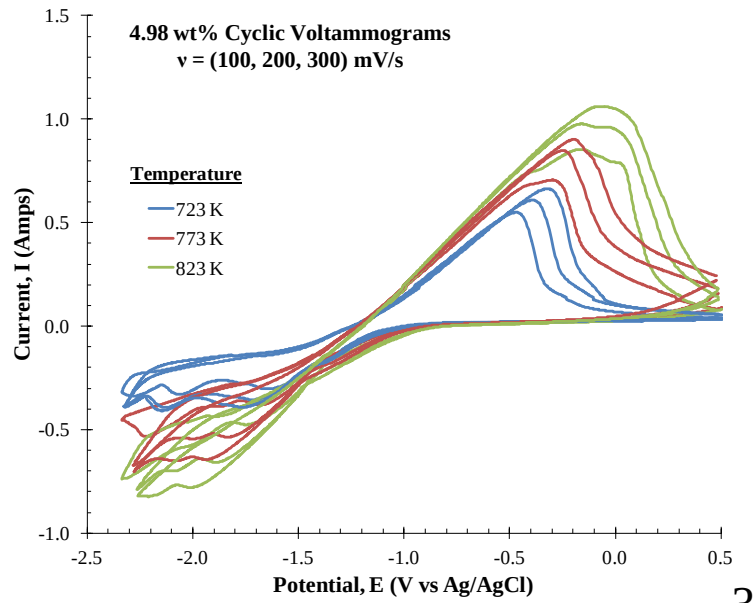




$ZrCl_4$ Concentration Effects







$ZrCl_4$ Temperature Effects