Electrochemical Detection and Analysis of a Molten Lithium Chloride - Potassium Chloride and Cadmium Metal System

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Introduction

Background

- Results of electrorefiner salt sample analyses can be quite delayed due to level of radioactivity, number of elements analyzed, and facility availability.
- Electrochemical methods have strong potential to provide compositional information, which could yield results more quickly.
- Much electrochemical research related to pyroprocessing has focused on salt mixtures of fixed concentration and without a cadmium pool.

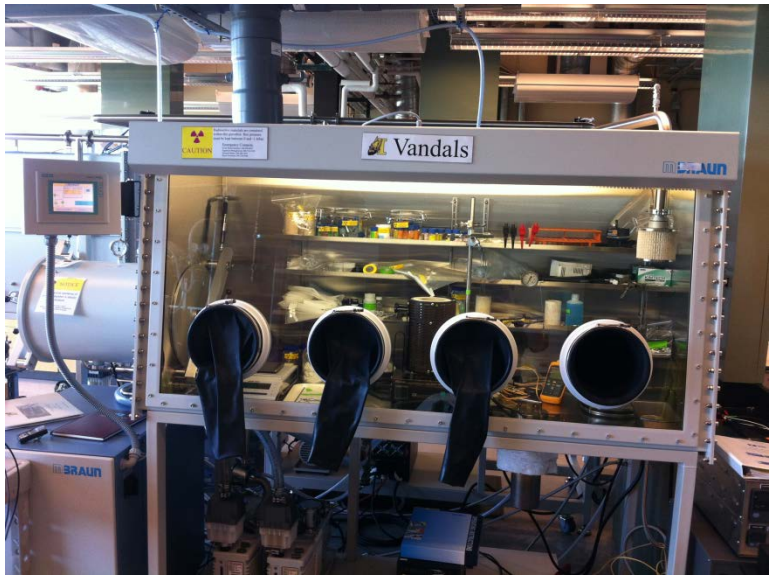
Motivation

- A basis of transient conditions in the molten salt-cadmium system is crucial for enabling a deployable technology and ensuring an efficient and secure treatment process.

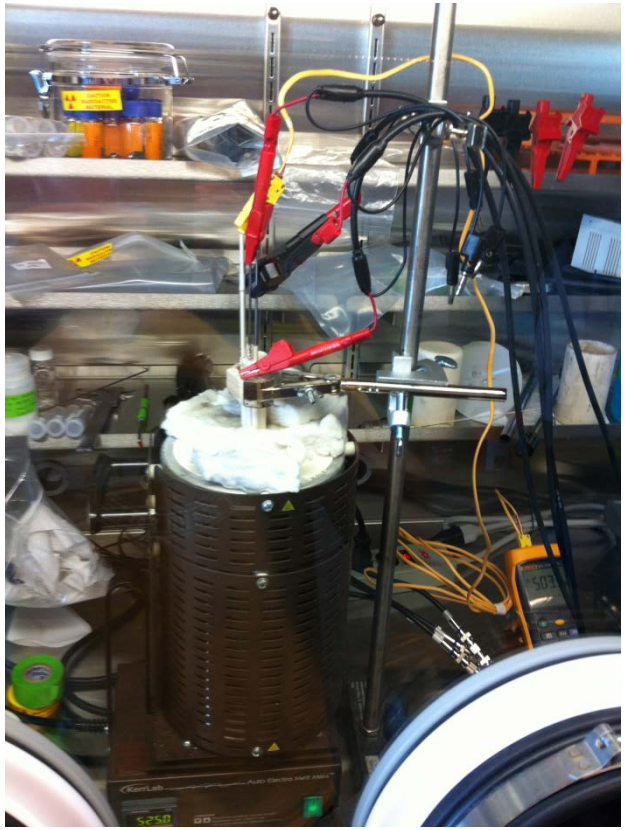
Objective

- Demonstrate usefulness of electrochemical techniques in a molten salt-cadmium system of which the concentration of analytes change during the experiment.

Experimental Equipment



- MBraun glovebox
- Argon atmosphere
- < 5 ppm O_2 and H_2O



- Kerrlab melting furnace
- 1100 ° C max temp.
- 120 V

Experimental Equipment and Materials

Materials

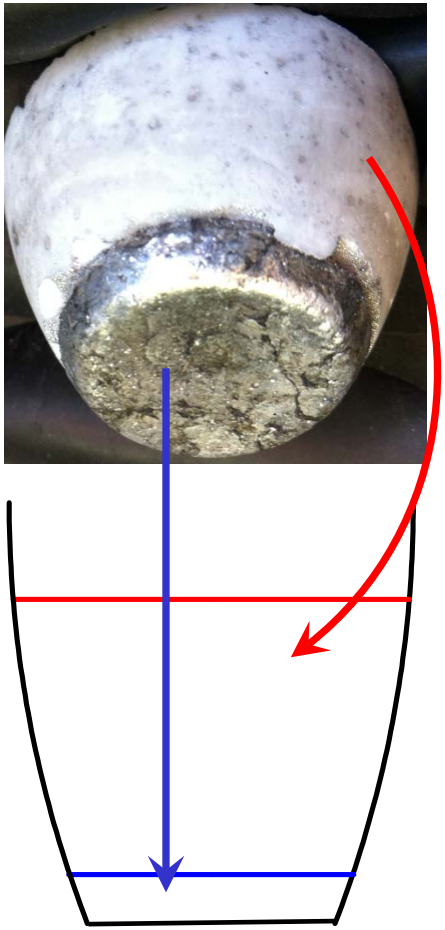
- YCl_3 and $LaCl_3$ beads
- $EuCl_3$ powder
- UCl_3-LiCl-KCl
  - 25 % LiCl-KCl eutectic by mass
  - 75 % UCl_3
- Al_2O_3 crucible
- 60 g LiCl-KCl eutectic
- 30 g cadmium shot

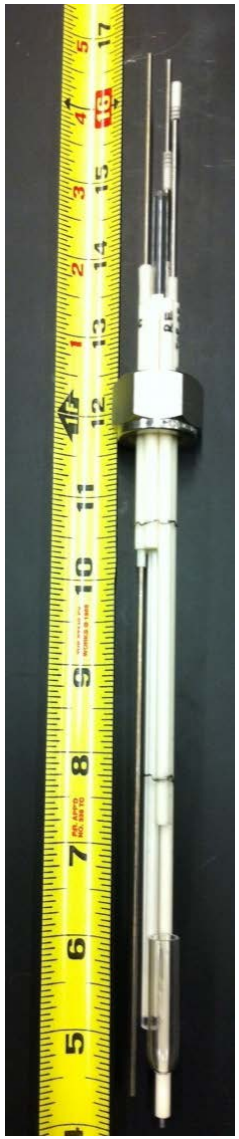
Used for all tests.

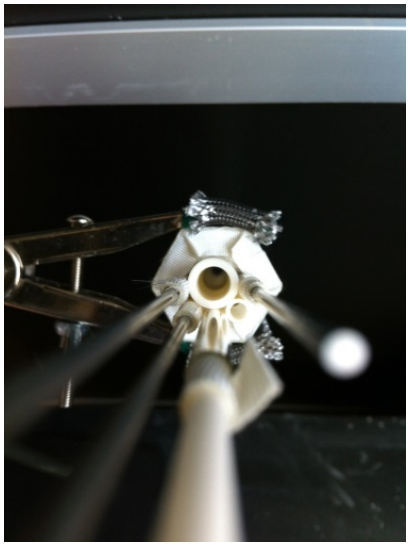
Electrode Assembly

- *Tungsten rods*: 2 mm diameter, 30 cm length
- Al_2O_3 tube (sheathing)
- Al_2O_3 paste (sealant)
- Pyrex (reference electrode)
- *Silver wire*: 1mm diameter
- 5 mol % Ag/AgCl
- Alumina sheathed type K thermocouple

Experimental Equipment and Materials



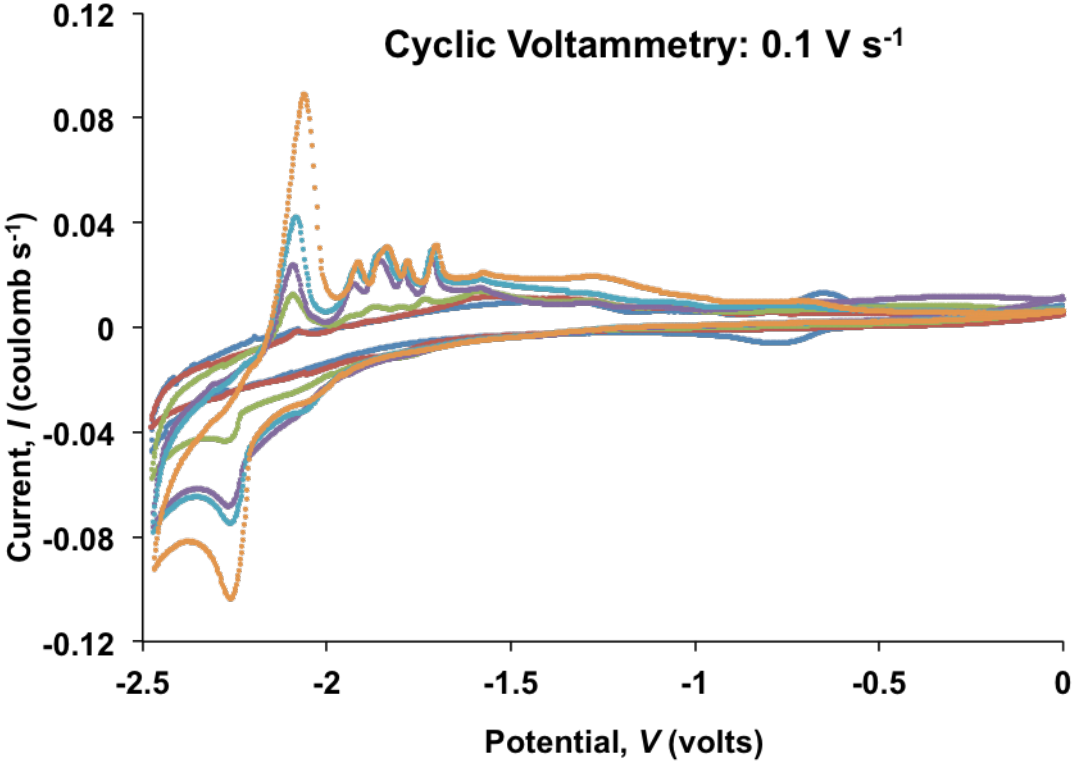




Procedure and Measurements: YCl_3 Experiment

Procedure

- Temperature = 500 ° C
- No YCl_3 in the molten salt initially
- Add YCl_3 in three increments
- 1.5 wt % max YCl_3 concentration
- Record CV data throughout duration
- 11 hr duration



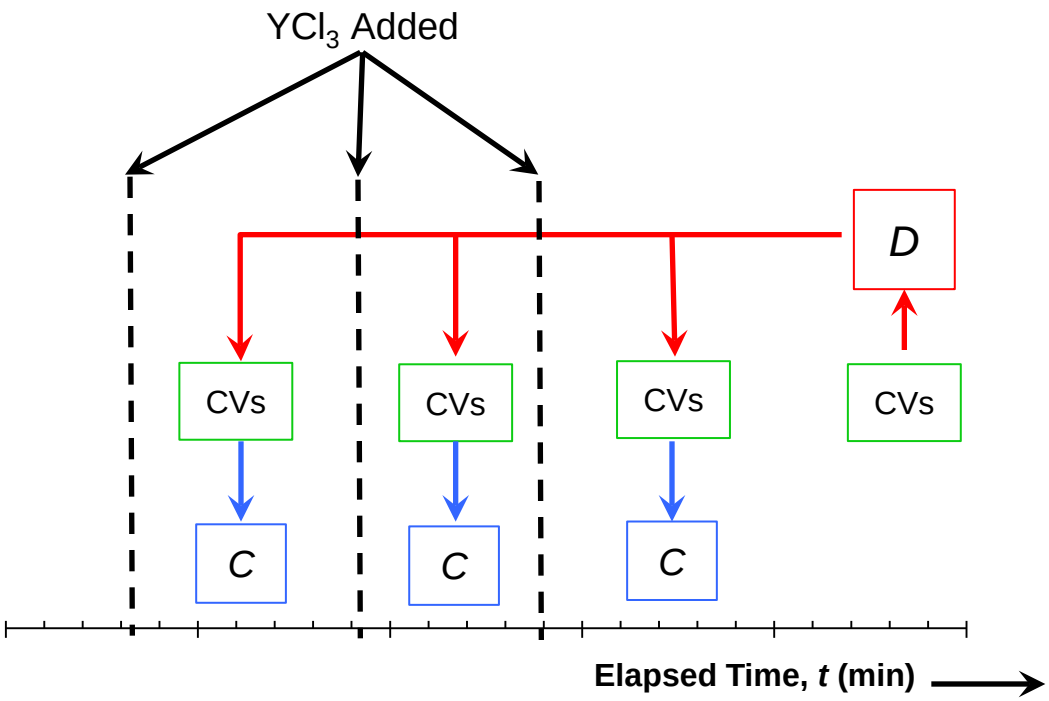
Calculations: YCl_3 Experiment

$$i_p = 0.4463nFAC\sqrt{\frac{n\nu DF}{RT}} \qquad (1)$$

(Reversible, Ref. 1)

$$i_p = 0.61nFAC\sqrt{\frac{n\nu DF}{RT}} \qquad (2)$$

(Reversible, Ref. 2)



Step 1: CVs recorded throughout experiment.

Step 2: Use Eqs.1 and 2 to calculate *D* from CVs at the end of the duration. Assume maximum *C.*

Step 3: Use equations to calculate *C*, from CVs preceding the final, based on *D* from Step 1.

Calculations: YCl_3 Experiment

This Study

Note: Values are based on anodic and cathodic peak currents.

Table 1

	Average Diffusion Coefficient, ($D \pm \sigma$) × 10^6 cm^2 s^{-1} @ 500 °C	
	Equation 1	Equation 2
Y^{3+}	9.2 ± 2.8	4.9 ± 1.5

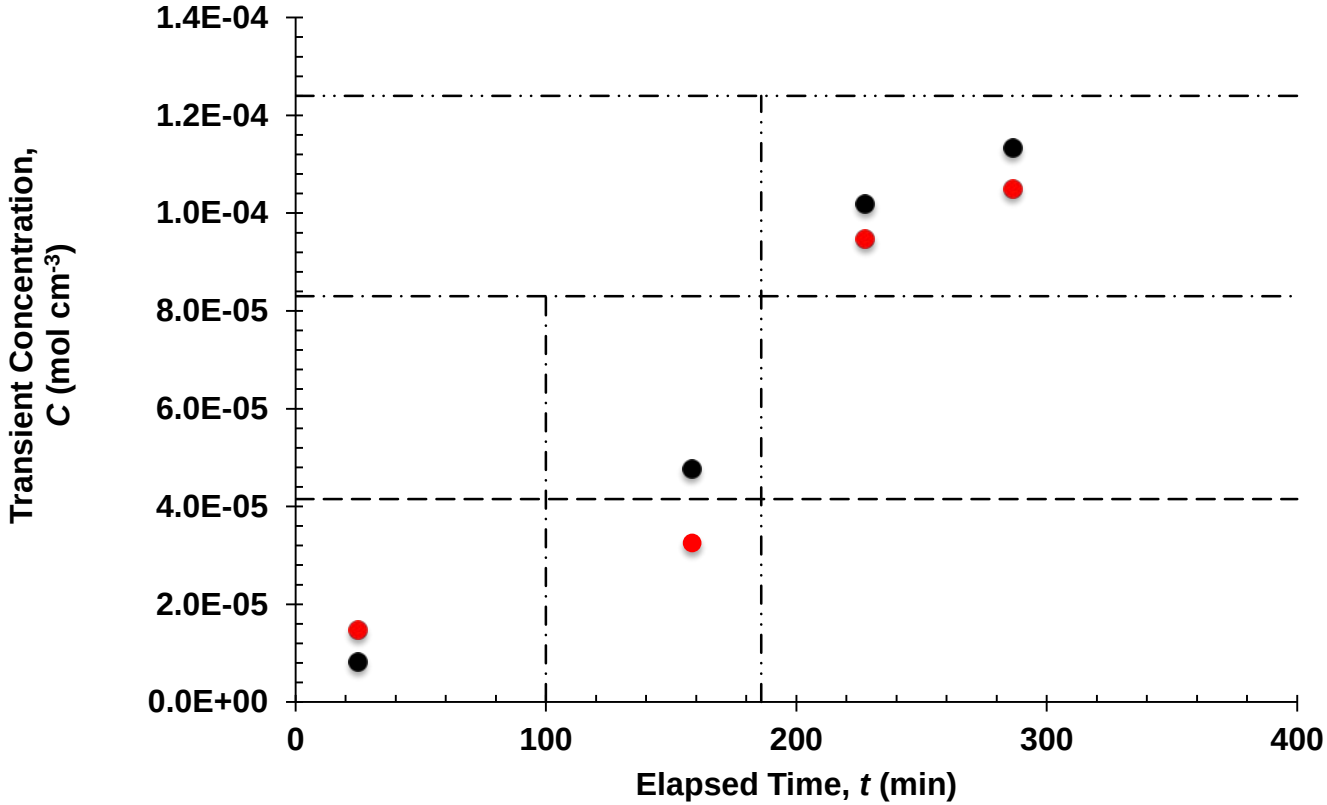
Literature

Table 2

	Diffusion Coefficient, D × 10^6 cm^2 s^{-1} @ 500 °C
Lantelme et al. (Ref. 3)	7.69 ± 2
Castrillejo et al. (Ref. 4)	12.9

Calculated YCl_3 Concentration in the Salt

- t < 0, no YCl_3 in salt.
- t = 0, 0.3 g YCl_3 added.
- t = 100 min, 0.3 g YCl_3 added.
- t = 186 min, 0.3 g YCl_3 added.

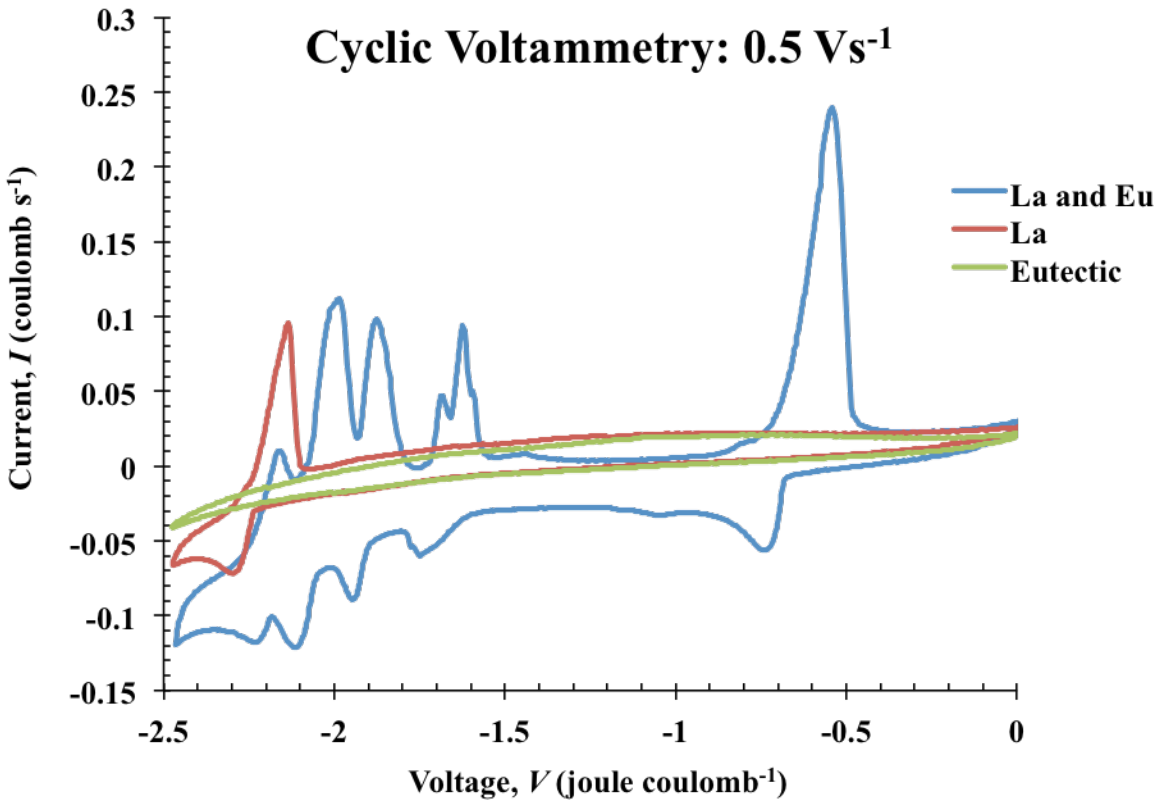


Eq. 1

Eq. 2

Procedure and Measurements: $EuCl_3$ – $LaCl_3$ Experiment

- Operating temperature = 500 °C
- 1 wt% each of $EuCl_3$ and $LaCl_3$ in molten salt initially
- Add 0.05 g of Li metal to reduce all Eu^{3+}
- Add 0.05 g of Li metal to reduce all La^{3+}
- Record CV and OCP data throughout
- 16 hr duration



Calculations: $EuCl_3$ - $LaCl_3$ Experiment

Europium Diffusion Coefficient

Note: Values are based on cathodic peak currents.

Table 3: Values of *D* from this study.

	Average Diffusion Coefficient, $D \times 10^5$ cm^2 s^{-1} @ 500 °C	
	Equation 1	Equation 2
Eu^{3+}	8.35	4.48

Table 4: Values of *D* from literature.

Eu^{3+}	Diffusion Coefficient, $D \times 10^5$ cm^2 s^{-1} @ 500 °C	Method
Caravaca et al. (Ref. 5)	2.04	Convolution
	0.588	Chronopotentiometry

Calculations: $EuCl_3$ - $LaCl_3$ Experiment

Lanthanum Diffusion Coefficient

Note: Values are based on anodic and cathodic peak currents.

Table 5: Values of *D* for this study.

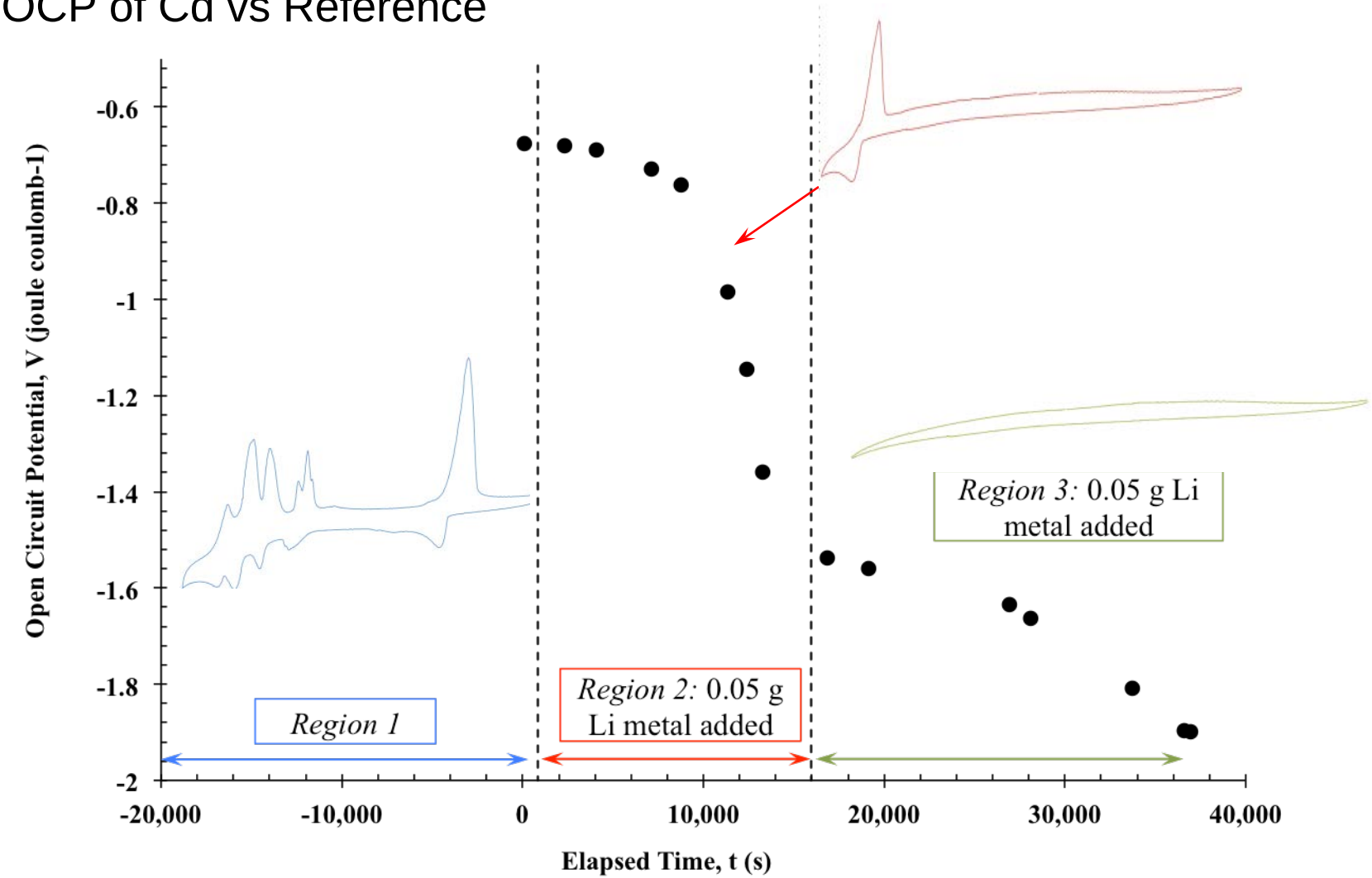
	Average Diffusion Coefficient, $D \times 10^6$ cm^2 s^{-1} @ 500 °C	
	Equation 1	Equation 2
La^{3+}	5.28	2.83

Table 6: Values of *D* from literature.

La^{3+}	Diffusion Coefficient, $D \times 10^6$ cm^2 s^{-1} @ 500 °C
Fanxing et al. (Ref. 6)	16.2
Masset et al. (Ref. 7)	8.0
Lantelme et al. (Ref. 3)	20.3

Measurements: $EuCl_3$ – $LaCl_3$ Experiment

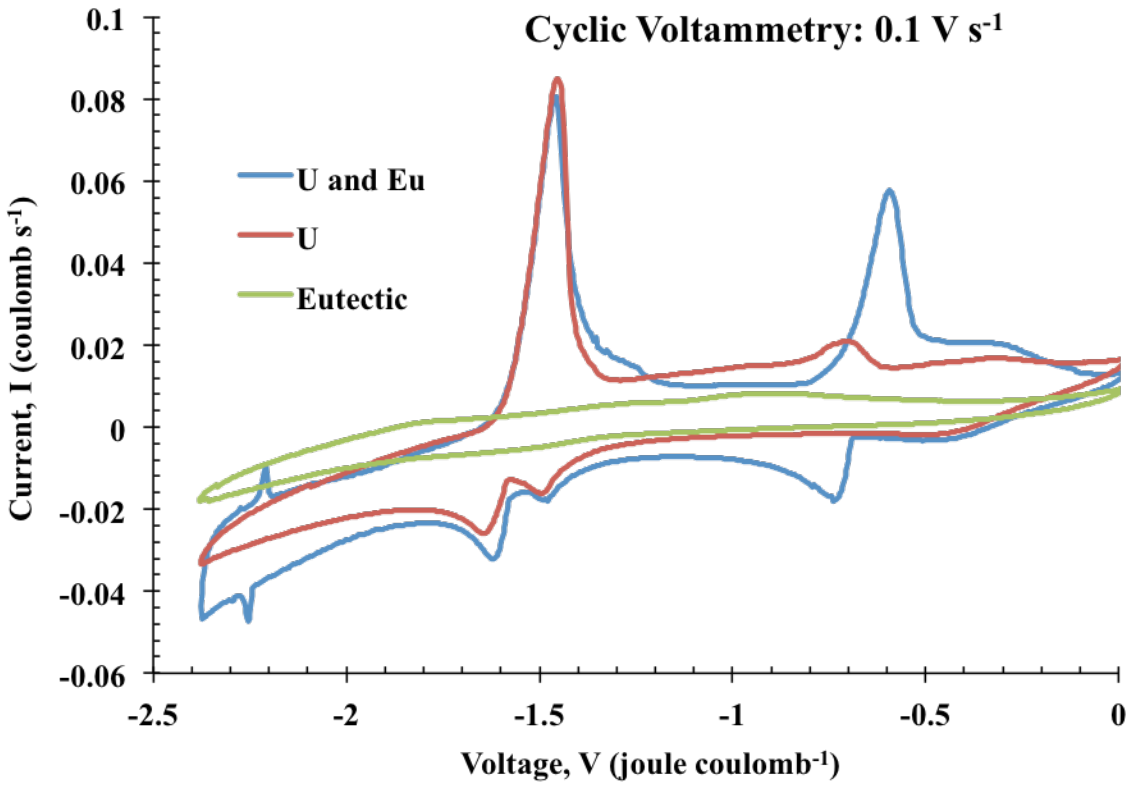
- OCP of Cd vs Reference



Procedure and Measurements: $EuCl_3$ – UCl_3 Experiment

- Operating temperature = 500 °C
- 0.5 wt% $EuCl_3$ and 0.66 wt% UCl_3 in molten salt initially

- Add 0.025 g of Li metal to reduce all Eu^{3+}
- Add 0.025 g of Li metal to reduce all U^{3+}
- Record CV and OCP data throughout
- 14 hr duration



Calculations: $EuCl_3$ - UCl_3 Experiment

Europium Diffusion Coefficient

Note: Values are based on anodic and cathodic peak currents.

Table 7: Values of *D* from this study.

	Average Diffusion Coefficient, $D \times 10^5$ cm^2 s^{-1} @ 500 °C	
	Equation 1	Equation 2
Eu^{3+}	5.95	3.19

Table 8: Values of *D* from literature.

Eu^{3+}	Diffusion Coefficient, $D \times 10^5$ cm^2 s^{-1} @ 500 °C	Method	Electrode
Caravaca et al. (Ref. 5)	2.04	Convolution	Tungsten
	0.588	Chronopotentiometry	

Calculations: $EuCl_3$ - UCl_3 Experiment

Uranium Diffusion Coefficient

Note: Statistical values are based on cathodic peak currents.

Table 9: Values of *D* from this study.

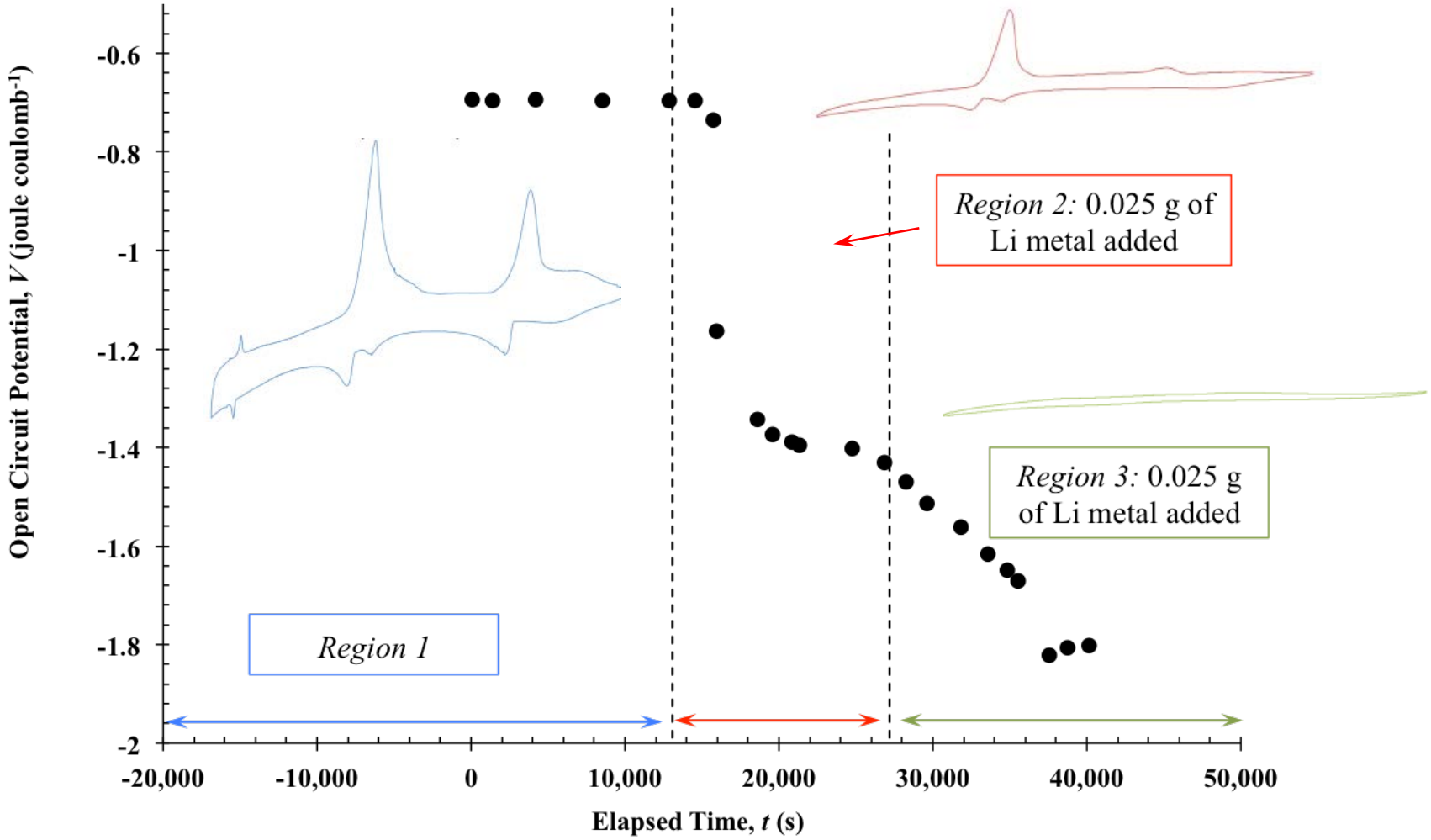
	Average Diffusion Coefficient, $D \times 10^6$ cm^2 s^{-1} @ 500 °C	
	Equation 1	Equation 2
U^{3+}	0.83	0.44

Table 10: Values of *D* from this study.

U^{3+}	Diffusion Coefficient, $D \times 10^6$ cm^2 s^{-1} @ 500 °C
Hoover et al. (Ref. 8)	1.04 ± 0.17
Caligara et al. (Ref. 9)	1.031

Measurements: $EuCl_3$ – UCl_3 Experiment

- OCP of Cd vs Reference



Summary

- Changes in composition of the salt and cadmium phases were measured electrochemically.
- Diffusion coefficients calculated via cyclic voltammetry were comparable to literature values.
- Calculated transient concentrations are reasonable.
- Drawdown reactions were monitored by CV measurements in the salt.
- Open circuit potential measurements of the cadmium phase correlated to drawdown of Eu^{3+}, La^{3+}, and U^{3+} from the salt phase.

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