

Electroanalytical Measurements of Uranium and Plutonium in Molten LiCl-KCl Eutectic

M.M. Tylka, N. A. Smith, J.L. Willit, M.A. Williamson
Chemical Sciences and Engineering Division
Argonne National Laboratory

Outline

- Overview of methods used to ensure high precision measurements
- Improvements in experimental setup
- Importance of proper cleaning procedure
- Method used to control working electrode area
- Selecting a preferred electroanalytical method
- Results from U^{3+} and Pu^{3+} concentration measurements
 - Compare electroanalytical with ICP-MS results
- Voltammetry at higher concentrations
- Examination of new techniques to improve data analysis



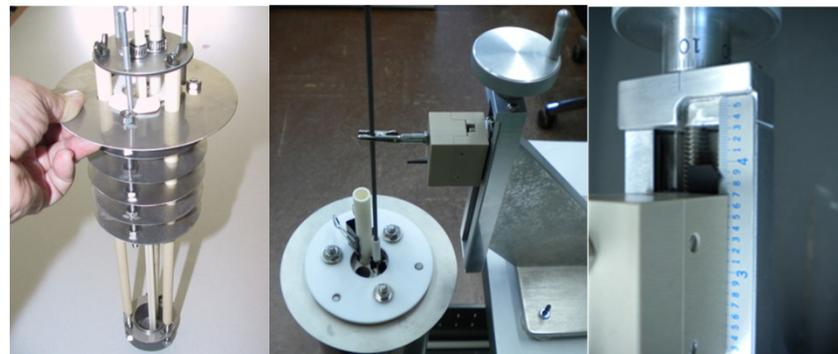
High Precision Measurements

- Methods and approaches used to improve precision of the measurements:
 - Developed a pre-treatment protocol to ensure representative solution conditions at the interface and reproducible electrode surface
 - Control of the active electrode area by standard area addition
 - Counter reaction that does not interfere with the reaction occurring at the working electrode (ex. $U^0 \rightarrow U^{3+}$)
 - Improved precision of the equipment used for varying immersion depths
 - Using a wide range of immersion depths
 - Stable and durable reference electrode
 - Selecting proper electrochemical method



Experimental Setup

- Three electrode configuration: reference, working and counter electrode.
- Improvements made:
 - Adding a vertical translator allowed for a simpler and more precise adjustment of the working electrode immersion depth.
 - A variety of reference electrodes were examined and changed to a quasi-reference:
 - Very short lifetime of Vycor tube
 - Additional redox peaks present after introducing mullite tube to the salt.
 - Both tungsten wire and Pt wire used as a quasi-reference and both showed similar performance.

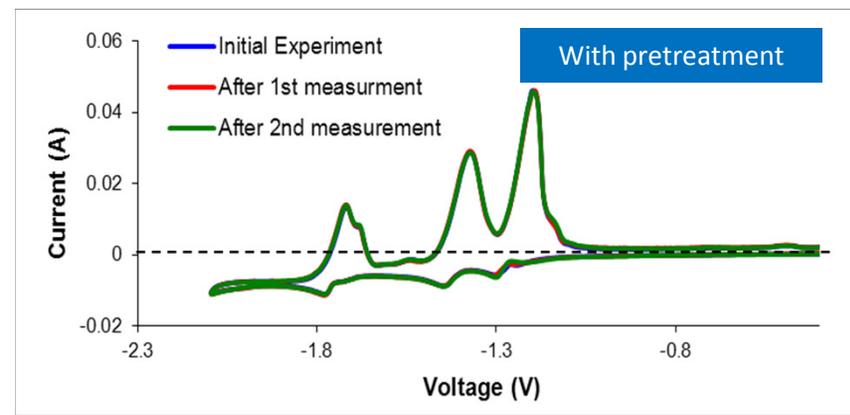
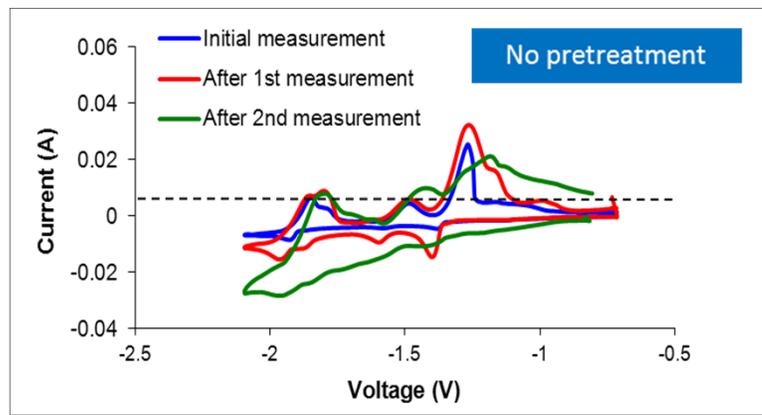
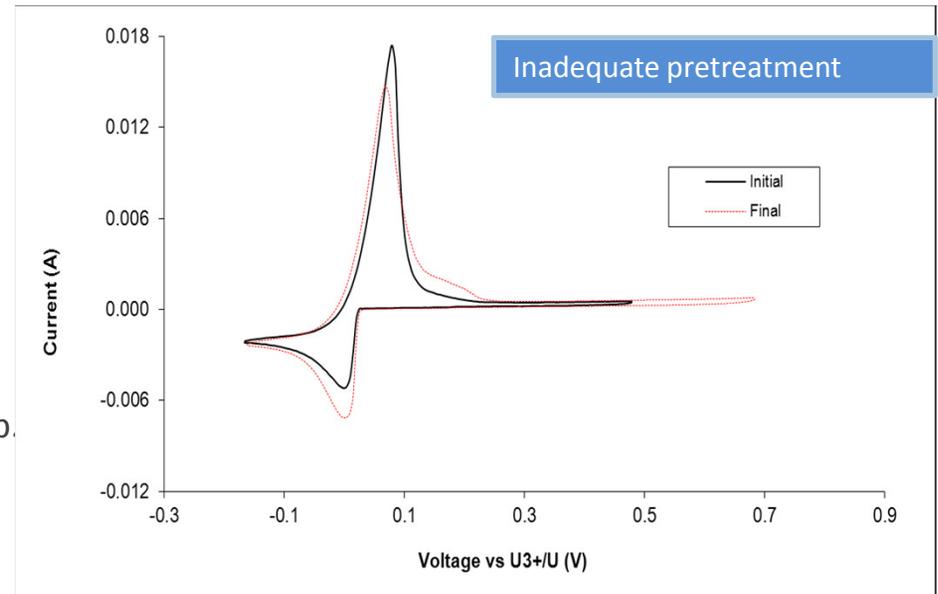


The addition of the new vertical translator and the change to a quasi-reference electrode allowed for greater control of electrode area and eliminated the extraneous voltammetric peaks due to the presence of Vycor or mullite in the cell



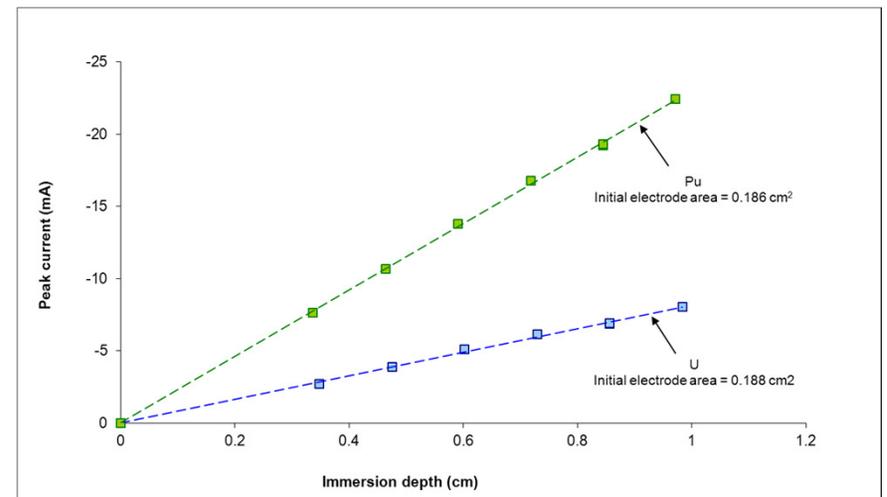
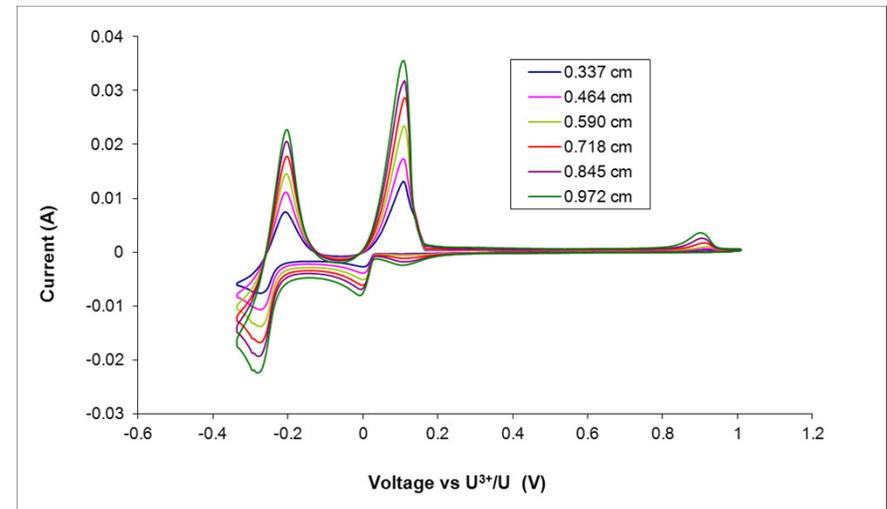
Importance of the Proper Cleaning Procedure

- Developed a pre-treatment protocol to ensure
 - reproducible electrode surface
 - representative solution conditions at the interface
- Two-step protocol
 - apply an appropriate cleaning potential
 - rest for defined time at open circuit
- A modification of the protocol is required at each salt composition by changing the waiting period and/or modifying the time and amplitude of the cleaning step.
- Proper choice of the cleaning potential is very important.
 - selecting inadequate cleaning potential also results in irreproducible data



Controlled Working Electrode Area

- Determine working electrode area *in situ* – using Cyclic Voltammetry
 - Current peaks measured at different immersion depths (under constant concentration and scan rate)
 - Linear relationship between current and immersion depth allow us to calculate the height of the electrode
 - Area calculated from the height and known diameter of the electrode.
 - Both peaks in U-Pu voltammogram give the same initial surface area
 - With sufficient measurements over a range of immersion depths, relative error in slope is extremely small
 - Wide range of immersion depths
 - Multiple runs



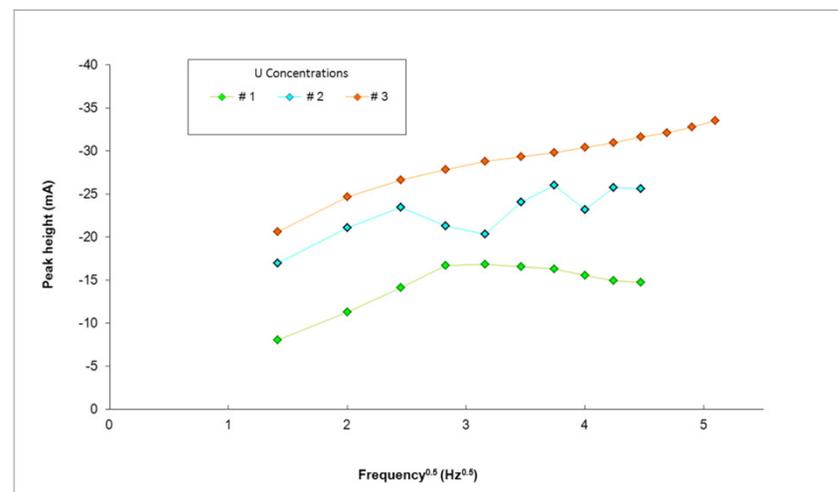
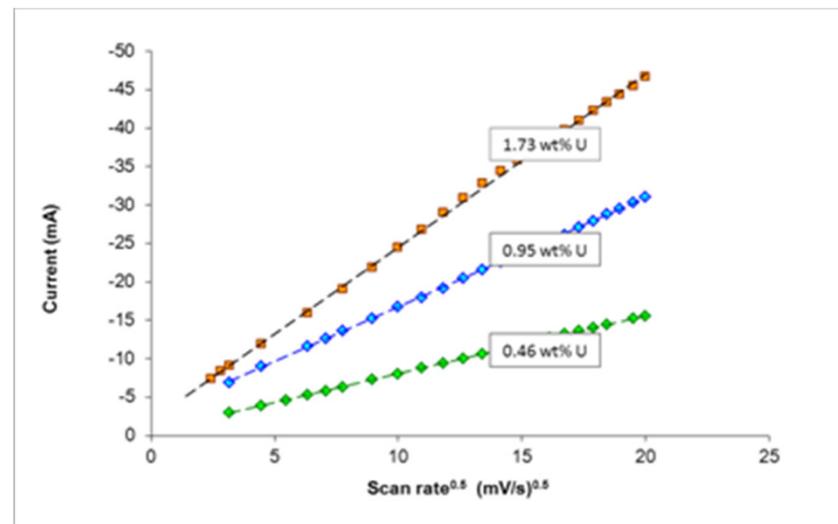
Preferred Method - Cyclic Voltammetry

- The proportionality between peak height and concentration constitutes the basis of electroanalytical methods.
- Theory is well developed for several electroanalytical methods: CV, SWV, NPV, DPV, etc. - they can be used as long as the linearity between concentration and peak height is confirmed.
- The CV selected as a preferred approach since it consistently gives the most reliable data over a wide range of conditions.

Berzins-Delahay **CV** peak current equation (reduced species is insoluble)

$$i_p = 2AC_O \sqrt{F^3 n^3 D v / RT \pi} \quad (1)$$

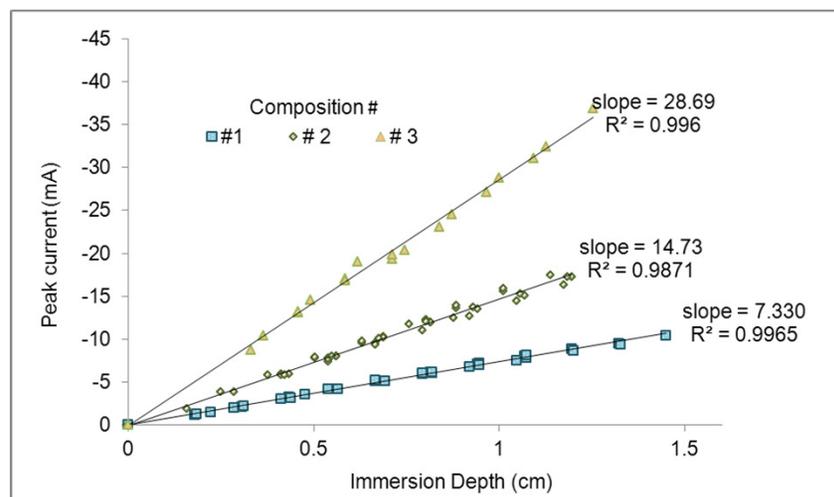
$$\frac{di_p}{dh} = 4rC_O \sqrt{F^3 n^3 \pi D v / RT} \quad (2)$$



Concentration Measurements of U³⁺ and Pu³⁺

Compositions Studied

Composition #	U ³⁺ (wt%)	Pu ³⁺ (wt%)
1	0.46	-
2	0.95	-
3	1.73	-
4	-	1.33
5	0.51	1.33



- With a 99.9% confidence interval, the error in measured concentrations averages ~1%.
- The *in situ* electrochemical concentration measurements have a higher degree of precision and are in agreement with sample analysis by ICP-AES.

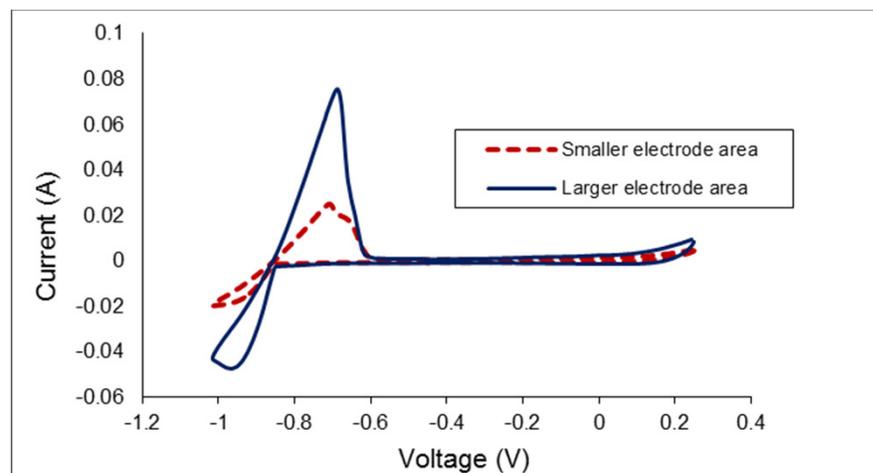
Composition #	Species	Slope ± (99.9% C.I.)	wt% (ICP-OES)	wt% (CV)	Relative % Error
1	U ³⁺	7.330 ± 0.043	0.46 ± 0.05	0.4515 ± 0.0027	0.65
2	U ³⁺	14.73 ± 0.14	--	0.9074 ± 0.0085	0.94
3	U ³⁺	28.69 ± 0.12	1.73 ± 0.2	1.767 ± 0.026	1.5
4	Pu ³⁺	22.71 ± .21	1.33 ± .13	1.336 ± 0.013	0.97
5	U ³⁺	8.280 ± 0.23	0.51 a	0.510 ± 0.014	2.8
5	Pu ³⁺	22.91 ± 0.29	1.33 ± 0.13	1.345 ± 0.017	1.3



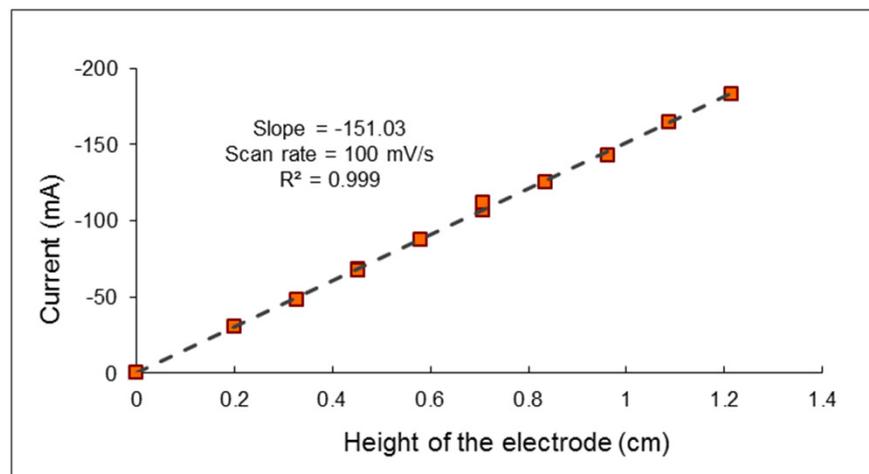
Working with Higher Concentrations

- The higher the concentration of the electroactive species in the salt, the more extensive the cleaning protocol has to be applied:
 - Longer and/or repeated rest periods.
 - Additional oxidizing steps.
- Delahay equation is valid only for the reaction limited by mass transport
 - A distinct peak has to be observed in the Voltammogram
 - A peak height has to be a linear function of a scan rate^{0.5}
 - Almost always the case for relatively low concentrations.
- At higher concentrations additional steps may be required to ensure mass transport limitations:
 - Increasing the scan rate
 - Using electrode with higher surface area

Example of CV – **10wt% U** with and without mass transfer limitations (different electrode areas):



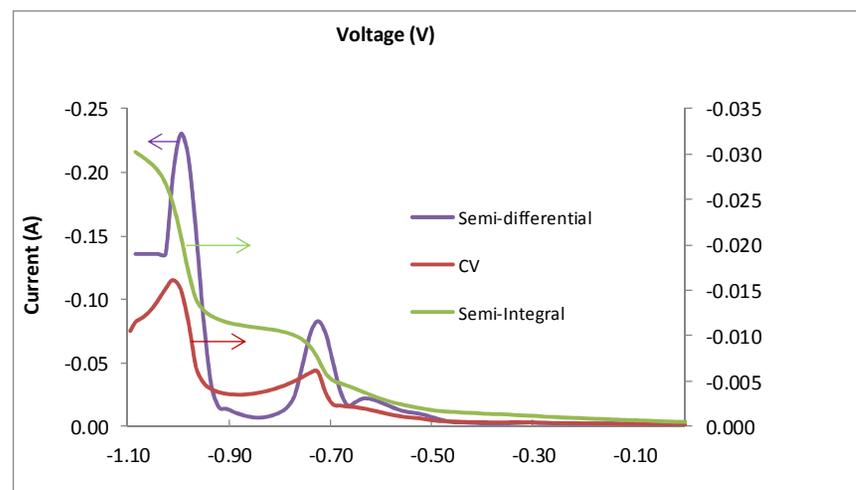
Linear plots obtained after applying proper cleaning procedure and ensuring reaction is limited by diffusion



Improving the data analysis

- Accurate peak height measurements require a reliable baseline from which to measure the peak heights.
- Determination of the baseline for the U^{3+}/U^0 peak is straightforward and reliable because it is the first peak in the series.
- The baseline for the Pu^{3+}/Pu^0 reduction peak is affected by the tail from the U^{3+}/U^0 peak.
- New method of data analyzing is being investigated:
 - Increases the peak height/width ratio
 - Provides a better baseline for the Pu^{3+}/Pu^0 peak.
 - A semi-integration of the current is followed by a first derivative:
 - dI/dE – convoluted current differentiated with respect to potential (E)
 - dI/dt – convoluted current differentiated with respect to time (t)

Example of current vs. voltage plots of the original cyclic voltammetry data, the semi-integral data, and the semi-differential (dI/dE) data.



Using Nernst equation and definition of semi-integral of current an equation for a peak height can be derived:

$$e_p = \frac{n^2 F^2 A D^{0.5} c_0}{4RT}$$



Concluding Remarks

- Voltammetry (CV) is a very promising tool for *in situ* process monitoring of pyroprocess operations
- Voltammetric experiments were completed for a range of salt compositions
- Using the methods developed in combination with electrode area control, high precision measurements of U^{3+} and Pu^{3+} were obtained.
- With a 99.9% confidence interval, the error in measured concentrations averages ~1%.
- It was shown that the *in situ* electrochemical concentration measurements have a higher degree of precision and are in agreement with sample analysis by ICP-AES.
- Using voltammetry at higher concentrations is possible when proper procedures are applied.
- New method for analyzing CV data is being investigated.



Acknowledgements

Government License Notice

- The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory (“Argonne”). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.
- This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, under Contract DE-AC02-06CH11357.

