Feasibility Study of Pyrochemical Treatment on Fuel Debris by Performing U and Zr Electrochemistry in LiCl-KCl Molten Salt

Supathorn (Supy) Phongikaroon, Ph.D., P.E.
Associate Professor

VCU | Virginia Commonwealth University
Department of Mechanical & Nuclear Engineering

CAES
Center for Advanced Energy Studies

Vandals

International Experts Meeting on
Strengthening Research and Development Effectiveness
in the Light of the Accident at the Fukushima Daiichi Nuclear Power Plant
16–20 February 2015
Vienna, Austria

Outline

- Brief Background
- Motivation and Goal
- Experimental Program
- Basic Electrochemistry
- Results and Discussion
- Conclusion

Background

- In the light of the accident at the Fukushima Daiichi NPP,
  - 3 Phases existed for mid- and long-term plans

1st: 2 years
Fuel removal from the pool

2nd: Next 10 years
Removal of fuel debris

3rd: In 30 – 40 years
Removed, processed, and disposed fuel debris with proper waste management

- Technical plans in various aspects:
  - Direction on recovery and treatment,
  - Characterization,
  - Conditions and long term performances, and
  - **Possibility of treatment path for toxicity reduction**.

Separation Methods

- Possible fuel debris treatments due to previous studies on debris samples in TMI-2.
- Aqueous and Pyrochemical separation methods
  - PUREX –dissolving in nitric acid and fluoric acid showing that neither 6 N HNO_3 nor 3 M HNO_3 + 1 M HF mixture could be used to dissolve the actual debris.
  - Japan Atomic Energy Agency (JAEA) and Central Research Institute of Electric Power Industry (CRIEPI) – advantage on pyrochemical treatment in term of solubility of debris and secondary waste volume through oxide reduction tests.

Motivation and Goal

- No fundamental experiment to further gain insight in reprocessing of the fuel debris after electrolytic oxide reduction step.

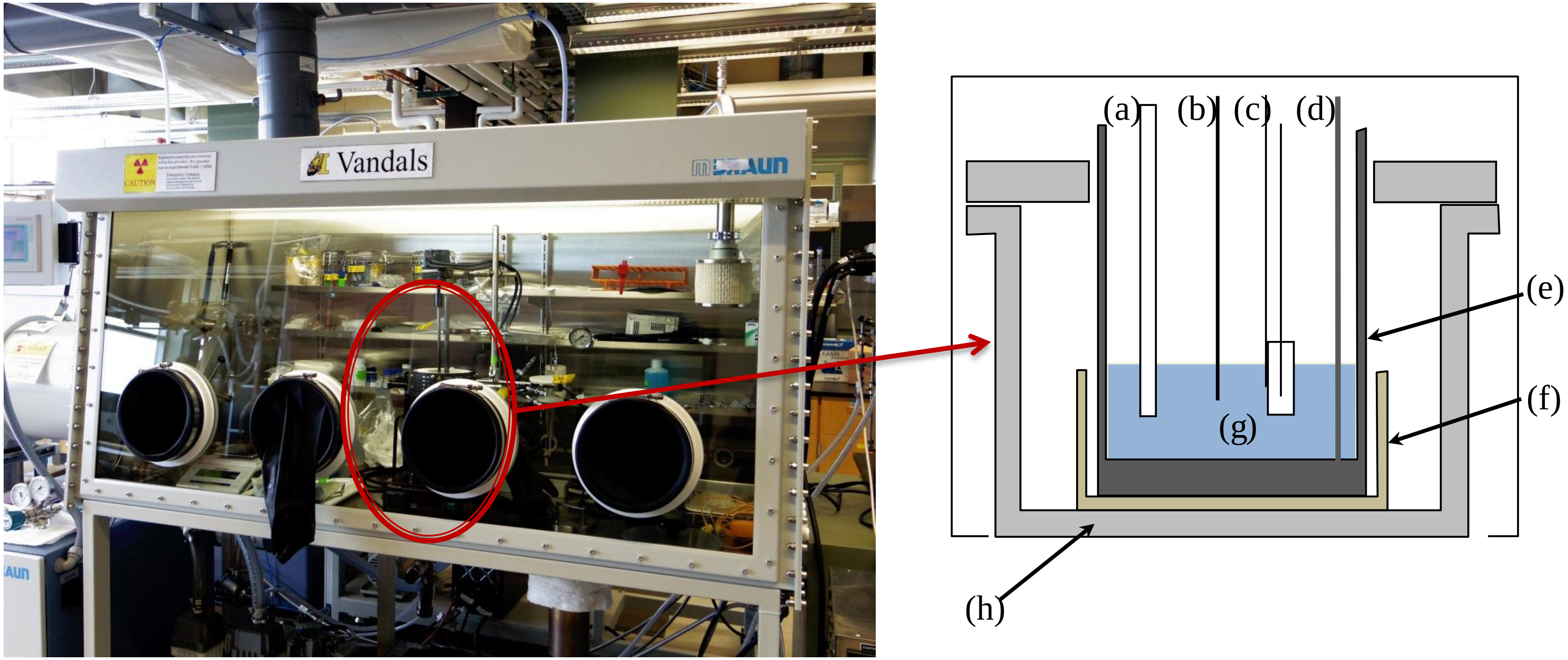
Motivation

Explore concentration effects on thermodynamic and electrochemical properties for U and Zr in LiCl-KCl molten salt system under common electroerefiner's conditions.

Goal

Gain fundamental understanding and path forward in applying pyrochemical process in order to separate U and Zr efficiently.

Experimental Program



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

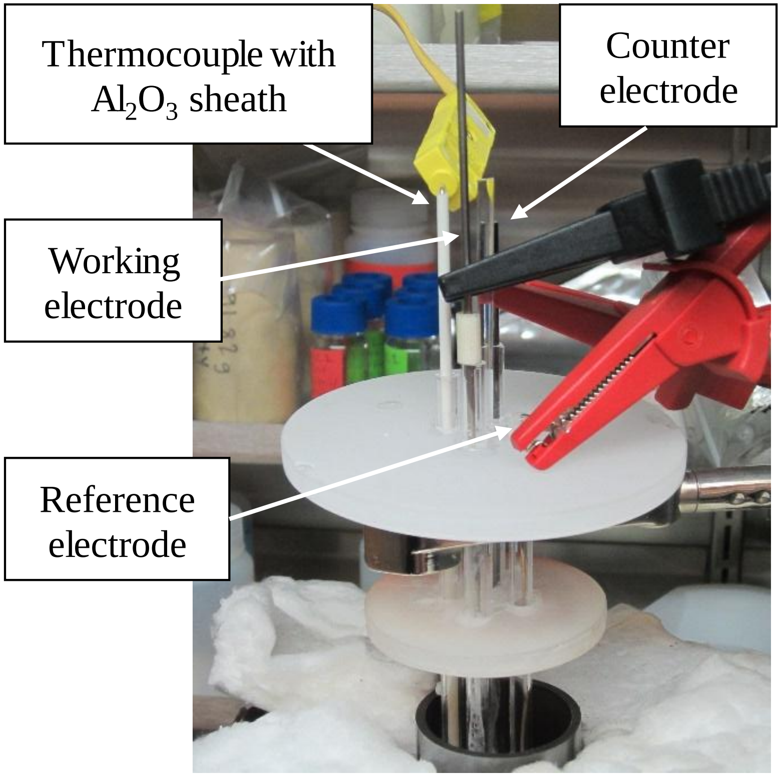
f) MgO secondary crucible

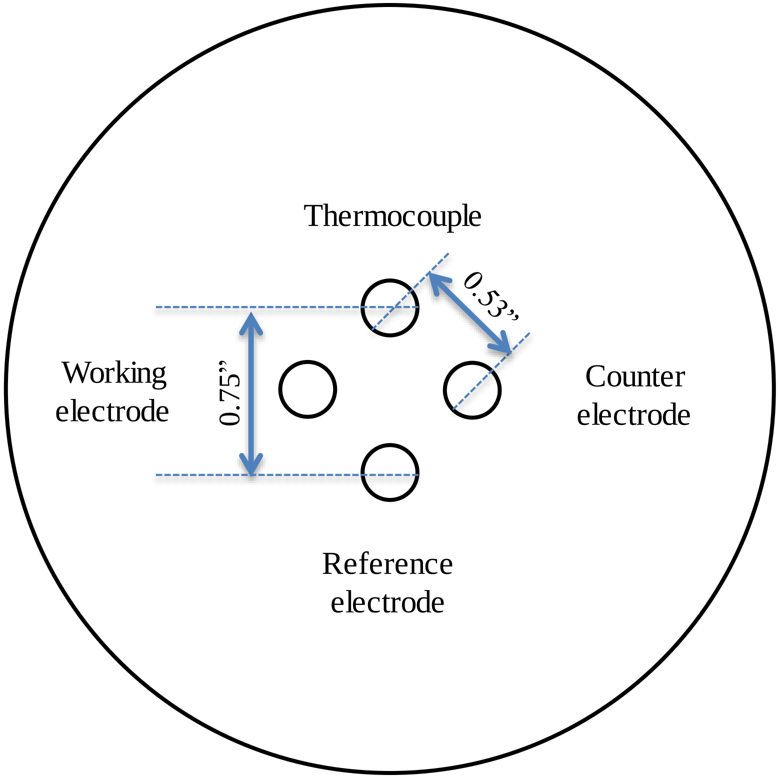
g) Eutectic LiCl-KCl (99.99%) containing $dUCl_3$ (75 wt%) or $ZrCl_4$ (99.95+%)

h) Kerrlab furnace

Experimental Equipment

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





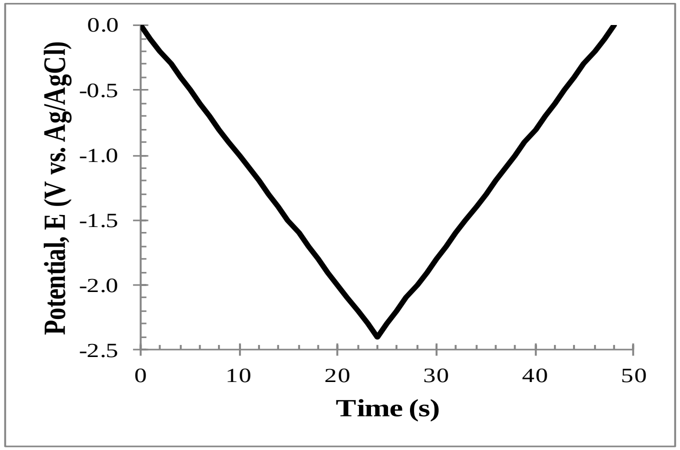
Data Collection

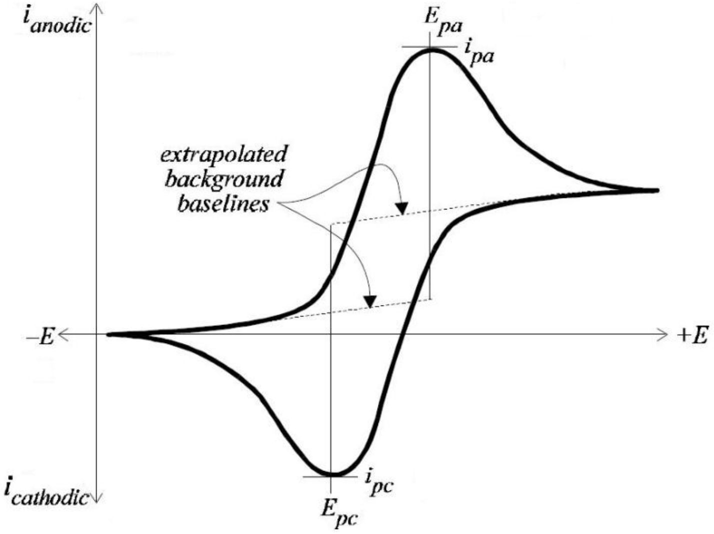
- All experiments were performed and all data was collected with a Princeton Applied Research VersaSTAT 4-400 potentiostat and *VersaStudio* software.
- The raw data was imported into Excel for further analysis.
- Following the electrochemical data collection, the working electrode was removed from the salt and the wetted length was measured to determine the active surface area.

Cyclic Voltammetry (CV)

- A common electrochemical technique that can be used to determine information about the reactions that occur in an electrochemical cell.
- Potential is repeatedly scanned from one vertex potential to another at a constant scan rate, ν.
- Reduction and oxidation reactions occur at the electrode surface resulting in cathodice (negative current) and anodic (positive current) peaks, respectively.
- Equilibrium potential

$$E = \frac{E_{pa} + E_{pc}}{2}$$





From the resulting current, reaction information can be determined.

- Reversible: soluble/soluble
  - Randles-Sevcik equation

$$\frac{I_{pc}}{\sqrt{\nu}} = 0.4463nFAC\sqrt{\frac{nFD_{ox}}{RT}}$$

$$\frac{I_{pa}}{\sqrt{\nu}} = 0.4463nFAC\sqrt{\frac{nFD_{red}}{RT}}$$

  - Apparent standard potential

$$E = E^{0*} + \frac{RT}{nF}\ln\left(\sqrt{\frac{D_{red}}{D_{ox}}}\right)$$

- Irreversible
  - Electrons transferred (irreversible)

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

  - Delahay equation (irreversible)

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

  - Peak Potential (irreversible)

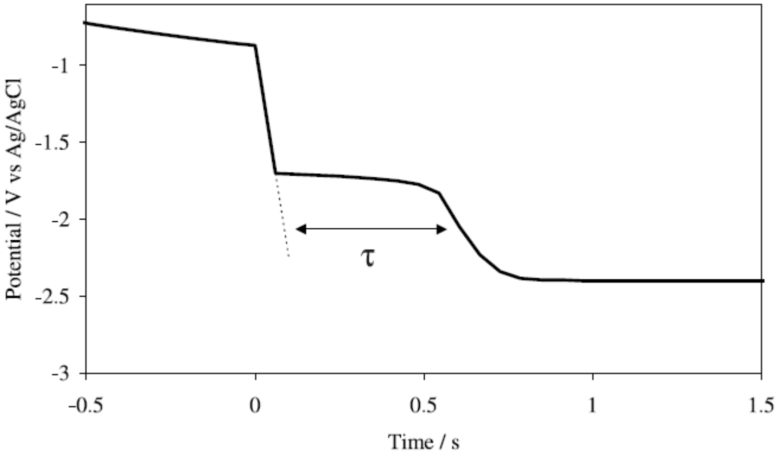
$$E_{pc} = E^{0*} - \frac{RT}{n\alpha F}\left[0.78 - \ln k_s + \ln\sqrt{\frac{n\alpha F\nu D_{ox}}{RT}}\right]$$

A	Electrode surface area	$E_{p/2}$	Half-peak potential
C	Concentration	k_s	Standard rate constant

Chronopotentiometry (CP)

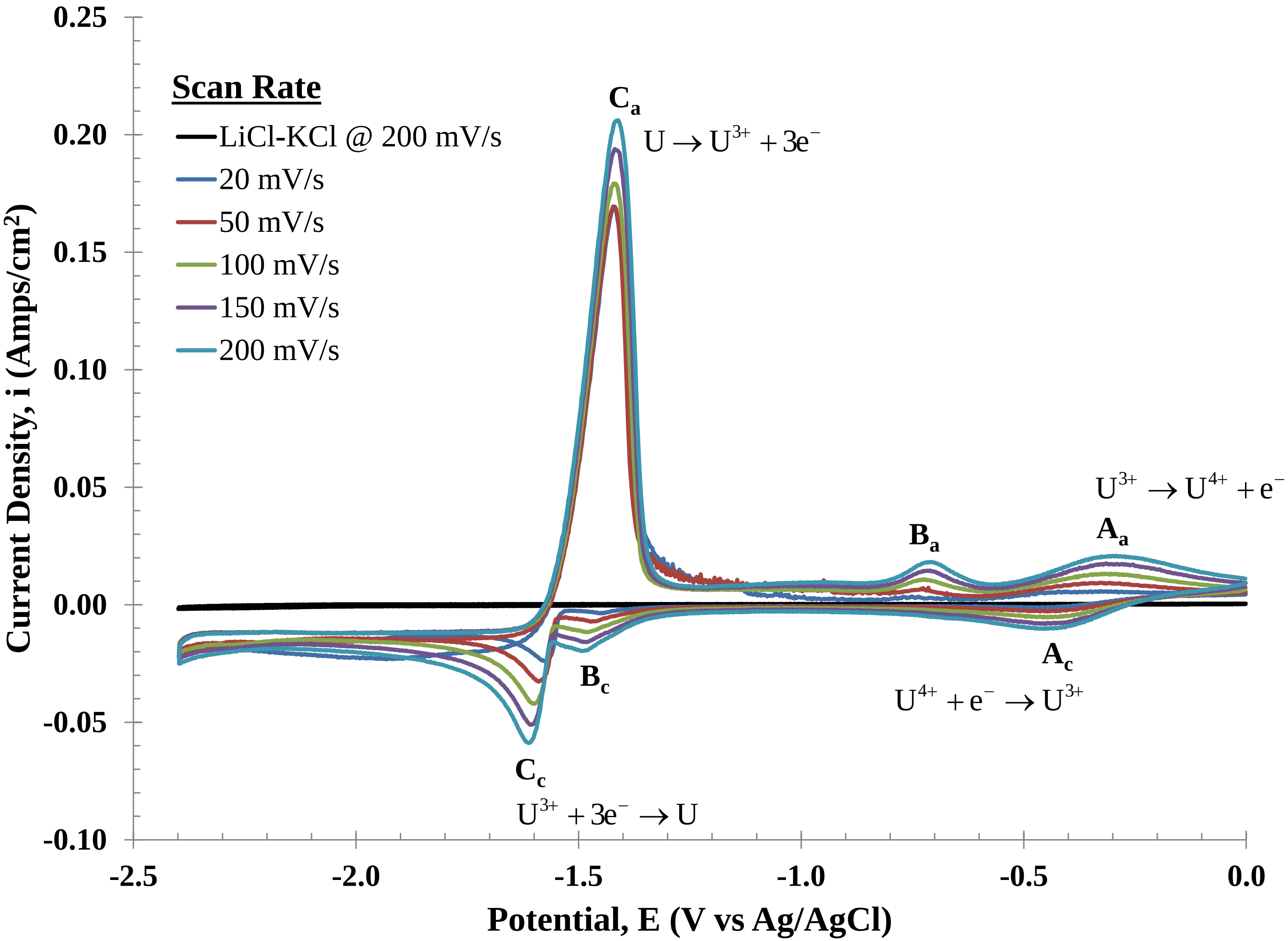
- An current-controlled technique that can be used to study time-dependent concentration change in a solution.
- A large driving current, I_d, is applied and the resulting potential is measured as a function of time.
  - To maintain the applied current, potential drops to a value at which ions of a given species are reduced.
  - When the ion is fully reduced at the electrode surface the potential further drops to reduce the next ion.
  - The time of this potential transition is the transition time, τ.

$$I_d\sqrt{\tau} = \frac{nFAC\sqrt{\pi D_{ox}}}{2}$$



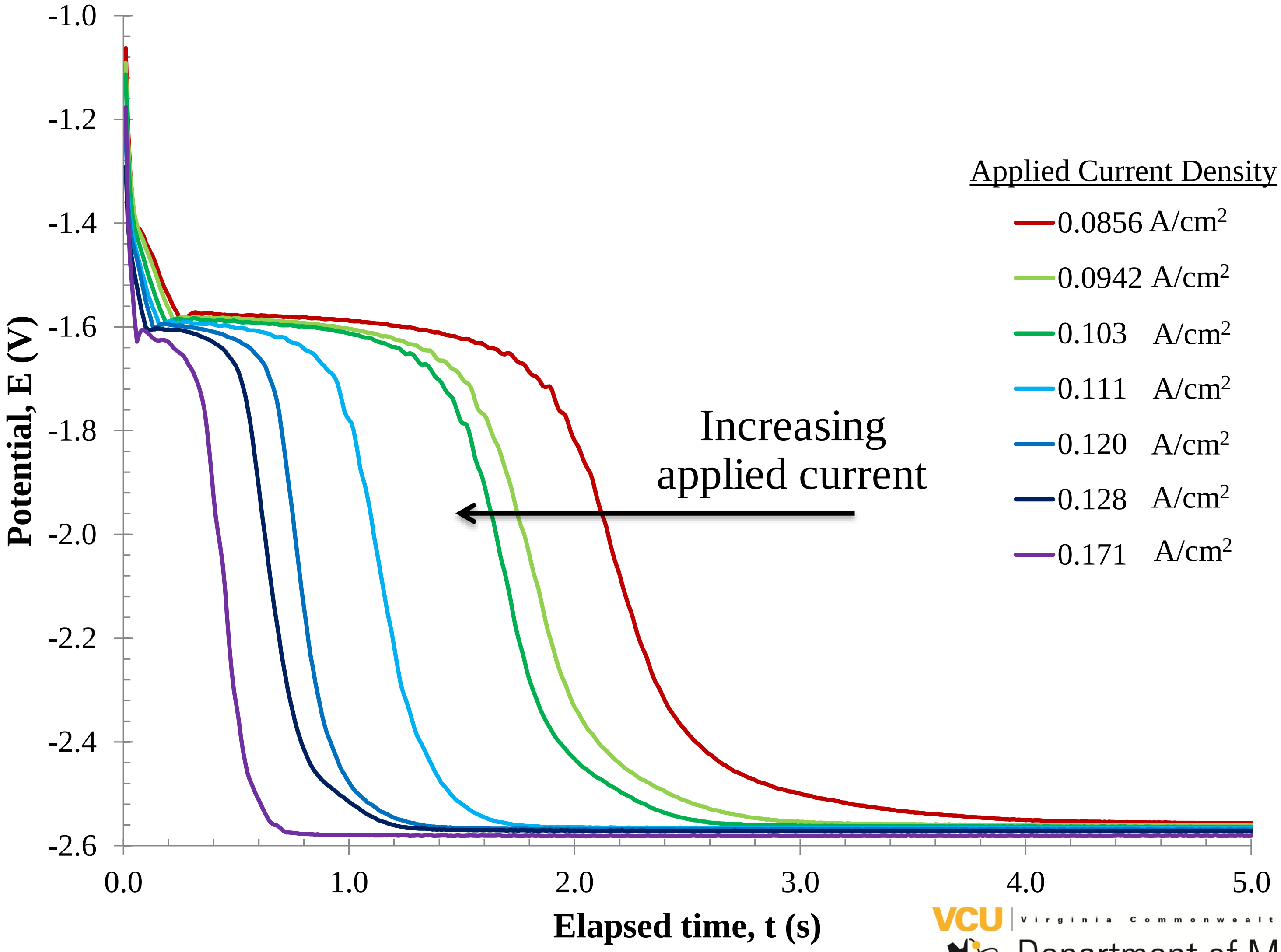
Ref: Serp, et al., "Electrochemical Behaviour of Plutonium Ion in LiCl-KCl Eutectic Melts," *Journal of Electroanalytical Chemistry*, **561** (2004).

Results: 1.0 wt% UCl_3 CV (773 K)

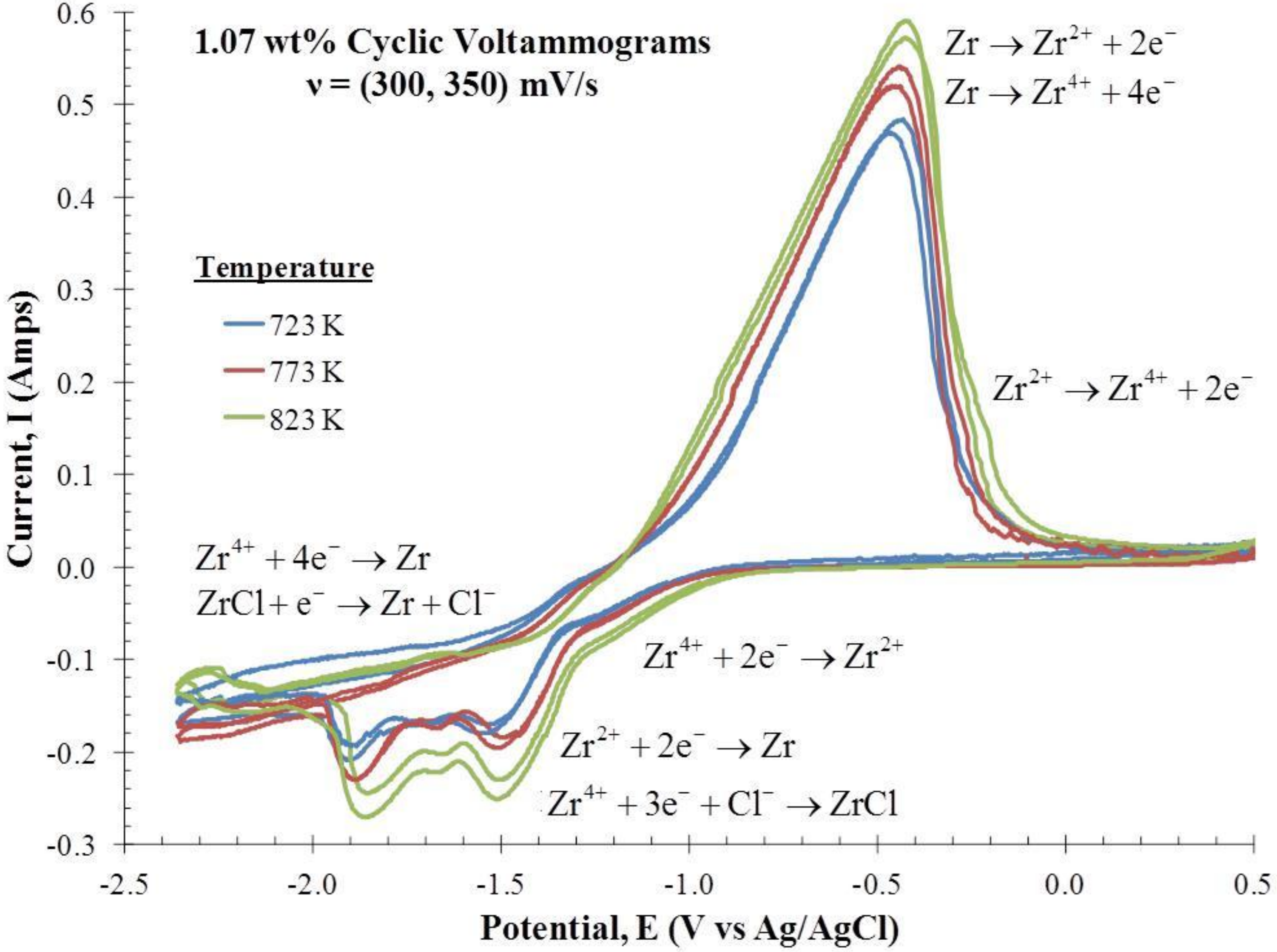


VCU | Virginia Commonwealth University
Department of Mechanical & Nuclear Engineering

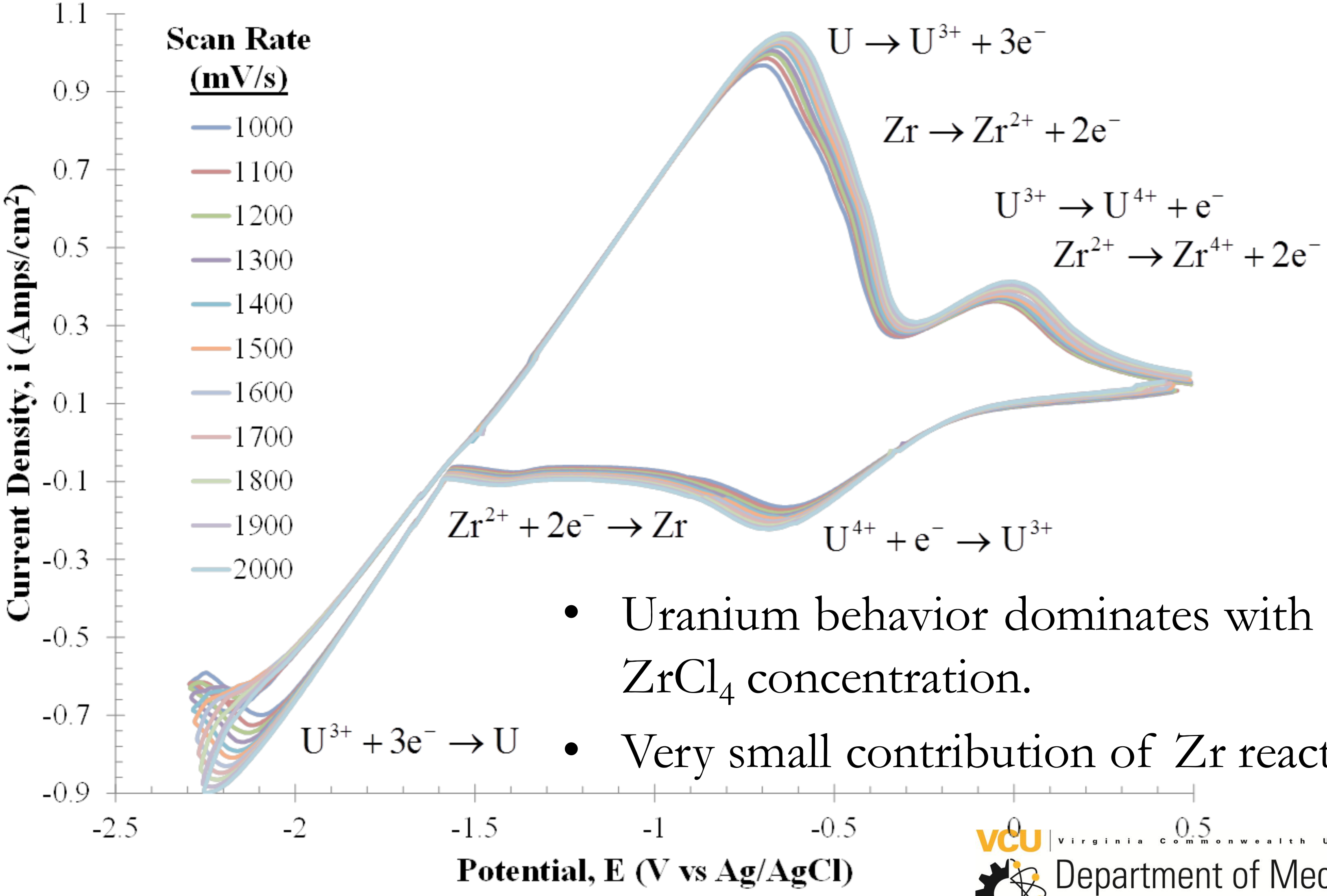
Results: 2.5 wt% UCl_3 CV (773 K)



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

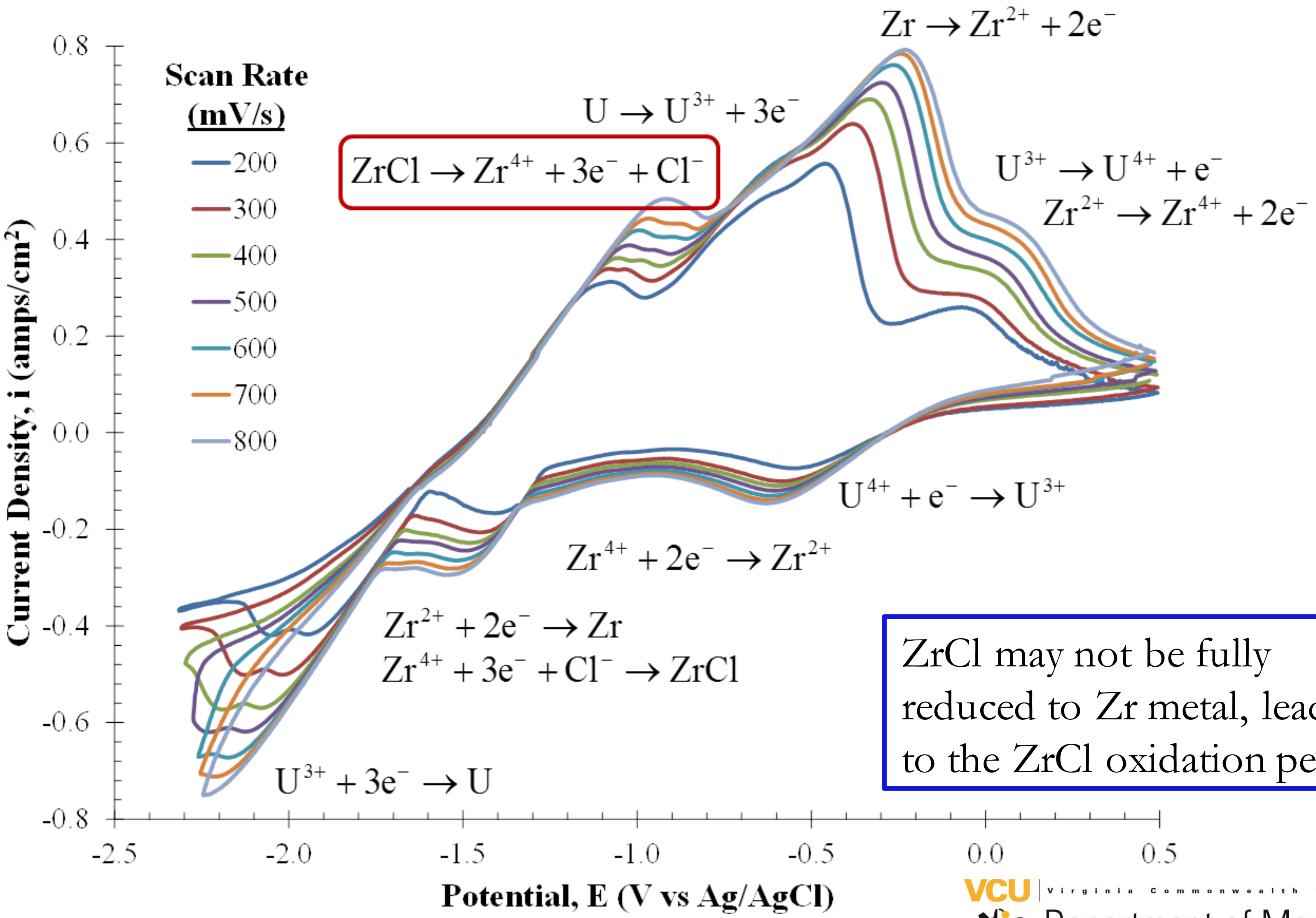


Results: 0.497 wt% $ZrCl_4$ and 9.80 wt% UCl_3



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

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



ZrCl may not be fully reduced to Zr metal, leading to the ZrCl oxidation peak.

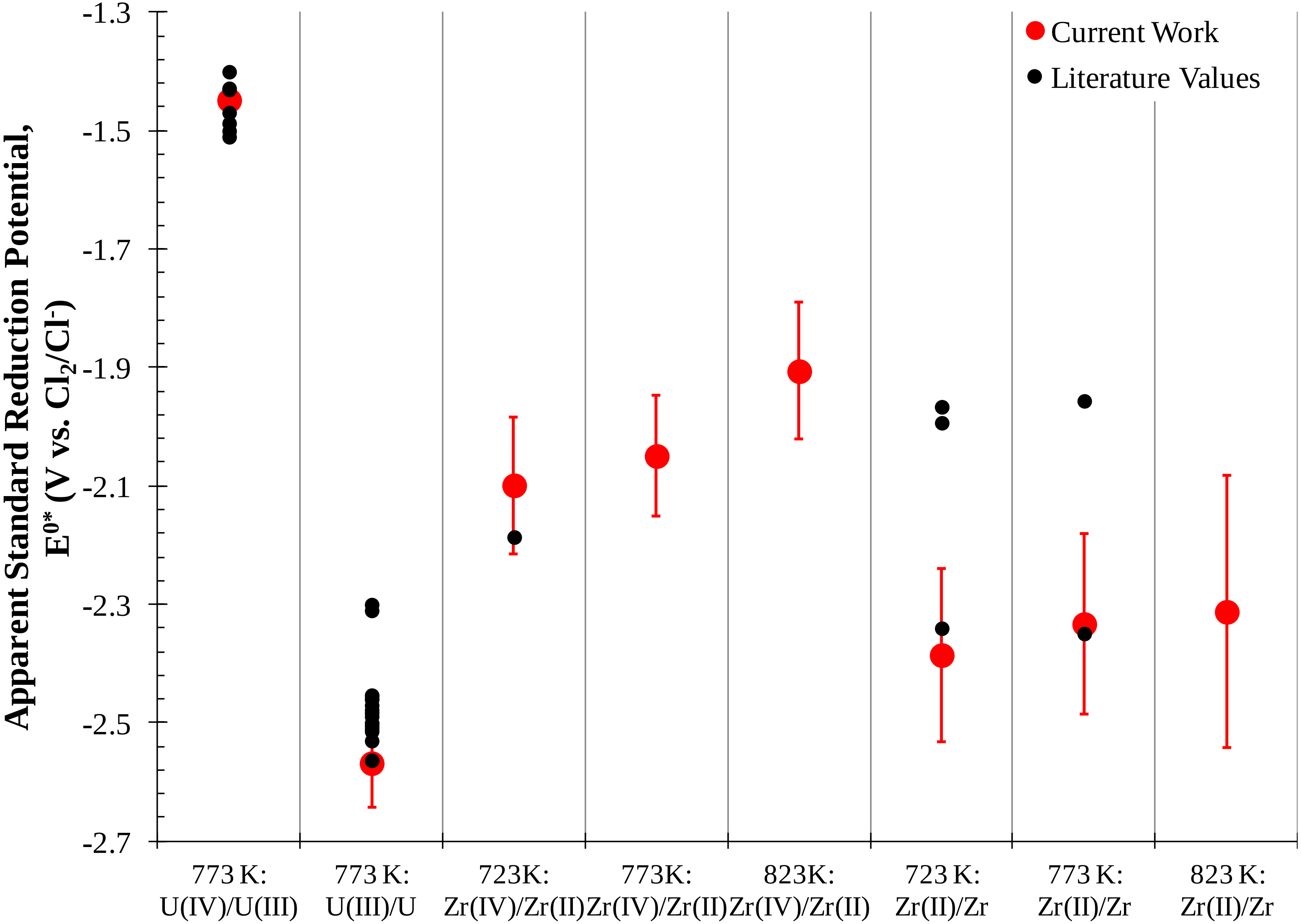
Summary

- CV cathodic and anodic peaks were identified.

	Peak	Cathodic Reaction, Location	Anodic Reaction, Location	Reversibility
U	A	$U^{4+} + e^- \rightarrow U^{3+}$, –0.5 V	$U^{3+} \rightarrow U^{4+} + e^-$, –0.3 V	Reversible
	B	Adsorption U^{3+}, –1.5 V	Desorption U^{3+}, –0.7 V	N/A
	C	$U^{3+} + 3e^- \rightarrow U$, –1.6 V	$U \rightarrow U^{3+} + 3e^-$, –1.4 V	Irreversible
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

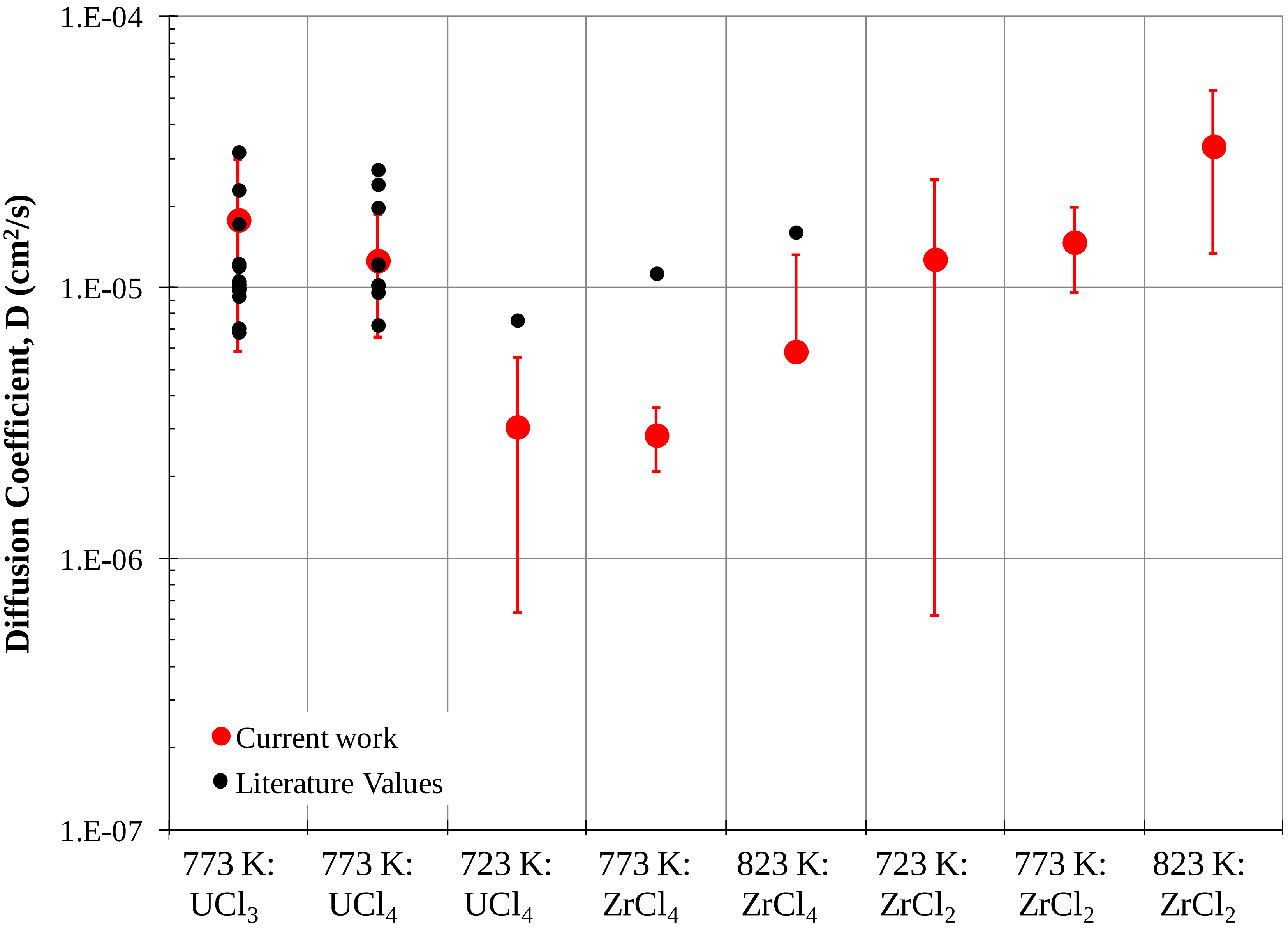
Summary

Apparent Standard Reduction Potential



VCU | Virginia Commonwealth University
Department of Mechanical
& Nuclear Engineering

Summary – Diffusion Coefficient



Acknowledgements

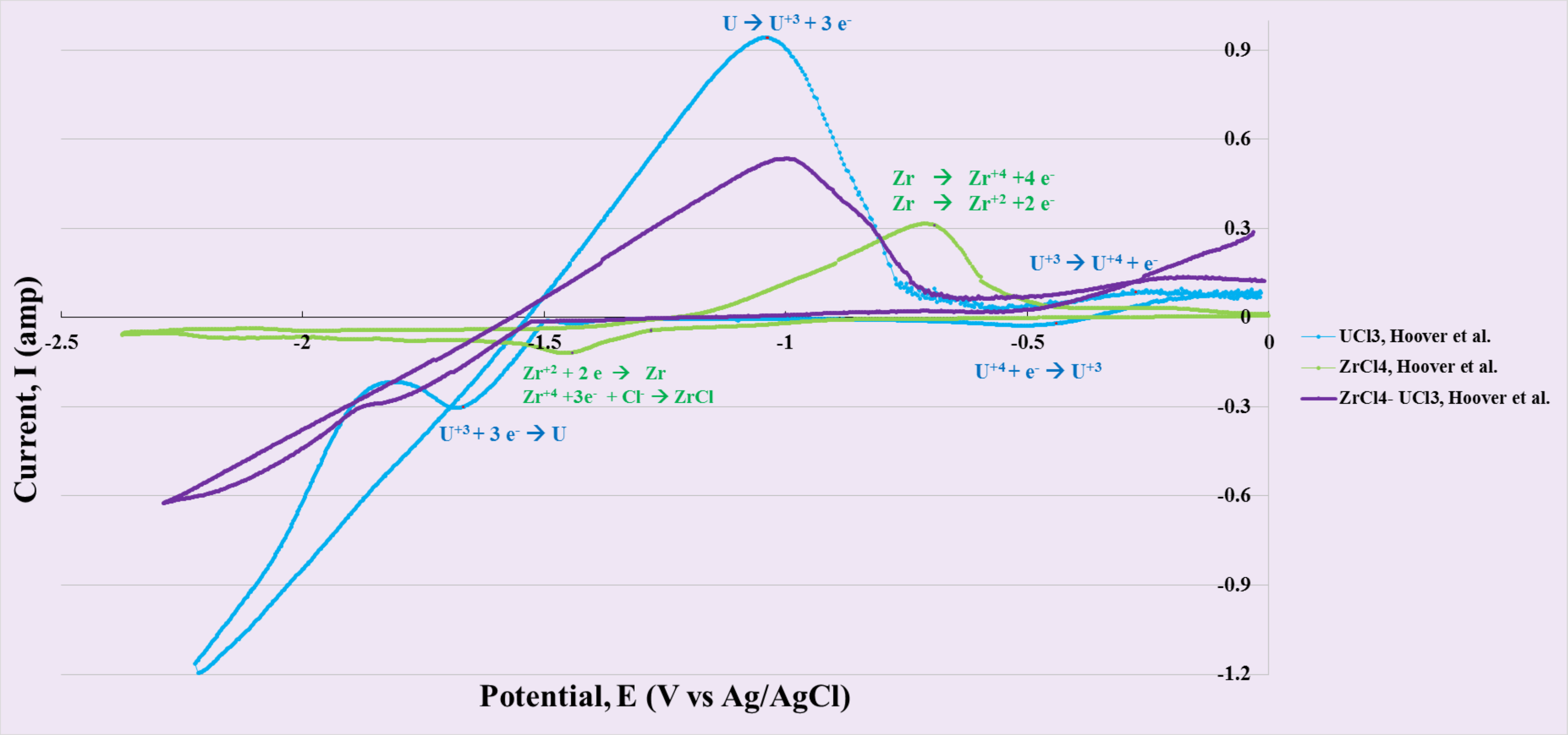
- This work was performed by University of Idaho as part of an International Nuclear Energy Research Initiative project (I-NERI 2010-001-K) with Idaho National Laboratory (INL), Seoul National University (SNU), and Korea Atomic Energy Research Institute (KAERI).
  - <u>Experimental conductor</u>: Dr. Robert Hoover
  - <u>Collaborators at INL:</u> Dr. Michael Simpson and Dr. Tae-Sic Yoo
  - <u>Collaborators at SNU</u>: Prof. Il-Soon Hwang, Jaeyeong Park, Sungyeol Choi
  - <u>Collaborators at KAERI</u>: Dr. Kwang-Rag Kim

List of References:

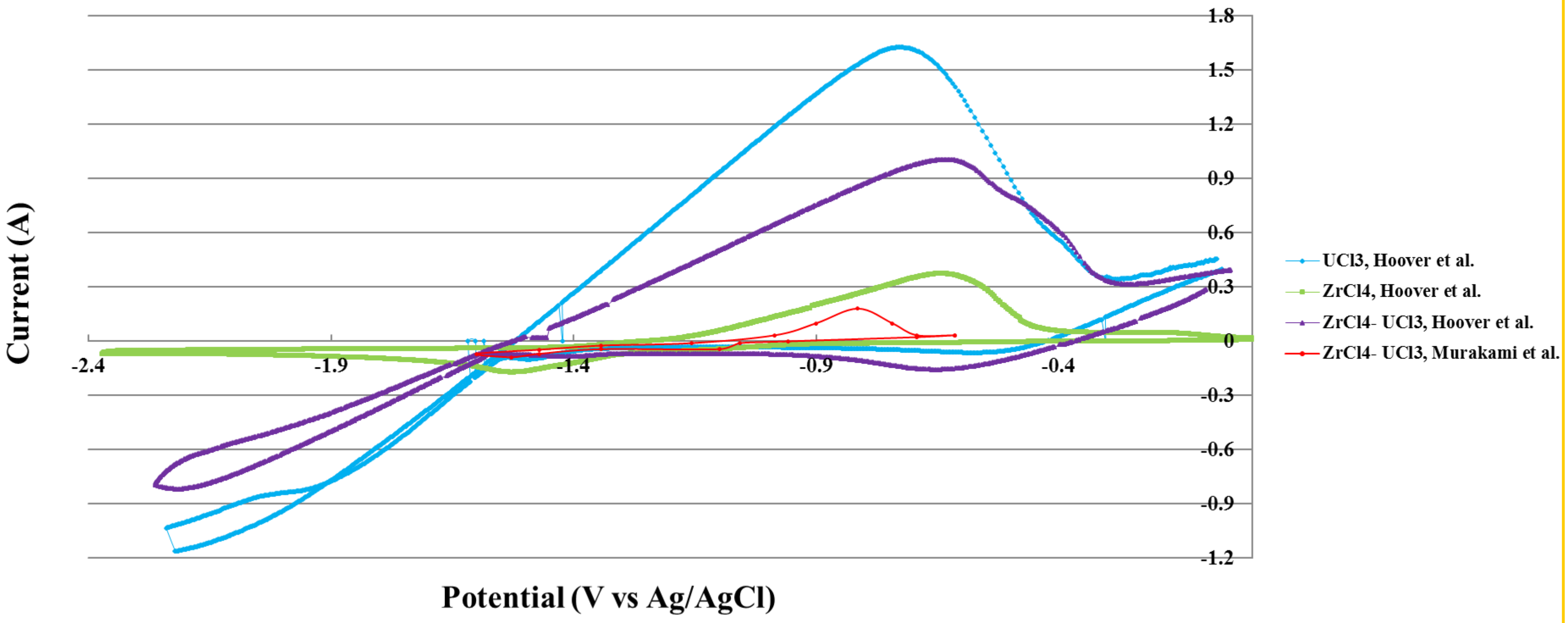
- Ahluwalia, et al., *Nucl. Tech.*, **126** (1999).
- Ahluwalia and Hua, *Nucl. Tech.*, **140** (2002).
- Akers, et al., EGG-OECD-9168, April (1992).
- Bard, “Encyclopedia of Electrochemistry of the Elements, Vol. X, Fused Salt Systems, Marcel Dekker, Inc. (1976).
- Bourg, S. IEM on Decommissioning and Remediation (2012).
- Bychkov, et al., Proceedings of the Workshop on Pyrochemical Separations, Avignon, France, March 14-16, 2000.
- Caligara, et al., *Bull. Soc. Chim. Belges*, **76** (1967).
- Choi, Proceedings of Global 2009, Paris, France, Sept. 6-11, 2009.
- Fujita, et al. , NUPYRO 2012
- Gao, et al., *J. Radioanal. Nucl. Chem.*, **280(1)** (2009).
- Hill, et al., *J. Electrochem. Soc.*, **107(8)** (1960).
- Iizuka, et al., *J. Nucl. Matls.*, **297** (2001).
- Inman and Bockris, *Can. J. Chem.*, **39** (1961).
- Janz and Bansal, *J. Phys. Chem. Ref. Data*, **11(3)** (1982).
- Kim, et al., *J. Nucl. Matls.*, **385** (2009)
- Kim, et al., *J. Radioanal. Nucl. Chem.*, **282** (2009).
- Kobayashi, et al., *J. Nucl. Sci. Tech.*, **32(7)** (1995).
- Kuznetsov, et al., *J. Electrochem. Soc.*, **152(4)** (2005).
- Masset, et al., *J. Electrochem. Soc.*, **152(6)** (2005).
- Masset, et al., *J. Nucl. Matls.*, **344** (2005).
- Masset, et al., *J. Nucl. Matls.*, **344**, (2005).
- McCardell, et al., *Nuc. Eng. Design*, **118** (1990).
- Murakami and Kato, *J. Electrochem. Soc.*, **155(7)**, (2008).
- Plambeck, *J. Chem. Eng. Data*, **12(1)**, (1967).
- Reddy, et al., *Electrochim. Acta*, **49**, (2004).
- Roy, et al, *J. Electrochem. Soc.*, **143(8)**, (1996).
- Sakamura, et al., *J. Alloys Comp.*, **271-273**, (1998).
- Shirai, et al., *J. Alloys Comp.*, **408-412**, (2006).
- Martinot and Duyckaerts, *Inorg. Nucl. Chem. Letters*, **6** (1970).
- Reddy, et al., *Electrochim. Acta*, **49** (2004).
- Thalmayer, et al., *J. Inorg. Nucl. Chemistry*, **26** (1964).
- Washiya, Int. Symposium on the Decommissioning of TEPCO’s Fukushima Daiichi NPP, March (2012).
- Yamada, et al., *J. Alloys Comp.*, **444-445** (2007).

Extra Slides

Cyclic Voltammetry of 0.5 wt% $ZrCl_4$, 10 wt% UCl_3, and a Mixture of 0.5 wt% $ZrCl_4$ and 10 wt% UCl_3 in LiCl-KCl at 773 K with 200 mV/S Scan Rate



Cyclic Voltammetry of 10 wt% UCl_3, and a Mixture of 0.5 wt% $ZrCl_4$ and 10 wt% UCl_3 with 2000 mV/s Scan Rate, 0.5 wt% $ZrCl_4$ with 500 mV/s Scan Rate (Hoover et al.), and a Mixture of 0.99 wt% $ZrCl_4$ and 0.79 wt% UCl_3 with 50 mV/S Scan Rate (Murakami et al.) in LiCl-KCl at 773 K



VCU | Virginia Commonwealth University
Department of Mechanical & Nuclear Engineering

Cyclic Voltammetry of 0.5 wt% $ZrCl_4$,10 wt% UCl_3, a Mixture of 0.5 wt% $ZrCl_4$ and 10 wt% UCl_3 with 200 mV/S Scan Rate (Hoover et al.), and a Mixture of 0.99 wt% $ZrCl_4$ and 0.79 wt% UCl_3 with 50 mV/S Scan Rate (Murakami et al.) in LiCl-KCl at 773 K