Feasibility Study of Pyrochemical Treatment on Fuel Debris by Performing U and Zr Electrochemistry in LiCl-KCl Molten Salt

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Outline

• Brief Background
• Motivation and Goal
• Experimental Program
• Basic Electrochemistry
• Results and Discussion
• Conclusion
Background

- In the light of the accident at the Fukushima Daiichi NPP,
  - 3 Phases existed for mid- and long-term plans

1st: 2 years                  2nd: Next 10 years                  3rd: In 30 – 40 years
FUEL REMOVAL FROM THE POOL   REMOVAL OF FUEL DEBRIS            REMOVED, PROCESSED, AND DISPOSED FUEL DEBRIS WITH PROPER WASTE MANAGEMENT

- Technical plans in various aspects:
  - Direction on recovery and treatment,
  - Characterization,
  - Conditions and long term performances, and
  - **Possibility of treatment path for toxicity reduction.**
Separation Methods

• Possible fuel debris treatments due to previous studies on debris samples in TMI-2.

• Aqueous and Pyrochemical separation methods
  – PUREX – dissolving in nitric acid and fluoric acid showing that neither 6 N HNO₃ nor 3 M HNO₃ + 1 M HF mixture could be used to dissolve the actual debris.

  – Japan Atomic Energy Agency (JAEA) and Central Research Institute of Electric Power Industry (CRIEPI) – advantage on pyrochemical treatment in term of solubility of debris and secondary waste volume through oxide reduction tests.
Motivation and Goal

• No fundamental experiment to further gain insight in reprocessing of the fuel debris after electrolytic oxide reduction step.

Motivation
Explore concentration effects on thermodynamic and electrochemical properties for U and Zr in LiCl-KCl molten salt system under common electrorefiner’s conditions.

Goal
Gain fundamental understanding and path forward in applying pyrochemical process in order to separate U and Zr efficiently.
a) Al₂O₃ sheathed thermocouple  
b) Tungsten (99.95%) working electrode  
c) Ag/AgCl (99.997%) reference electrode (5 mol%)  
d) Glassy carbon counter electrode lead  
e) Glassy carbon crucible/counter electrode  
f) MgO secondary crucible  
g) Eutectic LiCl-KCl (99.99%) containing dUCl₃ (75 wt%) or ZrCl₄ (99.95+%)  
h) Kerrlab furnace
Experimental Equipment

- A quartz electrode assembly was used to position the electrodes and thermocouples at reproducible locations.
Data Collection

- All experiments were performed and all data was collected with a Princeton Applied Research VersaSTAT 4-400 potentiostat and VersaStudio software.

- The raw data was imported into Excel for further analysis.

- Following the electrochemical data collection, the working electrode was removed from the salt and the wetted length was measured to determine the active surface area.
Cyclic Voltammetry (CV)

- A common electrochemical technique that can be used to determine information about the reactions that occur in an electrochemical cell.
- Potential is repeatedly scanned from one vertex potential to another at a constant scan rate, ν.
- Reduction and oxidation reactions occur at the electrode surface resulting in cathodic (negative current) and anodic (positive current) peaks, respectively.
- Equilibrium potential
  \[ E = \frac{E_{pa} + E_{pc}}{2} \]
From the resulting current, reaction information can be determined.

- **Reversible:** soluble/soluble
  - Randles-Sevcik equation
    \[
    I_{pc} = 0.4463nFAC \sqrt{\frac{nFD_{ox}}{RT}}
    \]
  - Apparent standard potential
    \[
    E = E^{0*} + \frac{RT}{nF} \ln \left( \sqrt{\frac{D_{red}}{D_{ox}}} \right)
    \]

- **Irreversible**
  - Electrons transferred (irreversible)
    \[
    |E_{pc} - E_{p/2}| = 1.857 \frac{RT}{n\alpha F}
    \]
  - Delahay equation (irreversible)
    \[
    I_{pc} = 0.4958nFAC \sqrt{\frac{n\alpha FD_{ox}}{RT}}
    \]
  - Peak Potential (irreversible)
    \[
    E_{pc} = E^{0*} - \frac{RT}{n\alpha F} \left[ 0.78 - \ln k_s + \ln \sqrt{\frac{n\alpha FvD_{ox}}{RT}} \right]
    \]

| A | Electrode surface area |
| C | Concentration |

| E_{p/2} | Half-peak potential |
| k_s | Standard rate constant |
Chronopotentiometry (CP)

- An current-controlled technique that can be used to study time-dependent concentration change in a solution.
- A large driving current, \( I_d \), is applied and the resulting potential is measured as a function of time.
  - To maintain the applied current, 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 further drops to reduce the next ion.
  - The time of this potential transition is the transition time, \( \tau \).

\[
I_d \sqrt{\tau} = \frac{nFAC\sqrt{\pi D_{\text{ox}}}}{2}
\]

Results: 1.0 wt% UCl$_3$ CV (773 K)

Scan Rate
- LiCl-KCl @ 200 mV/s
- 20 mV/s
- 50 mV/s
- 100 mV/s
- 150 mV/s
- 200 mV/s

Current Density, $i$ (Amps/cm$^2$)

Potential, $E$ (V vs Ag/AgCl)

$U \rightarrow U^{3+} + 3e^-$

$U^{3+} \rightarrow U^{4+} + e^-$

$U^{4+} + e^- \rightarrow U^{3+}$

$U^{3+} + 3e^- \rightarrow U$
Results: 2.5 wt% UCl₃ CV (773 K)

Increasing applied current
Results: 1.07 wt% ZrCl$_4$ CVs at 723, 773, & 823 K

1.07 wt% Cyclic Voltammograms

$\nu = (300, 350)$ mV/s

Temperature

- Blue line: 723 K
- Red line: 773 K
- Green line: 823 K

Chemical reactions:

- $\text{Zr} \rightarrow \text{Zr}^{2+} + 2e^-$
- $\text{Zr} \rightarrow \text{Zr}^{4+} + 4e^-$
- $\text{Zr}^{2+} \rightarrow \text{Zr}^{4+} + 2e^-$
- $\text{Zr}^{4+} + 4e^- \rightarrow \text{Zr}$
- $\text{ZrCl} + e^- \rightarrow \text{Zr} + \text{Cl}^-$
- $\text{Zr}^{4+} + 2e^- \rightarrow \text{Zr}^{2+}$
- $\text{Zr}^{2+} + 2e^- \rightarrow \text{Zr}$
- $\text{Zr}^{4+} + 3e^- + \text{Cl}^- \rightarrow \text{ZrCl}$
Results: 0.497 wt% ZrCl$_4$ and 9.80 wt% UCl$_3$

- Uranium behavior dominates with low ZrCl$_4$ concentration.
- Very small contribution of Zr reactions.
Results: 4.17 wt% ZrCl$_4$ and 8.34 wt% UCl$_3$ CVs

ZrCl may not be fully reduced to Zr metal, leading to the ZrCl oxidation peak.

ZrCl → Zr$^{4+}$ + 3e$^-$ + Cl$^-$

U → U$^{3+}$ + 3e$^-$

Zr$^{4+}$ + 2e$^-$ → Zr$^{2+}$

U$^{3+}$ + 3e$^-$ → U

Zr$^{2+}$ + 2e$^-$ → Zr

Zr$^{4+}$ + 3e$^-$ + Cl$^-$ → ZrCl

U$^{3+}$ → U$^{4+}$ + e$^-$

Zr$^{2+}$ → Zr$^{4+}$ + 2e$^-$

U$^{4+}$ + e$^-$ → U$^{3+}$
## Summary

- CV cathodic and anodic peaks were identified.

<table>
<thead>
<tr>
<th></th>
<th>Peak</th>
<th>Cathodic Reaction, Location</th>
<th>Anodic Reaction, Location</th>
<th>Reversibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>A</td>
<td>$U^{4+} + e^- \rightarrow U^{3+}, -0.5\ V$</td>
<td>$U^{3+} \rightarrow U^{4+} + e^-, -0.3\ V$</td>
<td>Reversible</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>Adsorption $U^{3+}, -1.5\ V$</td>
<td>Desorption $U^{3+}, -0.7\ V$</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>$U^{3+} + 3e^- \rightarrow U, -1.6\ V$</td>
<td>$U \rightarrow U^{3+} + 3e^-, -1.4\ V$</td>
<td>Irreversible</td>
</tr>
<tr>
<td>Zr</td>
<td>A</td>
<td>$Zr^{4+} + 2e^- \rightarrow Zr^{2+}, -1.06\ V$</td>
<td>$Zr^{2+} \rightarrow Zr^{4+} + 2e^-, \text{shoulder near } B_a$</td>
<td>Irreversible</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>$Zr^{2+} + 2e^- \rightarrow Zr$ and $Zr^{4+} + 3e^- + Cl^- \rightarrow ZrCl, -1.5\ V$</td>
<td>$Zr \rightarrow Zr^{4+} + 4e^-$ and $Zr \rightarrow Zr^{2+} + 2e^-, -0.5\ V$</td>
<td>Irreversible</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>$ZrCl + e^- \rightarrow Zr + Cl^-$ and $Zr^{4+} + 4e^- \rightarrow Zr, -1.85\ V$</td>
<td>NONE</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>
Summary

Apparent Standard Reduction Potential, $E_0^*$ (V vs. Cl₂/Cl⁻)

Current Work
- Literature Values

773 K: U(IV)/U(III)
773 K: U(III)/U
723 K: Zr(IV)/Zr(II)
773 K: Zr(IV)/Zr(II)
823 K: Zr(IV)/Zr(II)
723 K: Zr(II)/Zr
773 K: Zr(II)/Zr
823 K: Zr(II)/Zr
Summary - Diffusion Coefficient

Diffusion Coefficient, $D$ (cm$^2$/s)

- **Current work**
- **Literature Values**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Compound</th>
<th>Current work</th>
<th>Literature Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>773</td>
<td>UCl$_3$</td>
<td>$1.0 \times 10^{-7}$</td>
<td></td>
</tr>
<tr>
<td>773</td>
<td>UCl$_4$</td>
<td>$1.0 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>723</td>
<td>ZrCl$_4$</td>
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<tr>
<td>723</td>
<td>ZrCl$_2$</td>
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<tr>
<td>823</td>
<td>ZrCl$_2$</td>
<td>$1.0 \times 10^{-4}$</td>
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</table>
Acknowledgements

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  – **Collaborators at SNU:** Prof. Il-Soon Hwang, Jaeyeong Park, Sungyeol Choi
  – **Collaborators at KAERI:** Dr. Kwang-Rag Kim
List of References:

- Bourg, S. IEM on Decommissioning and Remediation (2012).
- Fujita, et al., NUPYRO 2012
Extra Slides
Cyclic Voltammetry of 0.5 wt% ZrCl$_4$, 10 wt% UCl$_3$, and a Mixture of 0.5 wt% ZrCl$_4$ and 10 wt% UCl$_3$ in LiCl-KCl at 773 K with 200 mV/S Scan Rate
Cyclic Voltammetry of 10 wt% UCl₃, and a Mixture of 0.5 wt% ZrCl₄ and 10 wt% UCl₃ with 2000 mV/s Scan Rate, 0.5 wt% ZrCl₄ with 500 mV/s Scan Rate (Hoover et al.), and a Mixture of 0.99 wt% ZrCl₄ and 0.79 wt% UCl₃ with 50 mV/S Scan Rate (Murakami et al.) in LiCl-KCl at 773 K
Cyclic Voltammetry of 0.5 wt% ZrCl$_4$, 10 wt% UCl$_3$, a Mixture of 0.5 wt% ZrCl$_4$ and 10 wt% UCl$_3$ with 200 mV/S Scan Rate (Hoover et al.), and a Mixture of 0.99 wt% ZrCl$_4$ and 0.79 wt% UCl$_3$ with 50 mV/S Scan Rate (Murakami et al.) in LiCl-KCl at 773 K