ESTIMATION OF URANIUM AND PLUTONIUM EXCHANGE CURRENT DENSITIES ON SOLID ELECTRODES

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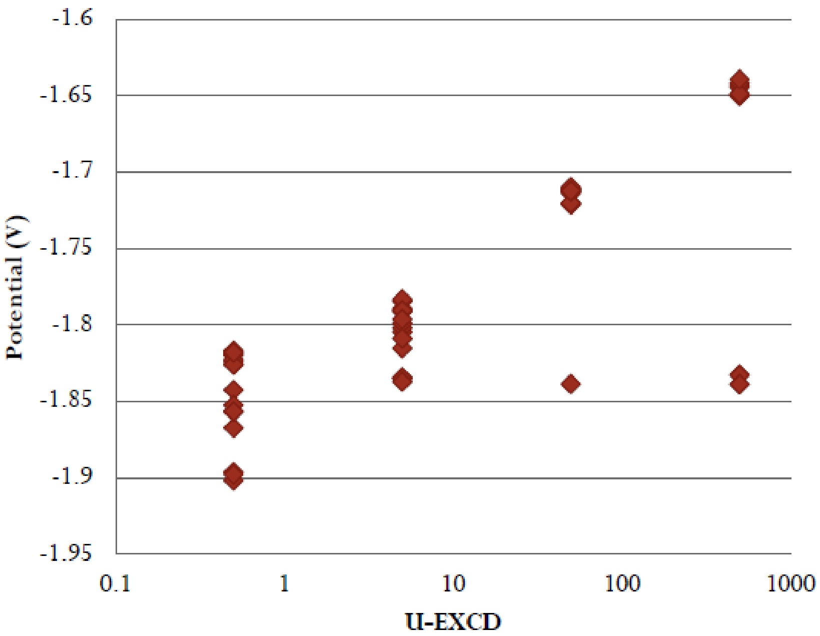
Overview

- Motivation
- Method
  - Assumptions
  - Possible interfering phenomena
  - Data Sources
- Results
  - Uranium
  - Plutonium
- Summary

Motivation

- Exchange current density is important in determining electrorefiner behavior
- The various estimations of exchange current density vary over a wide range
  - 500A/m^2 –I. Choi et al
  - 1A/m^2—Hoover et al
- No Plutonium estimate yet

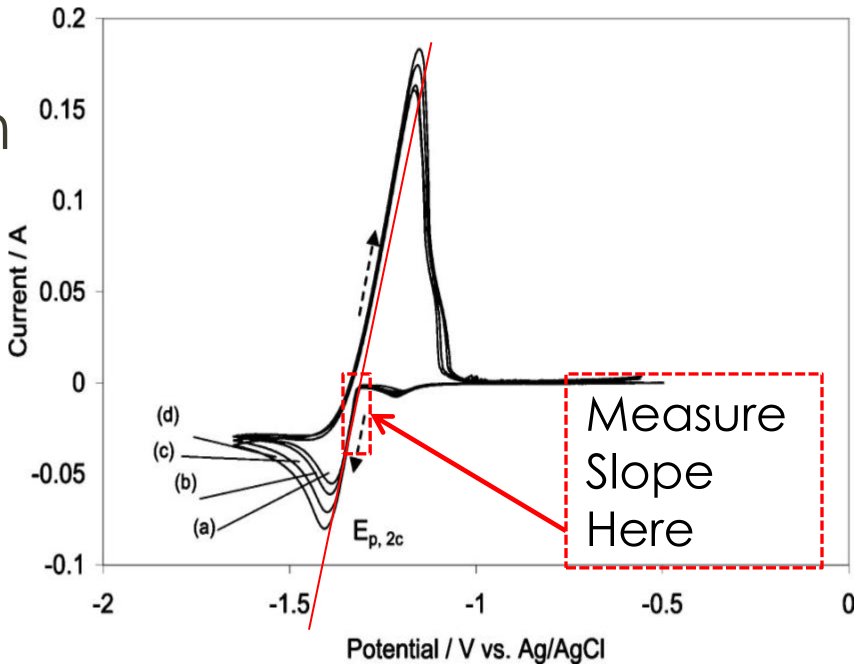


A plot from Devin Rappleye showing the effect of uranium exchange current density on average cathode potential.

Method

Method

- Based on linear approximation to Butler-Volmer equation
- If sweep rate sufficiently fast (.1V/s), diffusion will have minimal effect
- Therefore at base of peak, slope should correspond to linear approximation



Linear Approximation Method

- Liner Approximation:

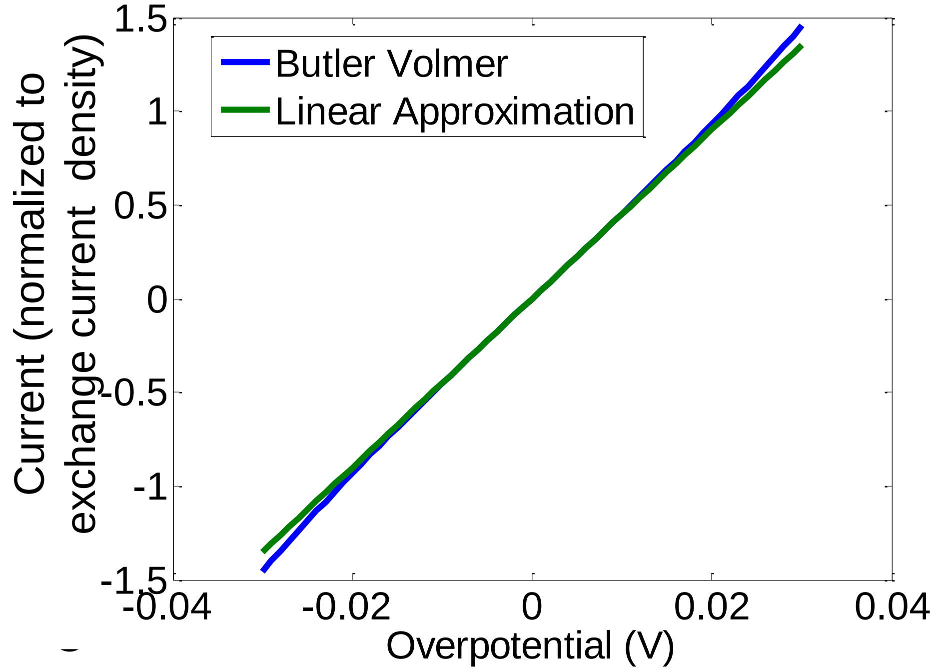
$$i = i_0 \frac{nF}{RT} \eta$$

- Small Deviation in potential produces:

$$\Delta i = i_0 \frac{nF}{RT} \Delta \eta$$

- Finally we arrive at:

$$i_0 = \frac{RT}{nF} \frac{\Delta i}{\Delta \eta}$$



Plot of linear approximation to the Butler-Volmer equation vs actual solution for n=3, T=773K, $\alpha=0.5$.

“Normalized” Exchange Current Density

- “Standard Exchange Current Density” Could have multiple ways of being defined
- We will simply normalize by molar concentration to obtain a value that does not vary with concentration.

$$i_{0norm} = \frac{i_0}{[x]^\alpha}$$

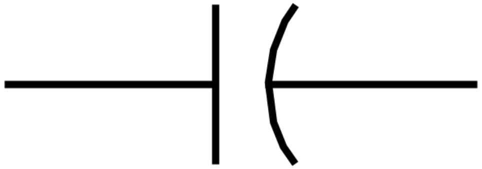
- Thus we can avoid using the activity coefficient. (Values sometimes vary)

Assumptions

- No other reactions can be taking place
  - Must be cathodic peak (if cathodic CV), and the current must start near 0
- Concentration must remain constant
  - Sweep must be quick
  - >.1V/s
- Linear approximation must be applicable
  - <0.03V from peak base
- Charge transfer coefficients
  - $\alpha=0.5$

Does Double Layer Capacitance Affect Result?

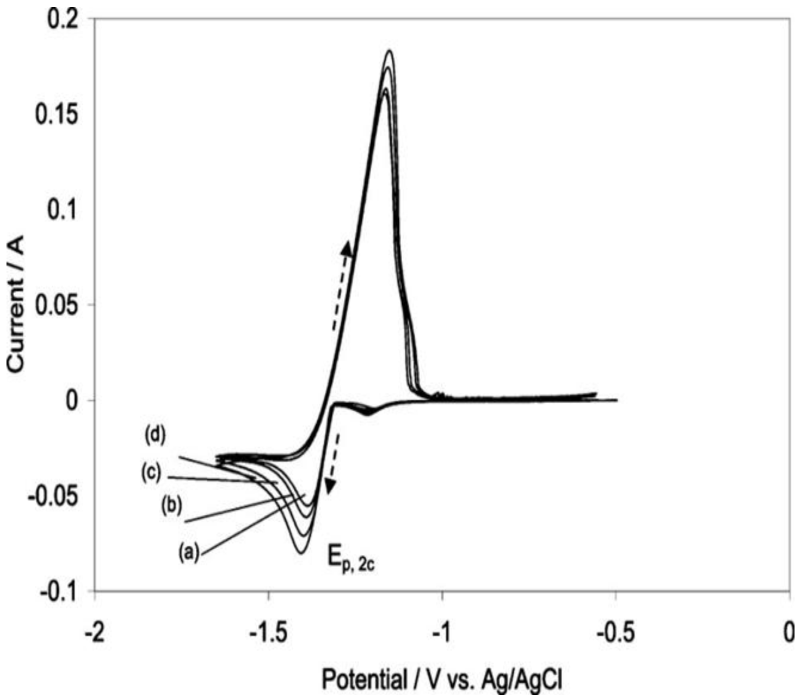
- In a cyclic voltammogram, the voltage sweep rate is constant—unlike EIS
- Current due to the double layer capacitance will be constant
- Therefore, it will not enter into the line slope to find the exchange current



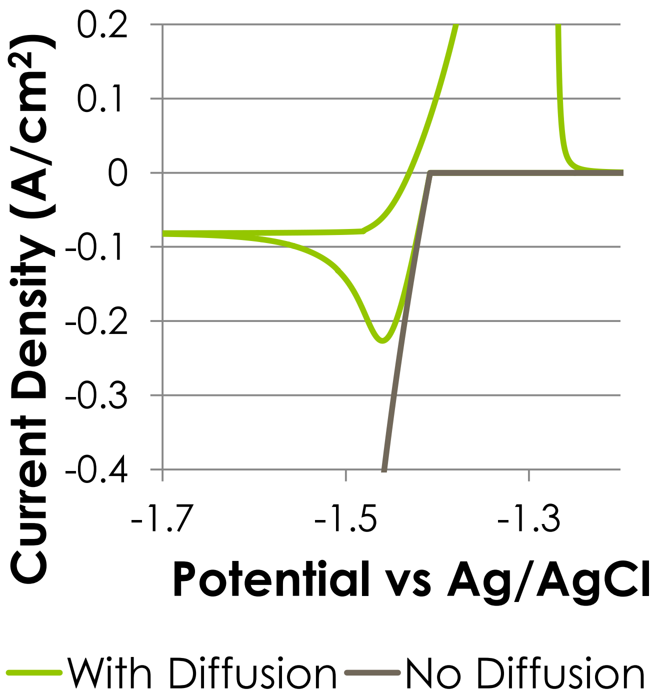
- $I = C\frac{dV}{dt}$

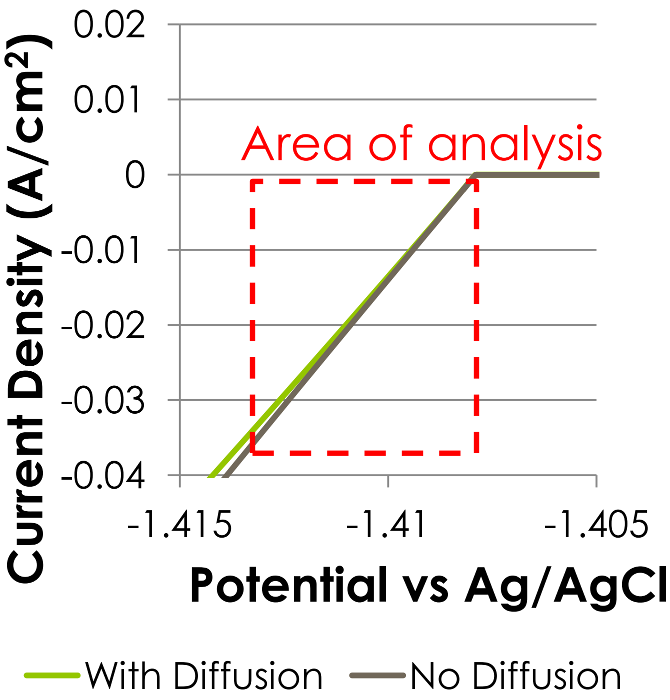
Does Diffusion Affect Result?

- At low scan rates, diffusion restricts mass transport
- When sweep rate is higher than 0.1 V/s, this effect is reduced
- Possible 10% reduction in final value (20% at most)
  - Based on simulation using ERAD
  - We are only getting a ballpark estimate anyway
- CV's with multiple sweep rates may help gauge this error
  - Similar slope implies little effect from diffusion



REFIN/ERAD Simulation





Zoomed in view

Data Sources Used for Uranium

Study	Figure	$CdCl_2$?
L. Cassayre et al. / Journal of Nuclear Materials 378 (2008) 79–85	2	N?
P. Masset, D. Bottomly et al ./Journal of The Electrochemical Society, 152.6 (2005) A1109-A1115	1	N
P. Masset, D. Bottomly et al ./Journal of The Electrochemical Society, 152.6 (2005) A1109-A1115	2	N
Y. Sakamura et al. / Journal of Alloys and Compounds 271 –273 (1998) 592 –596	1	N?
I Choi et al. / Global 2009 Paris France Paper 9045	7	Y
O. Shirai et al. / Journal of Alloys and Compounds 271 –273 (1998) 685 –688	2	Y
S.A. Kuznetsov et al. / Electrochimica Acta 51 (2006) 2463–2470	1	Y
B. Prabhakara Reddy et al. / Electrochimica Acta 49 (2004) 2471–2478	2	Y
GY Kim et al. / Journal of Electroanalytical Chemistry 682 (2012) 128–135	2A	Y

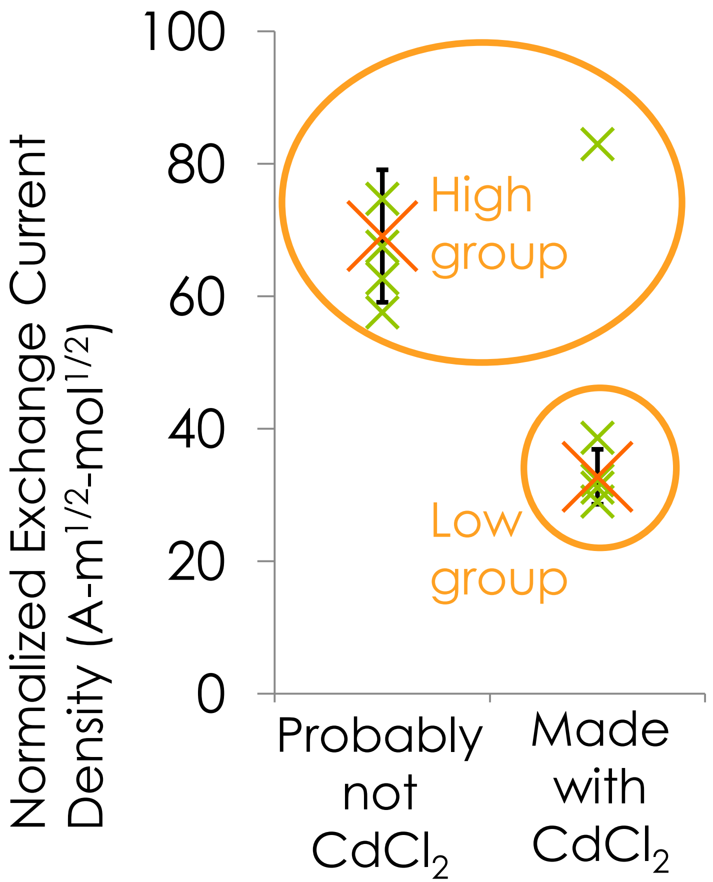
Data Sources Used for Plutonium

Study	**Figure**	**Al Electrode ?**
E. Mendes et al. / Journal of Nuclear Materials 420 (2012) 424–429 (4 Lines analyzed)	2	T
E. Mendes et al. / Journal of Nuclear Materials 420 (2012) 424–429	1	T
J. Serp et al. / Journal of Nuclear Materials 340 (2005) 266–270	1	F
J. Serp et al. / Journal of The Electrochemical Society, 152.3 (2005) C167-C172	2	F
J. Serp et al. / Journal of The Electrochemical Society, 152.3 (2005) C167-C172	2	T
J. Serp et al. / Journal of The Electrochemical Society, 152.3 (2005) C167-C172	3	T
J. Serp, RJM Konings et al. /Actinide and Fission Product Partitioning & Transmutation/ Jeju, Korea (2002)	1	F
O. Shirai et al. / Analytical Sciences 17 (2001) 51-57	2	F

Results

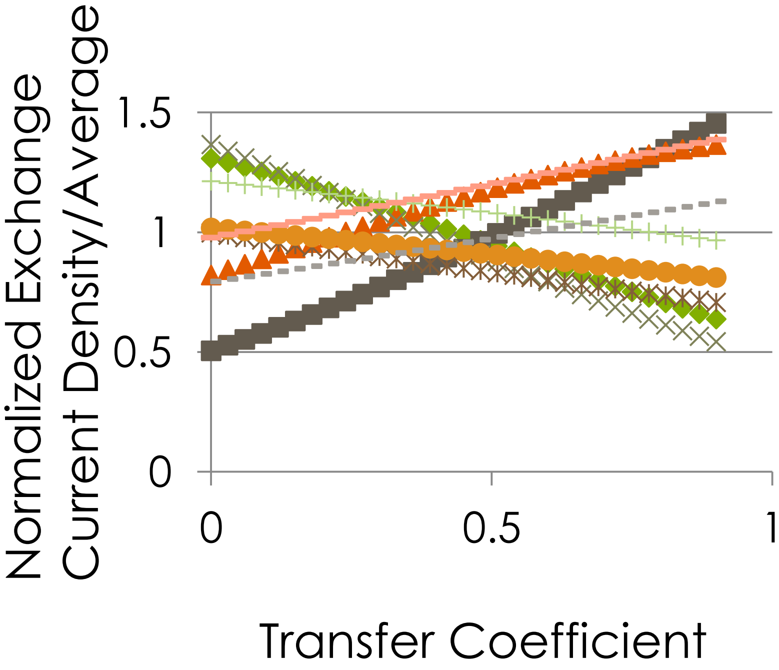
Results for Uranium

- Two groups are noticeable
- Reason for grouping may be related to whether the UCl_3 is produced using $CdCl_2$.
- Averages, and standard deviations are for high and low groups.



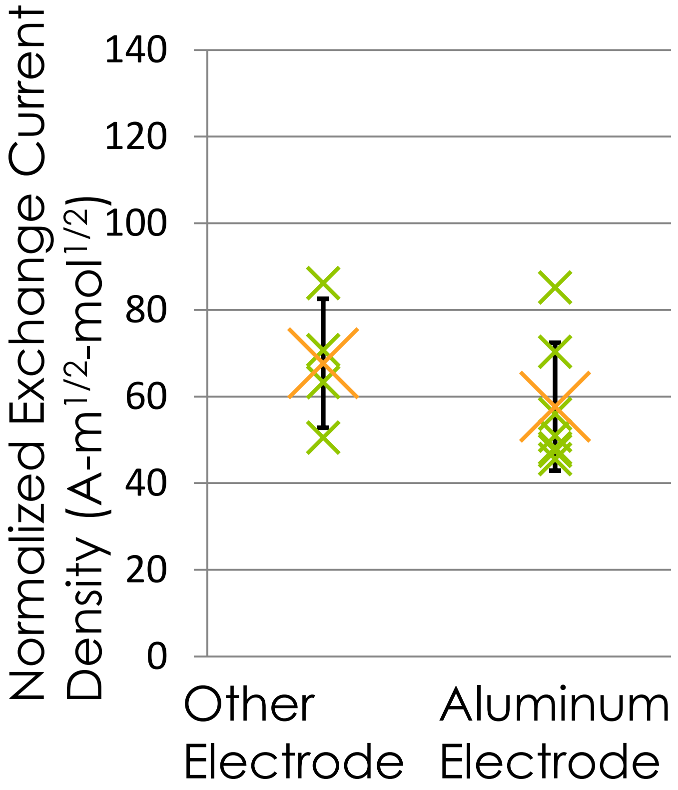
Uranium Transfer Coefficient

- At $\alpha \sim 0.5$, most exchange current densities approach averaged value
- This indicates that the cathodic transfer coefficient is 0.5.
- Shows that the methodology is sound



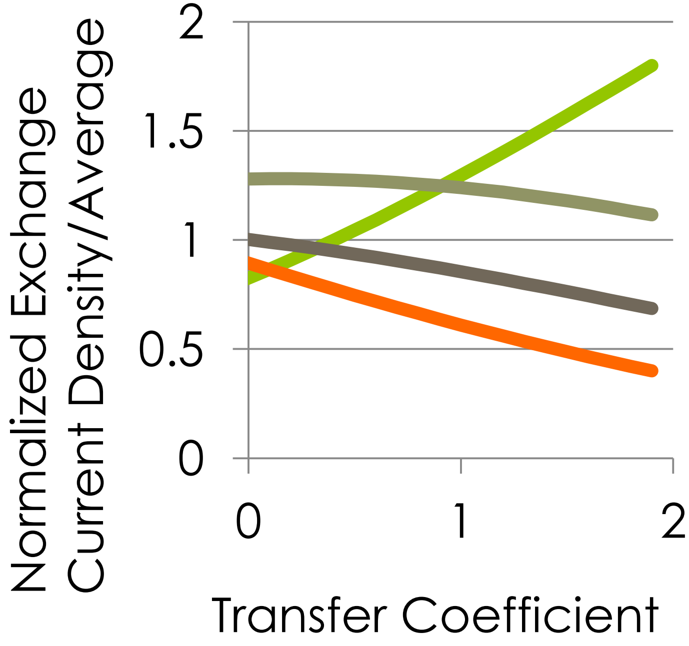
Plutonium Results

- Aluminum decreases deposition potential, so we treat it separately
- Aluminum exchange current density appears to be slightly lower



Plutonium Transfer Coefficient

- No value was found
- Possible that the same grouping that occurred with U also interfered
  - Unsure due to small sample size



Summary

- From this survey, we can estimate the value of uranium and plutonium exchange current density.
  - Previous range for U: 2.5 orders of magnitude
  - New ranges: 0.5 orders of magnitude
- Normalized exchange current densities found
  - Uranium: 30-100 A-$m^{1/2}$-$mol^{1/2}$
  - Plutonium: 40-100 A-$m^{1/2}$-$mol^{1/2}$
- It is believed that part of the uncertainty is due to diffusion but that another part is due to other phenomena
  - Use of graphical method
  - Electrode material
  - Additional species in salt
  - UCl_4