Electrochemical Zirconium Recovery Experiments in Molten Salt System

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Outline

• Introduction
• Motivation and Goal
• Experimental Setup
• Experimental Procedures
• Summary & Future Work
Introduction

- The Experimental Breeder Reactor-II (EBR-II) was a metallic fueled, sodium cooled fast reactor operated at Argonne National Laboratory-West (currently Idaho National Laboratory) from 1963-1994.
- This reactor was fueled with a sodium-bonded, uranium-zirconium alloy fuel.
- An electrochemical process was developed by Argonne National Laboratory to treat this stainless steel clad driver fuel.
- This electrochemical process is currently being used at Idaho National Laboratory to treat the used EBR-II driver fuel.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>80.596</td>
<td>III</td>
</tr>
<tr>
<td>Zr</td>
<td>10.805</td>
<td>IV</td>
</tr>
<tr>
<td>Na</td>
<td>2.160</td>
<td>I</td>
</tr>
<tr>
<td>Nd</td>
<td>0.930</td>
<td>III</td>
</tr>
<tr>
<td>Mo</td>
<td>0.771</td>
<td>III</td>
</tr>
</tbody>
</table>

EBR-II Used Fuel Treatment Process

Element Chopper

Electrorefiner

Cathode Processor

Casting Furnace

Depleted Uranium

Uranium Product

Spent Fuel

Element Segments

Cladding + Noble Metal + Fission Products

Salt w/ TRU + Fission Products + NaCl

Zeolite + Glass

Salt/Zeolite Blending

Zirconium

Metal Waste Furnace

Ceramic Waste Furnace

Ceramic Waste Form

Metal Waste Form

Uranium, Salt

Zirconiun
Mark-IV Electrorefiner (ER)

- **Anode**
  - $U \rightarrow U^{3+} + 3e^-$
  - $Zr \rightarrow Zr^{n+} + ne^-$

- **Cathode**
  - $U^{3+} + 3e^- \rightarrow U$
  - $Zr^{n+} + ne^- \rightarrow Zr$
Motivation and Goal

• Zirconium constitutes a large amount of the EBR-II used driver fuel at greater than 10 wt%.

• Over time, zirconium metal tends to build up within the Mark-IV ER and must periodically be removed.

• In developing a process to electrochemically recover pure zirconium, a knowledge of the Zr redox reactions that occur in the ER is necessary.

• To better understand this process, modeling is essential.

• In the electrochemical modeling process, there are several thermodynamic and electrochemical values that are required.
  - Standard Reduction Potential, \( E^0 \)
  - Diffusion Coefficient, \( D \)
  - Activity Coefficient, \( \gamma \)
• Nernst Equation:

\[ E = E^0 + \frac{RT}{nF} \ln(\gamma X_s) \]

- \( E \)  Equilibrium potential
- \( E^0 \)  Standard reduction potential
- \( R \)  Ideal gas constant
- \( T \)  Absolute temperature
- \( n \)  Number of transferred electrons
- \( F \)  Faraday’s constant
- \( \gamma \)  Activity coefficient
- \( X_s \)  Mole fraction at interface

• What is the standard reduction potential, \( E^0 \)?
  - The standard potential is the equilibrium potential, \( E \), of a given reduction reaction (i.e. \( \text{Zr}^{4+} + 4e^- \rightarrow \text{Zr} \)) at standard conditions.
    - Pure substance at 1 atm pressure
      - \( \gamma = 1 \) and \( X_s = 1 \)
    - This is related to the Gibbs free energy change of the same half-cell reaction.
      \[ \Delta G^0 = -nFE^0 \]
      \( \Delta G_i^0 \)  Gibbs energy change of reaction i
Mass Transfer:

\[ N = kA(C_s - C_{\text{salt}}) \]

\[ Sh = \frac{kd_e}{D} = 0.0791 \left( \frac{\omega d_e^2}{v} \right)^{0.7} (D)^{0.356} \]

What is the diffusion coefficient?

- Proportionality constant between molar flux and concentration gradient.
- Fick’s 1st Law:
  \[ N = -D \nabla C \]
- Follows the Arrhenius temperature dependence.

\[ D = D_0 \exp\left( -\frac{\Delta H_D}{RT} \right) \]

\begin{align*}
\text{N} & \quad \text{Molar mass transfer} \\
\text{k} & \quad \text{Mass transfer coefficient} \\
\text{C}_{\text{salt}} & \quad \text{Bulk salt concentration} \\
\text{Sh} & \quad \text{Sherwood number} \\
\text{d}_e & \quad \text{Equivalent electrode diameter} \\
\text{A} & \quad \text{Total electrode surface area} \\
\text{C}_s & \quad \text{Surface concentration} \\
\text{\omega} & \quad \text{Electrode rotation rate} \\
\text{v} & \quad \text{Viscosity of salt} \\
\text{D}_0 & \quad \text{Pre-exponential factor} \\
\Delta H_D & \quad \text{Activation energy for diffusion}
\end{align*}
# Available Literature Values

<table>
<thead>
<tr>
<th>Standard Reduction Potential, $E^0$ (V vs. Ag/AgCl)</th>
<th>Diffusion Coefficient, $D$ (cm$^2$/s)</th>
<th>Activity Coefficient, $\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(IV)/Zr</td>
<td>Zr(IV)/Zr(II)</td>
<td>Zr(II)/Zr</td>
</tr>
<tr>
<td>[2]</td>
<td>-1.22*</td>
<td>---</td>
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<tr>
<td>[3]</td>
<td>-1.064*</td>
<td>-1.121*</td>
</tr>
<tr>
<td>[4]</td>
<td>-0.838</td>
<td>---</td>
</tr>
<tr>
<td>[5]</td>
<td>-1.064*</td>
<td>-1.121*</td>
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<tr>
<td>[7]</td>
<td>-1.1</td>
<td>---</td>
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<tr>
<td>[8]</td>
<td>-1.22</td>
<td>---</td>
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<td>[9]</td>
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<td>---</td>
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<tr>
<td>[10]</td>
<td>---</td>
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</tr>
</tbody>
</table>

* Values reported are at 450 °C.

**References**

(a) Al$_2$O$_3$ sheathed thermocouple
   - Monitored with Fluke 52II
(b) Tungsten working electrode
(c) Ag/AgCl reference electrode
   (5 mol%)
(d) Glassy carbon counter electrode
   lead
(e) Glassy carbon crucible/counter electrode
(f) MgO secondary crucible
(g) Eutectic LiCl/KCl salt containing ZrCl$_4$
(h) Furnace
   - Kerrlab with graphite crucible
Procedures

• Loading LiCl/KCl eutectic and ZrCl\textsubscript{4}
  - (1.0, 2.5, and 5.0) wt% ZrCl\textsubscript{4}
  - LiCl/KCl eutectic, 44/56 wt% (Sigma-Aldrich, 99.99%)
  - ZrCl\textsubscript{4} (Alfa Aesar, Reactor Grade, 99.5+\%)
• Heating salt at 4 °C/min to 500 °C (± 2) in the salt.
• Lowering electrodes into the molten salt.
  - Tungsten Working Electrode
    - d = 2.0 mm (Alfa Aesar, 99.95%)
  - Glassy Carbon Counter Electrode Lead
    - d = 3.0 mm (HTW-Germany)
  - Ag/AgCl Reference Electrode
    - Ag wire, d = 1.0 mm diameter (Acros Organics, 99.9%)
    - 5 mol% AgCl in LiCl/KCl (Alfa Aesar, ultradry, 99.997%)
Electrochemistry

- Cyclic Voltammetry
  - Scan range: 0 V to -2.4 V
  - Scan rate: 300 mV/s to 2.0 V/s
- Chronopotentiometry
  - Driving current: 70 mA to 300 mA

Samples taken for ICP-MS analysis.

- Mixed:
  - 1.0 wt%
  - 2.5 wt%
  - 5.0 wt%

Analysis Results:

- (0.954 ± 0.117) wt%
- (2.49 ± 0.304) wt%
- (4.84 ± 0.585) wt%
Chloride Salt Ingots

Pure LiCl/KCl Eutectic
1.0 wt% ZrCl$_4$

2.5 wt% ZrCl$_4$

5.0 wt% ZrCl$_4$
Cyclic Voltammetry (CV)

- A common electrochemical technique that can be used to determine the reactions that can occur in the electrochemical cell.
- Potential is scanned through the range of interest and current is measured.
  - Potential Range Scanned: 0 V to -2.4 V
    - Li$^+$ Reduction: -2.561 V [12]
    - Cl$^-$ Oxidation: +1.065 V [12]
- From the resulting current, reaction information can be determined.
  - Randles-Sevcik equation
    \[
    \frac{I_p}{\sqrt{v}} = 0.446nFAC\sqrt{\frac{n\alpha FD}{RT}}
    \]
  - Delahay equation
    \[
    \frac{I_p}{\sqrt{v}} = 0.4958nFAC\sqrt{\frac{n\alpha FD}{RT}}
    \]
  - Equilibrium potential
    \[
    E = \frac{E_{p,a} + E_{p,c}}{2}
    \]
  - Apparent standard potential
    \[
    E = E^o' + \frac{RT}{nF} \ln(X)
    \]

Chronopotentiometry (CP)

- An electrochemical technique that can be used to determine the diffusion coefficient of ions within the electrolyte.
- A large driving current is applied and the resulting potential is measured.
  - To maintain the applied current, the 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 drops to a potential at which the next ion will reduce.
  - This creates a plateau in the measured potential.
  - The duration of this plateau, or transition time, $\tau$, is related to diffusion coefficient, $D$, through the Sand equation.

$$i\sqrt{\tau} = \frac{nFC\sqrt{\pi D}}{2}$$

- From the resulting potential response, transition time and diffusion can be determined.
Cyclic Voltammogram (1.0 wt% ZrCl$_4$)

**Scan Rate**
- LiCl/KCl 200 mV/s
- 300 mV/s
- 350 mV/s
- 400 mV/s
- 450 mV/s
- 500 mV/s
- 550 mV/s
- 600 mV/s
- 650 mV/s
- 700 mV/s
- 800 mV/s
- 900 mV/s
- 1.0 V/s

Electrode Surface Area: 0.53 cm$^2$

- $\text{Zr}^+ \rightarrow \text{Zr}^{4+} + 3e^-$
- $\text{Zr} \rightarrow \text{Zr}^{2+} + 2e^-$
- $\text{Zr} \rightarrow \text{Zr}^{4+} + 4e^-$
- $\text{Zr}^{2+} \rightarrow \text{Zr}^{4+} + 2e^-$
- $\text{Zr}^{4+} + 2e^- \rightarrow \text{Zr}^{2+}$
- $\text{Zr}^{4+} + 3e^- \rightarrow \text{Zr}^+$
1.0 wt\% ZrCl\textsubscript{4}

A $\text{Zr}^{4+} + 2e^- \rightarrow \text{Zr}^{2+}$
B $\text{Zr}^{2+} + 2e^- \rightarrow \text{Zr}$
$\text{Zr}^{4+} + 3e^- \rightarrow \text{Zr}^+$
C $\text{Zr}^+ + e^- \rightarrow \text{Zr}$
$\text{Zr}^{4+} + 4e^- \rightarrow \text{Zr}$
D $\text{Zr}^+ \rightarrow \text{Zr}^{4+} + 3e^-$
$\text{Zr} \rightarrow \text{Zr}^{2+} + 2e^-$

\[ i_p = 0.4958nFC\sqrt{\frac{n\alpha FD\nu}{RT}} \]

<table>
<thead>
<tr>
<th>Peak</th>
<th>Diffusion Coefficient, D (cm\textsuperscript{2}/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n = 1$</td>
</tr>
<tr>
<td>A</td>
<td>$9.26 \times 10^{-5}$</td>
</tr>
<tr>
<td>B</td>
<td>$1.50 \times 10^{-4}$</td>
</tr>
<tr>
<td>C</td>
<td>$1.52 \times 10^{-5}$</td>
</tr>
<tr>
<td>D</td>
<td>$1.19 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Cyclic Voltammogram (2.5 wt% ZrCl$_4$)

Scan Rate
- 400 mV/s
- 500 mV/s
- 800 mV/s
- 900 mV/s
- 1.0 V/s
- 1.1 V/s
- 1.5 V/s
- 2.0 V/s

Electrode Surface Area: 0.72 cm$^2$
Cyclic Voltammogram (5.0 wt% ZrCl$_4$)

Scan Rate
- 250 mV/s
- 350 mV/s
- 450 mV/s
- 550 mV/s
- 650 mV/s

Electrode Surface Area: 0.69 cm$^2$
Nernst Plot for Peaks B and D

- **Equation for Nernst Plot**: 
  \[ E = E^0 + \frac{RT}{nF} \ln(X) \]
  \[ E = -0.849 + 0.0389 \ln(X) \]
  \[ R^2 = 0.9829 \]

- **Apparent reduction potential**: 
  \[ E^0' = -0.849 \text{ V (vs Ag/AgCl)} \]

- **Average number of electrons transferred in the reaction(s)**: 
  \[ n = 1.71 \]
Chronopotentiometry (1.0 wt% ZrCl$_4$)

Applied Driving

- Current:
  - 70 mA
  - 80 mA
  - 90 mA
  - 100 mA
  - 150 mA

Electrode Surface Area: 0.53 cm$^2$
Summary

• An experimental setup and process has been designed to test properties relevant to the electrochemical recovery of zirconium in molten salt.

• Cyclic voltammetry has been performed on (1.0, 2.5, and 5.0) wt% ZrCl$_4$ in the molten LiCl/KCl eutectic salt at 500 °C.
  - Cyclic voltammograms show complex behavior of zirconium in the molten salt with presence of ZrCl$_4$, ZrCl$_2$, and ZrCl.
  - Range of diffusion coefficients in the LiCl/KCl eutectic was determined.
    • $D = 2.37 \times 10^{-7} - 1.48 \times 10^{-4}$ cm$^2$/s
  - Apparent standard reduction potential was determined for one pair of peaks.
    • $E^\circ' = -0.849$ V vs. Ag/AgCl

• Chronopotentiometry was performed and shows complex behavior.
## Summary

<table>
<thead>
<tr>
<th>Standard Reduction Potential, $E^0$ (V vs. Ag/AgCl)</th>
<th>Diffusion Coefficient, $D$ (m$^2$/s)</th>
<th>Activity Coefficient, $\gamma$</th>
<th>This Work</th>
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<td>$\text{Zr(IV)/Zr}$</td>
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<td>$\text{Zr(IV)}$</td>
</tr>
<tr>
<td>[2] -1.22*</td>
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<td>-1.12</td>
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<td>[3] -1.064*</td>
<td>-1.121*</td>
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<td>[4] -0.838</td>
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<td>-0.722</td>
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<tr>
<td>[5] -1.064*</td>
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<td>-1.007*</td>
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<td>[7] -1.1</td>
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<td>[9] ---</td>
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<tr>
<td>[10] ---</td>
<td>---</td>
<td>---</td>
<td>$1.13 \times 10^{-5}$</td>
</tr>
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</table>

* Values reported are at 450 °C.

Future Work

• Further analysis of chronopotentiometry data.
• Further work with ZrCl$_4$ at additional concentrations.
• Zirconium electrodeposition experiments with transparent setup to analyze zirconium deposit morphology.
• Experiments to optimize/maximize zirconium recovery.
  • Cathode material, operating temperature, applied potential.
• Electrochemistry experiments/analysis with UCl$_3$ in LiCl/KCl eutectic.
• Final phase of this work will explore the electrochemical recovery of zirconium in the presence of uranium.
Acknowledgements

• This work was performed as part of I-NERI Project 2010-001-K in conjunction with Seoul National University and Korea Atomic Energy Research Institute.

• Thanks to all those who have helped with this project including Debbie Lacroix, Sean Martin, Ammon Williams, Josh Versey, Mike Pack, Cindy Hanson, and Dalsung Yoon.
Thanks!
Activity Coefficient

• Nernst Equation

\[ E = E^0 + \frac{RT}{nF} \ln(\gamma X_s) \]

• What is the activity coefficient, \( \gamma \)?
  - A factor included in order to take account of deviations from solution ideality in the liquid phase.
  - It is related to the excess Gibbs energy, \( G^E \), the difference between the actual and ideal Gibbs energy of a solution.

\[ \bar{G}^E = RT \ln(\gamma) \quad \text{G}^E \text{ Excess Gibbs energy} \]

- It is defined as a ratio of the fugacity of the species in solution and its mass fraction in solution times its pure species fugacity.

\[ \gamma \equiv \frac{\hat{f}}{xf} \quad \hat{f} \text{ Fugacity in solution} \]
\[ x \text{ Mass fraction in solution} \]
\[ f \text{ Fugacity of pure species} \]