Measurements of $CeCl_3$ in LiCl-KCl Eutectic Salt via Cyclic Voltammetry and Electrochemical Impedance Spectroscopy

Dalsung Yoon and Supathorn Phongikaroon

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Idaho Falls, ID

VCU | Virginia Commonwealth University
Department of Mechanical & Nuclear Engineering

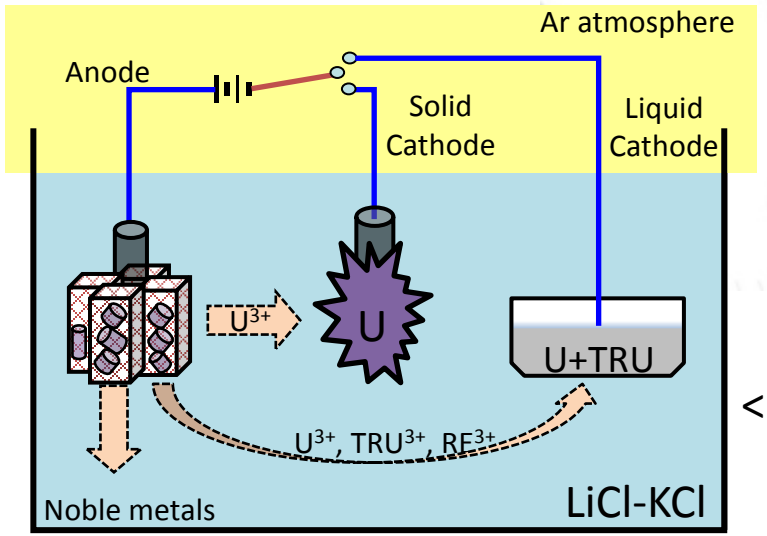
NEUP | Nuclear Energy University Programs
U.S. Department of Energy

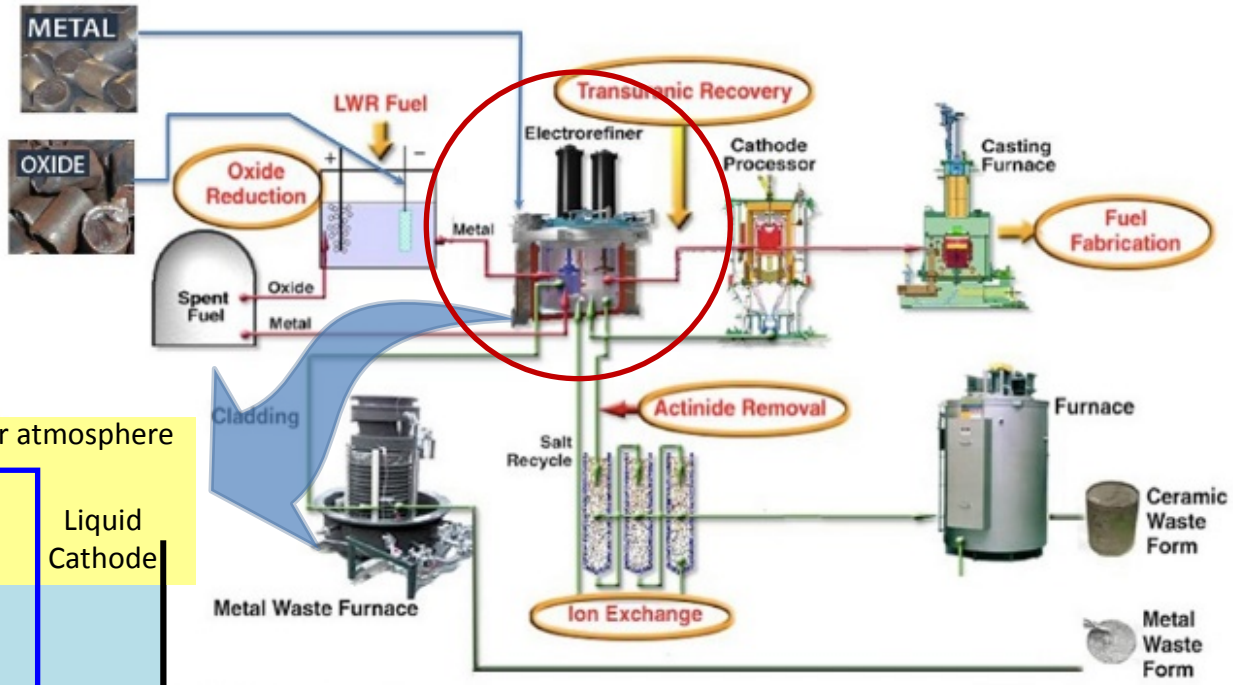
Presentation Outline

- Background
  - Pyroprocessing
  - Motivation
  - Objective
- Experimental
  - Materials & chemicals
  - Experimental setup
- Results & Discussion
  - Cyclic-voltammetry
  - Electrochemical impedance spectroscopy
- Summary & Future works

Background

- Pyroprocessing





<EBRII used-fuel treatment process at INL>

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Motivation

- Understand kinetic and electrochemical properties of uranium on solid and liquid electrode.
- Exchange current density of uranium has not been studied and documented.

Goals

- Determine kinetic parameters of uranium :
  Diffusion coefficients, apparent standard potentials.
- Develop experimental method to measure exchange current density.

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Approach

- Cyclic voltammetry to determine kinetic parameters : Diffusion coefficients, apparent standard potentials
- EIS technique to measure the exchange current density.

Task 1

- Cerium
- Solid Cathode

Task 2

- Cerium
- Liquid Cadmium Cathode

Task 3

- Uranium
- Solid/Liquid Cathode

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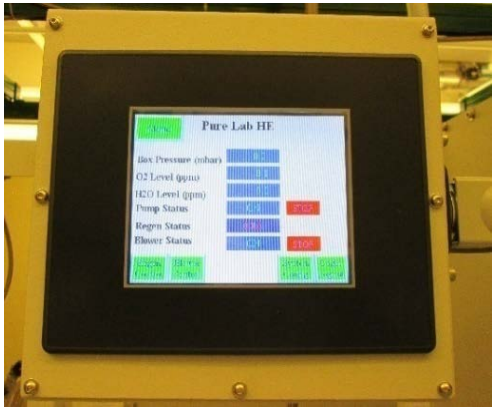
Experimental Setup

Apparatus

Glove box (RAM 1)



Glove box control panel

Potentiostat/Galvanostat (VSP-300, Biologic)

Furnace & electrode assembly

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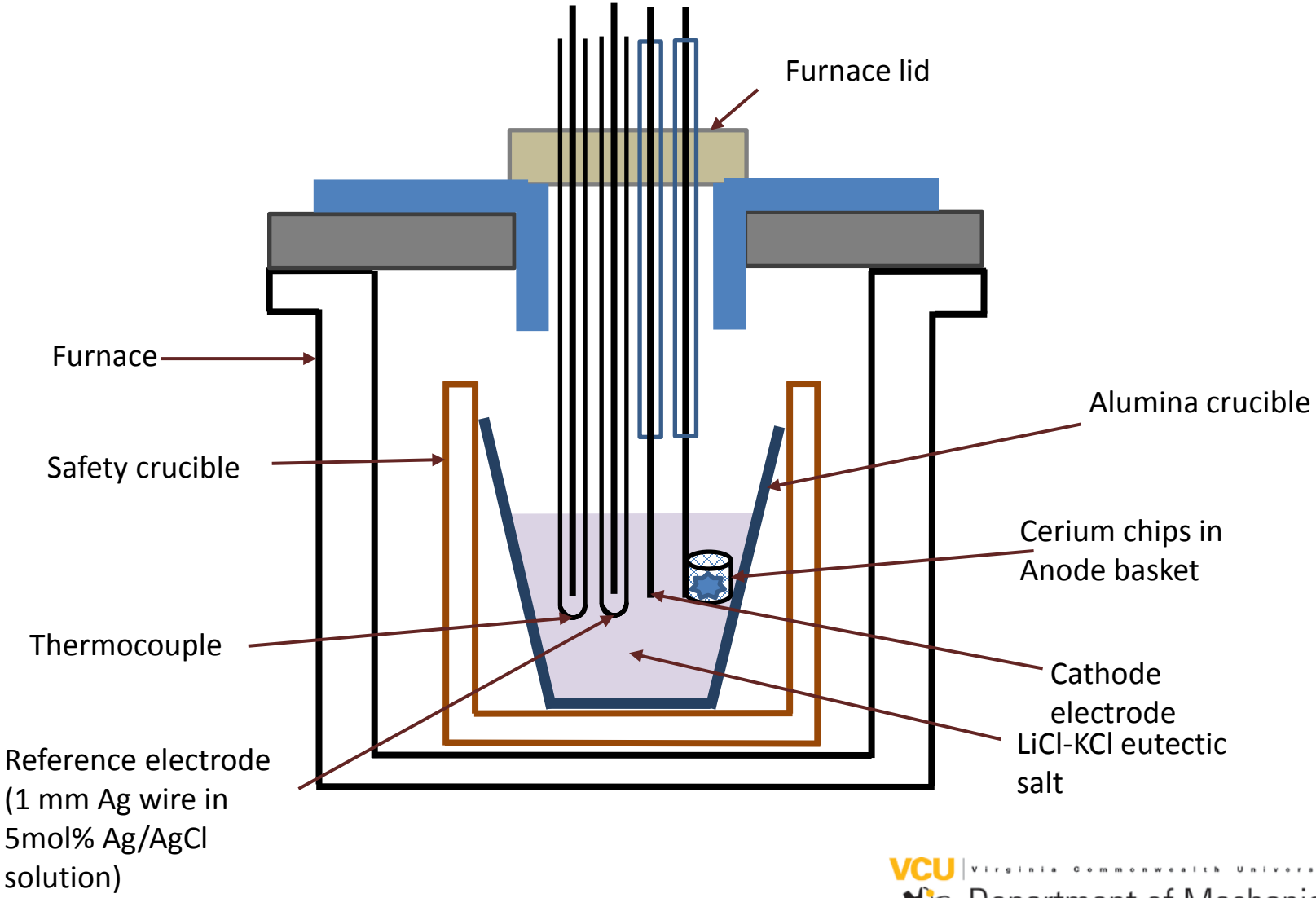
Sketch of Electrode Assembly



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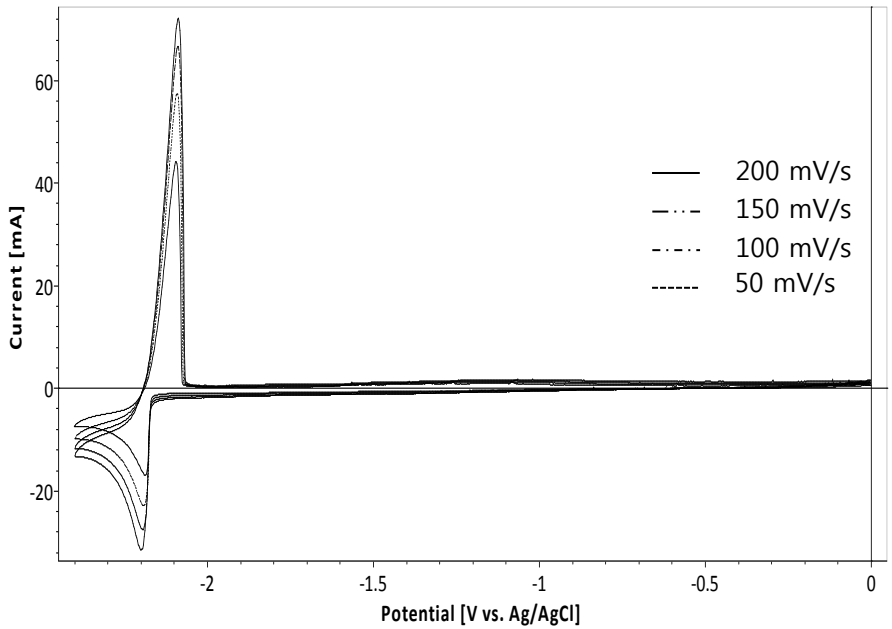
Summary of Materials & Chemicals

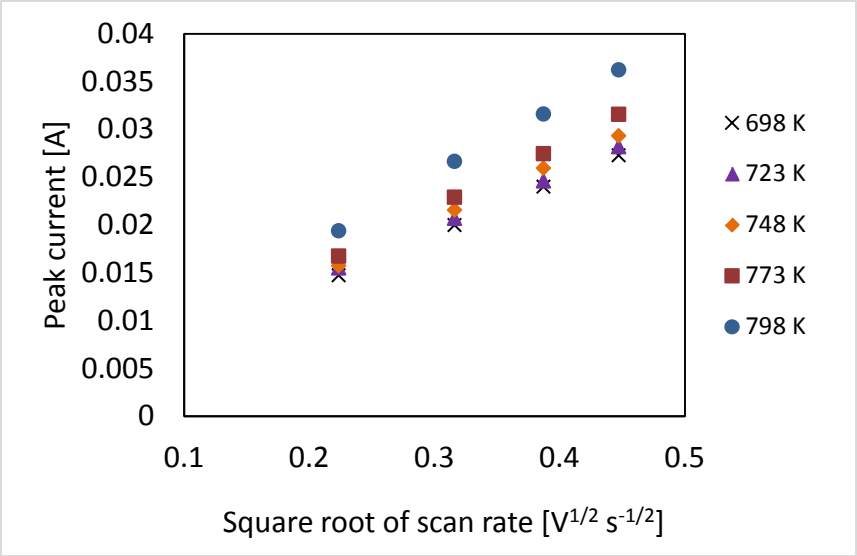
Electrochemical cell configuration	Material/Description	Photos
Vessel	Al_2O_3 crucible, 99.99%	
Safety crucible	Al_2O_3 crucible	
Cathode electrode	2mm tungsten rod, 99.95%	
Anode electrode	Cerium metal chips in meshed Mo basket	
Reference electrode	1mm Ag wire in 5 mol% AgCl-LiCl-KCl	

Chemicals	Preparation
LiCl, KCl Alfa Aesar 99.995%	LiCl-KCl(58.2:41.8 mol %)
$CeCl_3$, Sigma Aldrich 99.99%	0.5wt % $CeCl_3$ in LiCl-KCl
AgCl, Sigma Aldrich 99.998%	5 mol% AgCl in LiCl-KCl

Cyclic-voltammetry

Determine reversibility and diffusion coefficient, and apparent standard potential from 698 to 798 K.





Cyclic voltammograms of 0.5 wt% $CeCl_3$ (X_{CeCl3} = 1.17 x 10^{-3}) in LiCl-KCl eutectic salt with scan rate; 50, 100, 150, 200 mV/s

Dependence of the current versus square root of scan rate

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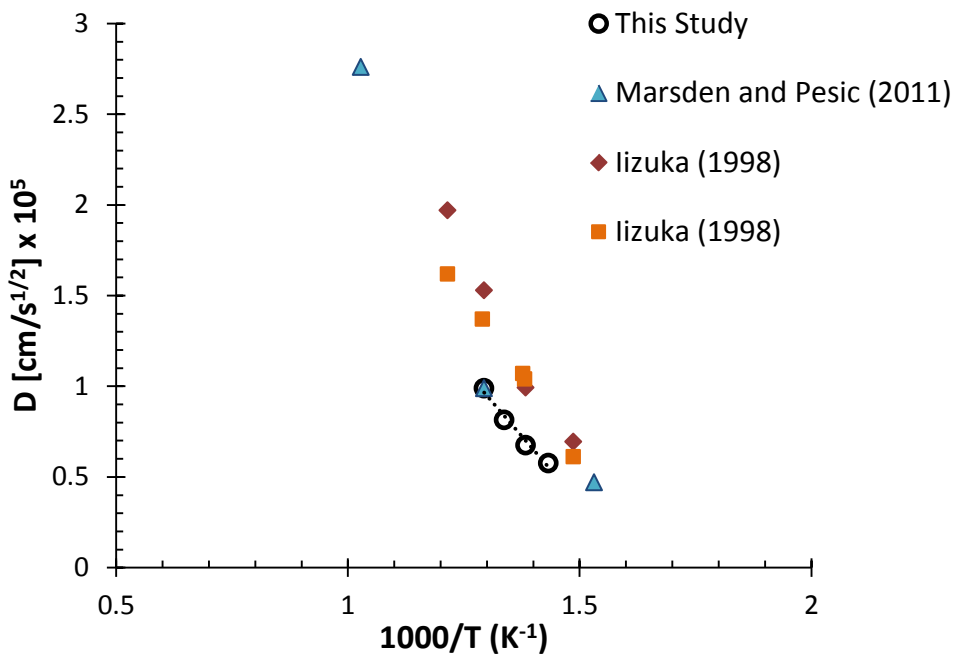
Diffusion coefficients were calculated by using Randles-Sevick equation and compared with other studies.

$$i_p = 0.611nFAC_0\left(\frac{nFvD}{RT}\right)^{\frac{1}{2}}$$

i_p : the cathodic peak current [V]
C_0 : $CeCl_3$ concentration [=3.32x10^{-5} mol/cm^3]
v: the scan rate [V/s]
A: the cathode area[cm^2]
D: the diffusion coefficient [cm^2/s]



Diffusion coefficients of Ce^{3+}/Ce in LiCl-KCl.
Error range of D = ± 2.14%

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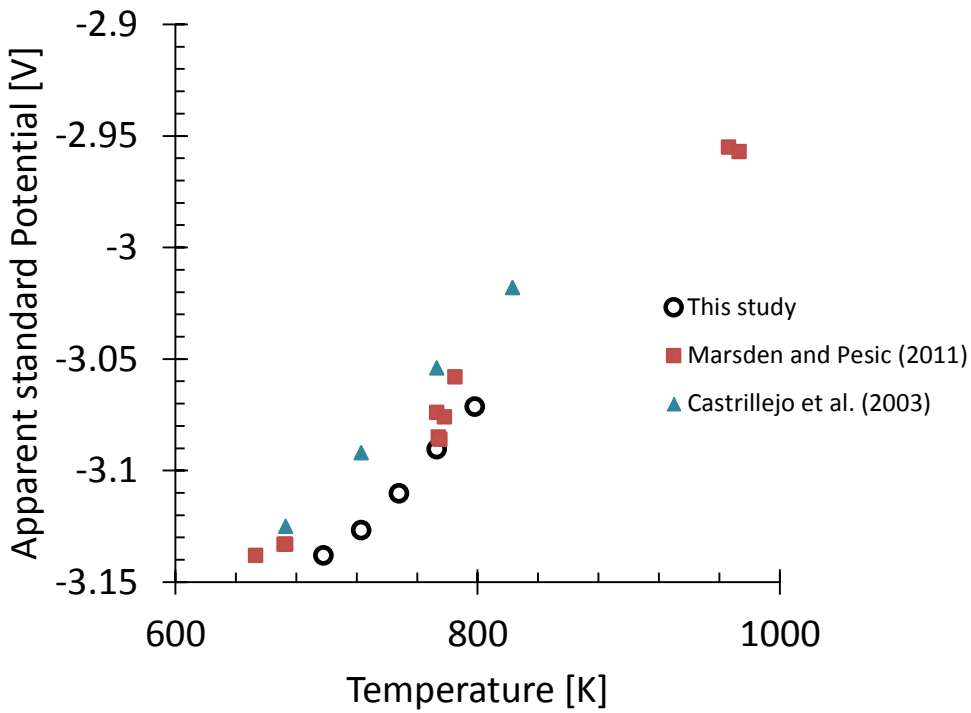
Apparent standard potentials were determined by

$$E_p = E^0_{CeCl_3} + \frac{RT}{nF}\ln X_{CeCl_3} - 0.854\frac{RT}{nF} + E^0_{AgCl} - \frac{RT}{F}\ln X_{AgCl}$$

E : the equilibrium potential [V]
E^0_{MClx} : an apparent standard potential[V]
R : the gas constant [J/mol K]
T : the absolute temperature [K]
n : the number of electrons transferred
F : Faradays' constant [C/mol]
X_{MClx} : mole fraction



Apparent standard potentials of Ce^{3+}/Ce in LiCl-KCl (3.32×10^{-5} mol/cm^3).

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Electrochemical Impedence Spectroscopy (EIS)

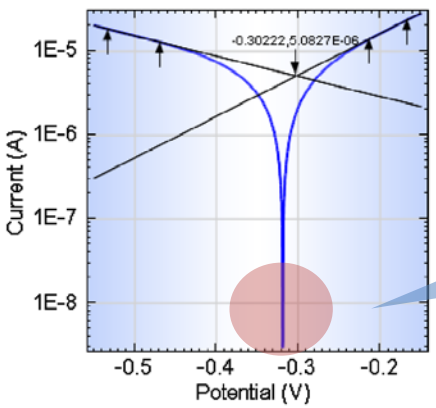
Exchange current density : The current in the absence of net electrolysis and at zero overpotential

$$i = \frac{RT}{\alpha}\ln i_0 - \frac{RT}{\alpha F}\ln i$$

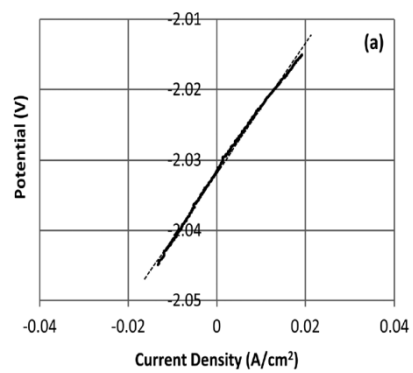
Small η

$$R_{ct} = \frac{RT}{nFi_0}$$

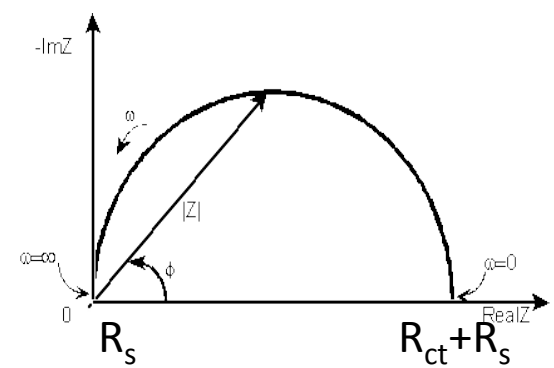
i_0 : the exchange current density [A/cm^2]
R_{ct} : the charge transfer resistance [Ohm]
α : the activity coefficient



Tafel plot for anodic and cathodic branches



Polarization curve



Impedance spectra

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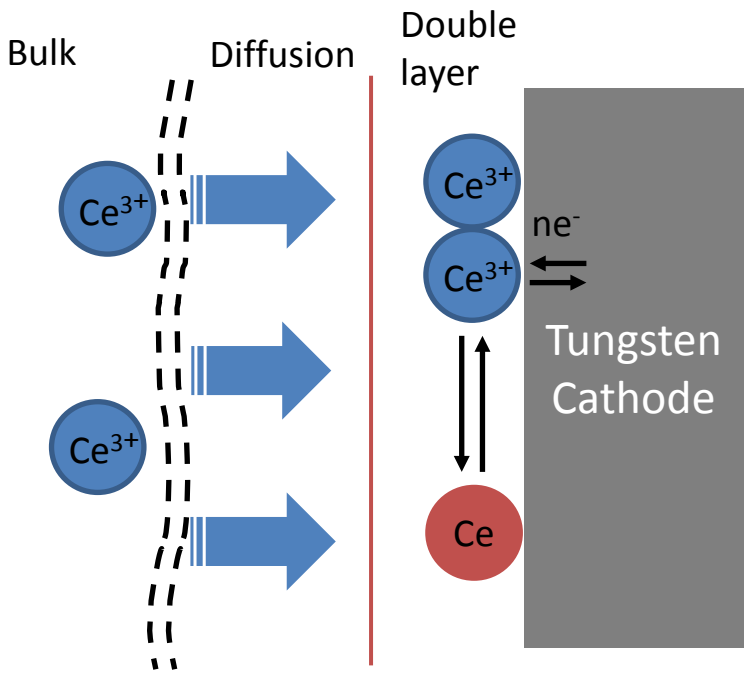
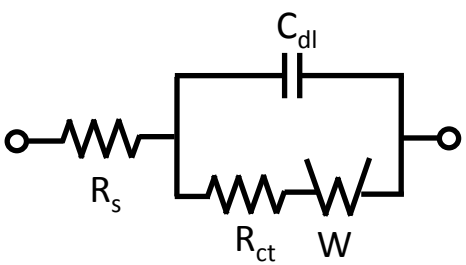
Approaches

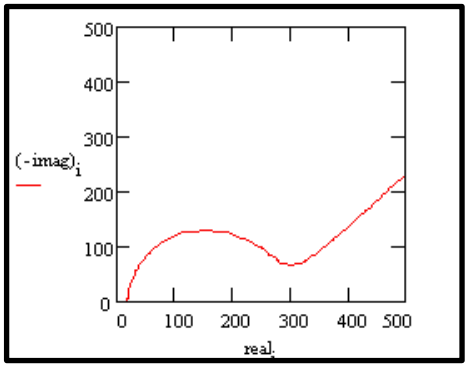


Components	Impedance Eq.
Resistor	$Z = R$
Capacitor	$Z = \frac{1}{i\omega C}$
Warburg	$Z = \sigma(\omega)^{-\frac{1}{2}}(1 - j)$

where C is the Farad, ω is the angular frequency, *j* is equal to $(-1)^{1/2}$ and σ is called Warburg constant



Expected Nyquist plot



Electrochemical system that includes electron transfer along with its equivalent circuit

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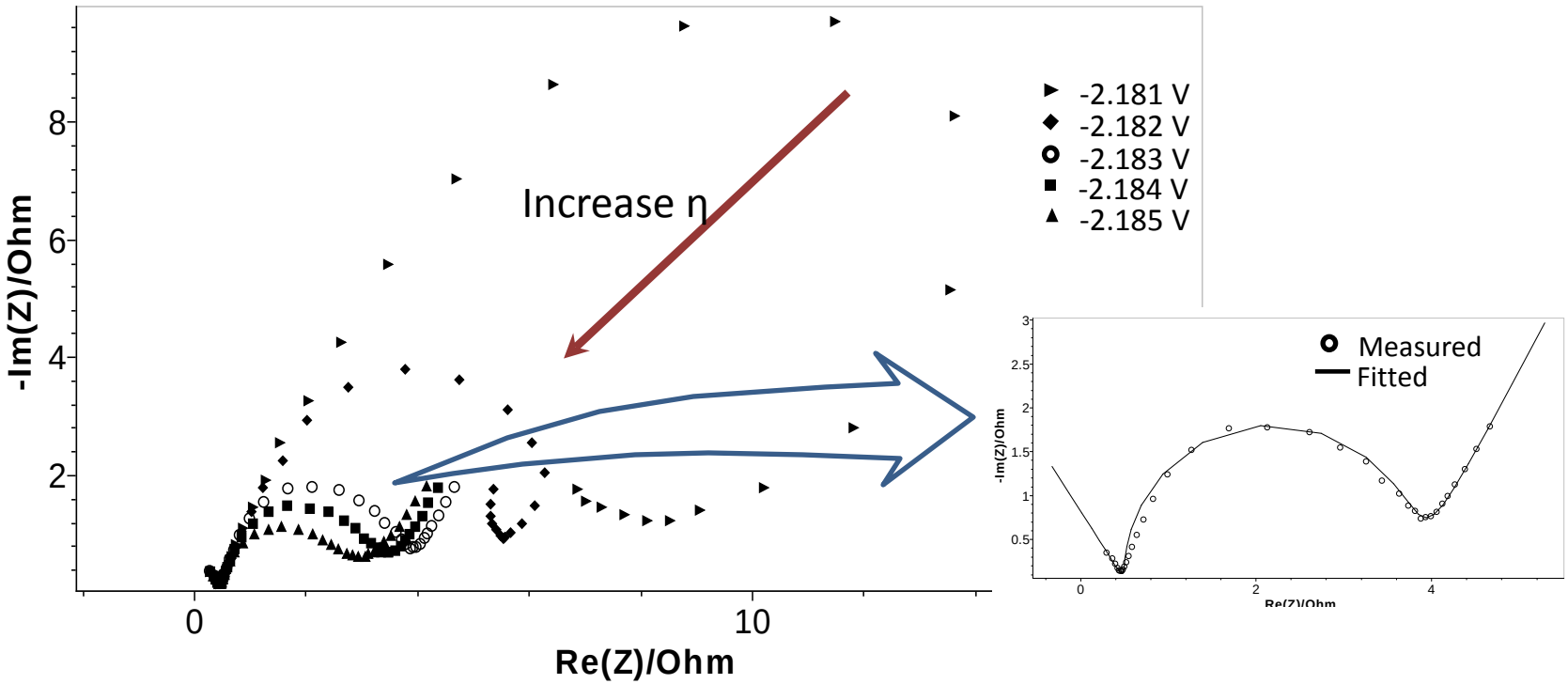
How to measure R_{ct} at Open Circuit Potential?



Nyquist plot for 0.5wt% $CeCl_3$ in LiCl-KCl at 698 K on W electrode, and fitted Nyquist plot. OCP : -2.179 V

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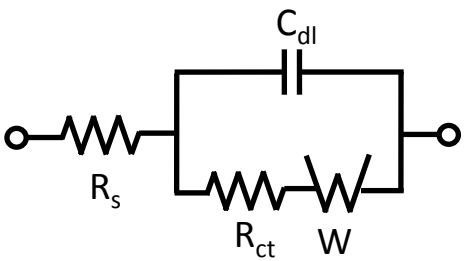
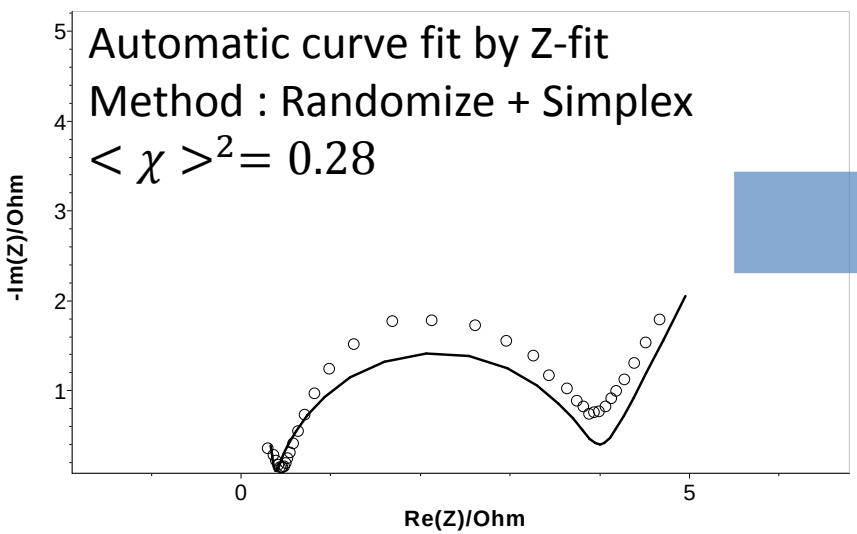
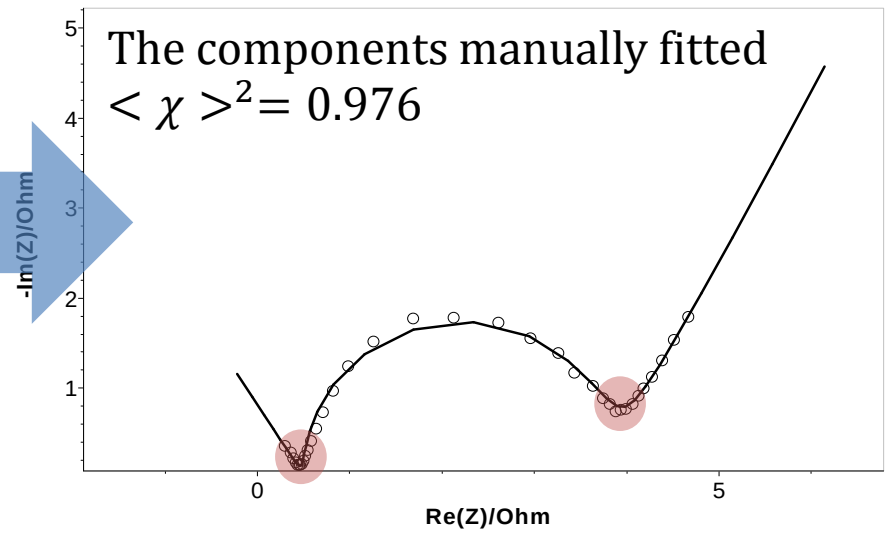
Curve fitting method (Z-fit, EC-Lab software)



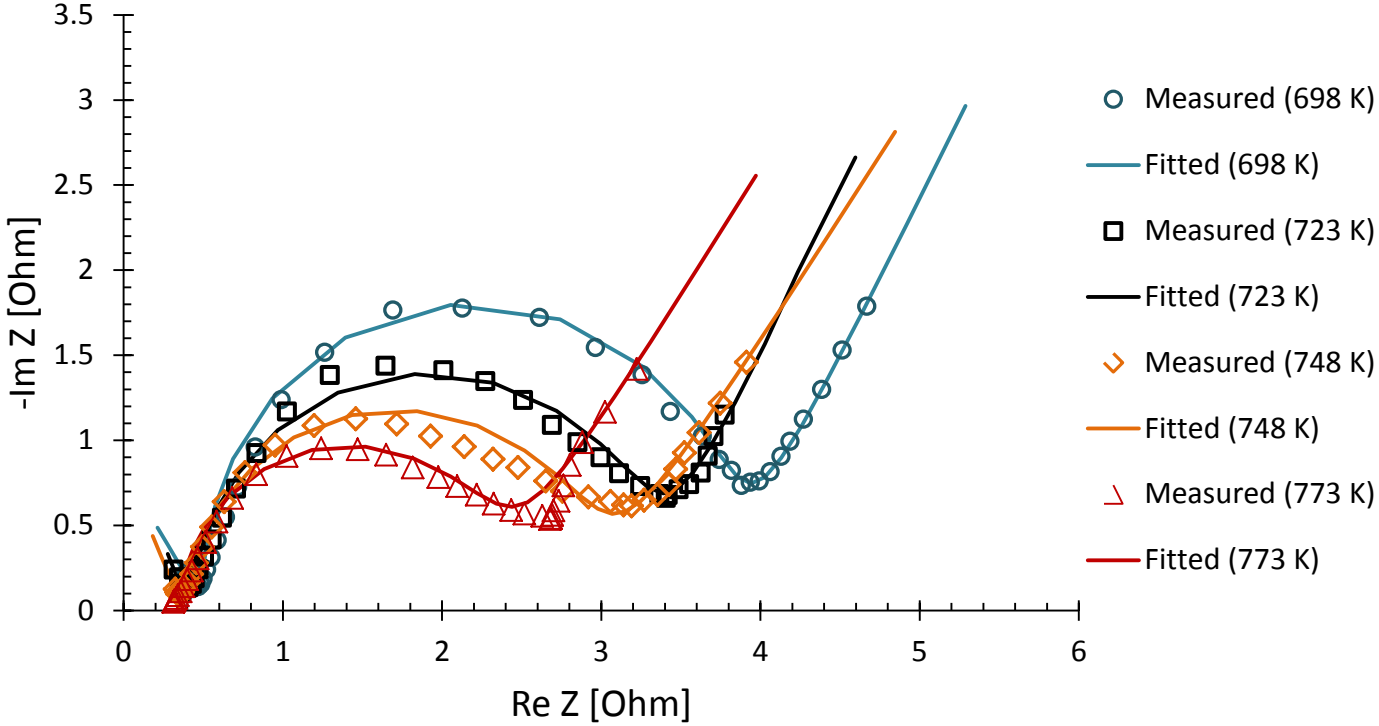
Components	**Impedance Eq.**
Resistor	$Z = R$
Capacitor	$Z = \frac{1}{i\omega C}$
Warburg	$Z = \sigma(\omega)^{-\frac{1}{2}}(1-j)$

$$Z_{CPE} = \frac{1}{Q(j\omega)^a}$$





Selected Nyquist curves & fit the curves by using EC-Lab curve fitting software.



Nyquist plot for 0.5wt% $CeCl_3$ in LiCl-KCl at 698, 723, 748, 773K on W electrode. Frequency : 50kHz~50mHz, $< \chi >^2 = 0.931 \sim 0.976$

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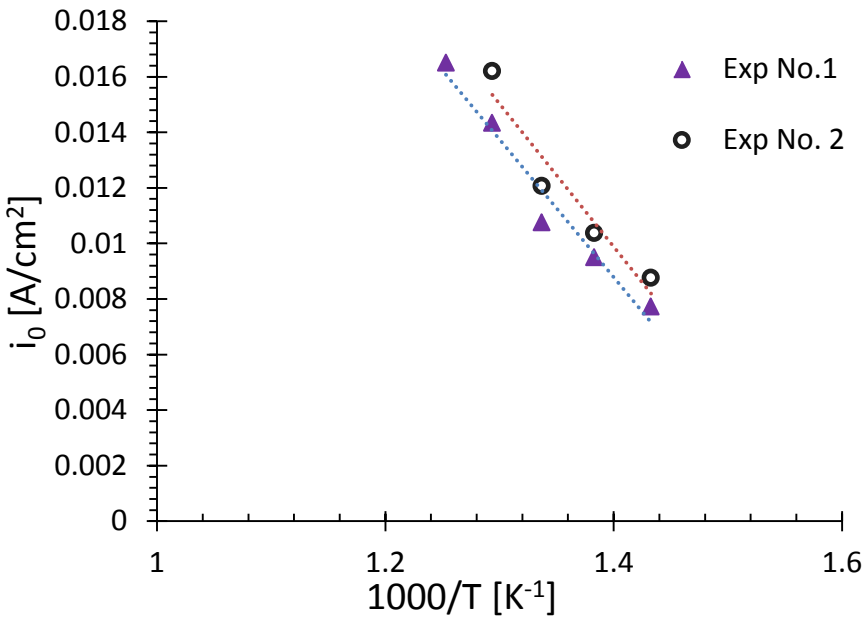
Charge transfer resistances were measured by fitting the Nyquist plots and exchange current densities were calculated by

$$R_{ct} = \frac{RT}{nFi_0} = \frac{RT}{n^2F^2Ak^0C_{Ce}^{1-\alpha}}$$

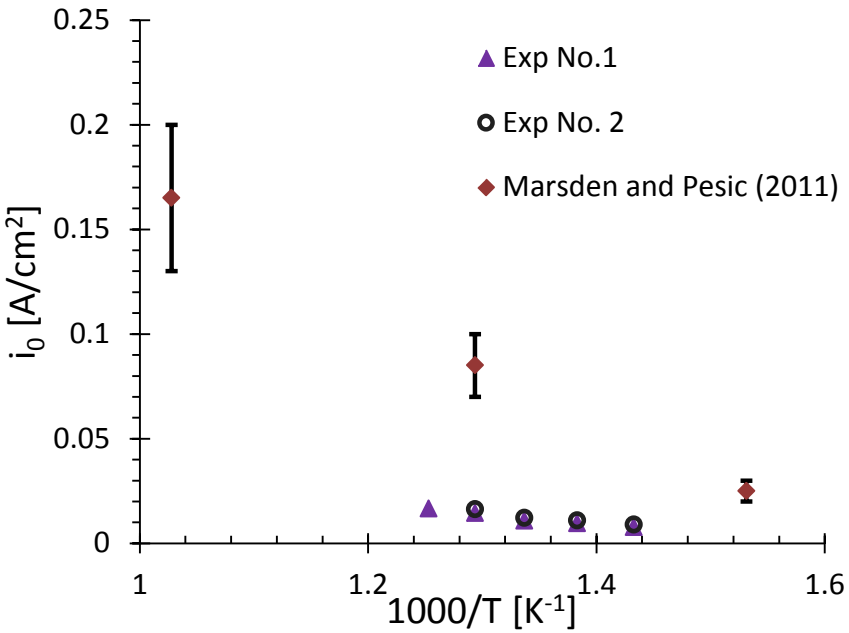
i_0 : the exchange current density [A/cm^2]
R_{ct} : the charge transfer resistance [Ohm]
α : the activity coefficient
k^0 : the rate constant for Ce^{3+}/Ce

T (K)	η [mV]	R_{ct} [Ω]	i_0 [A/cm^2] x10^2	k^0 [cm/s] X 10^6
698	4	3.34	0.91	5.45
723	5	2.92	1.08	6.46
748	4	2.53	1.29	7.72
773	5	2.18	1.54	9.25

Plot exchange current densities with respect to temperature



Plots of the exchange current densities with respect to 1000/T.



Various exchange current densities. (linear polarization method was used in Marsden and Pesic)

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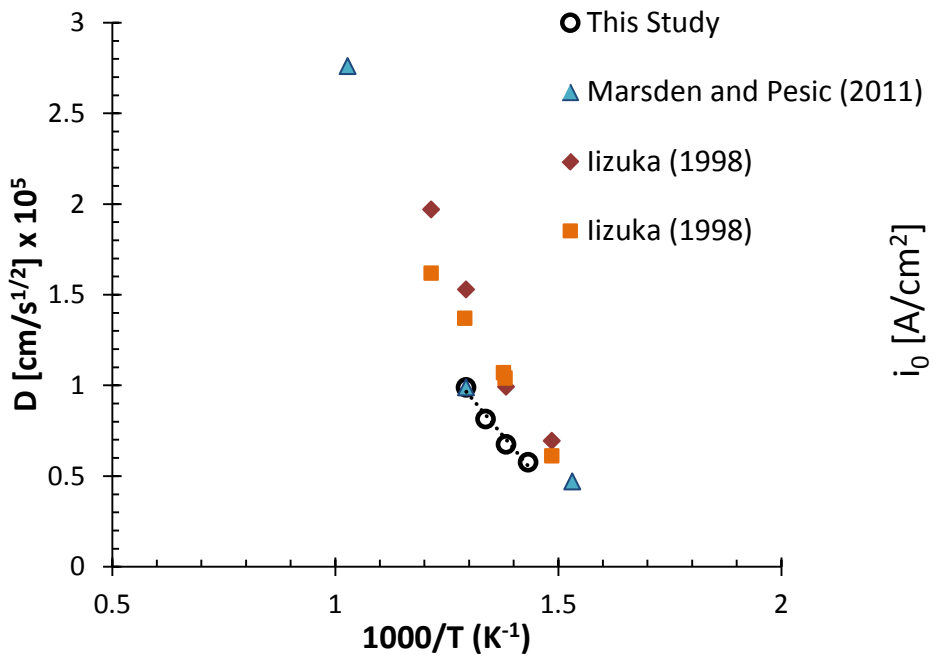
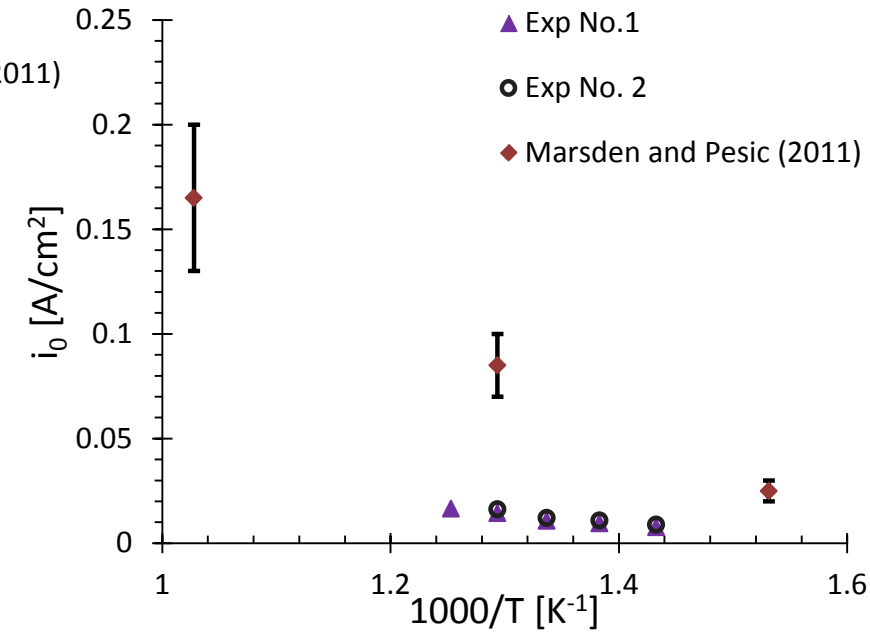
Summary

The electrochemical properties of $CeCl_3$ in a LiCl-KCl salt at different temperatures were studied.



Measured diffusion coefficients of Ce^{3+}/Ce



Measured exchange current densities of Ce^{3+}/Ce

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Future work

- Proof the repeatability of impedance spectra to measure exchange current densities.

- Determine the exchange current densities in different concentration of $CeCl_3$.

- Assess electrochemical and kinetic properties with liquid cadmium cathode.

- Assess electrochemical and kinetic properties of URANIUM.

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- Colleague Students: Ammon Williams, Keith Bryce

Reference

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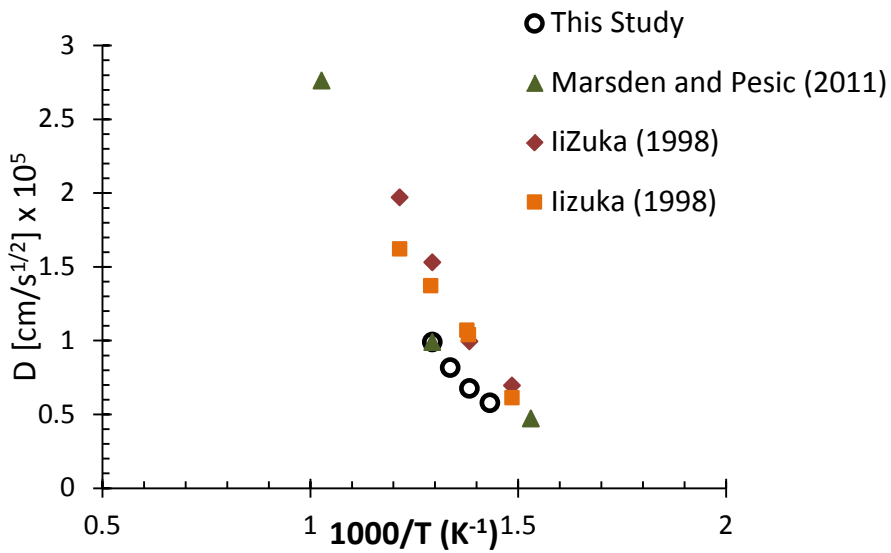
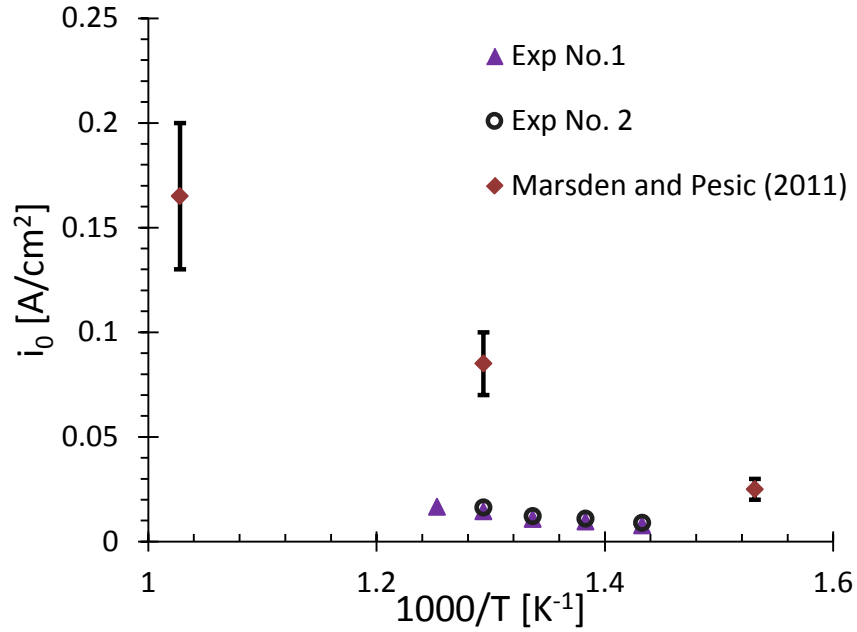
The electrochemical properties of $CeCl_3$ in a LiCl-KCl salt at different temperatures were studied.



Measured diffusion coefficients of Ce^{3+}/Ce



Measured exchange current densities of Ce^{3+}/Ce

QUESTIONS?

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