Zirconium(IV) electrochemical behavior and electrorefining in molten fluoride salts
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Electrochemical behavior of zirconium in molten fluoride

Delphine QUARANTA¹, Eric MENDES¹, Laurent MASSOT², Mathieu GIBILARO², Jérôme SERP¹

¹ CEA Marcoule, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes, 30207 Bagnols-sur-Cèze, France
² Laboratoire de Genie Chimique, Université de Toulouse, UPS, CNRS, INPT, 118 Route de Narbonne, 31062, Toulouse Cedex 9, France
Zircaloy

- Material constituting nuclear fuel claddings
- Main composition of Zircaloy-4
  - Non-irradiated

<table>
<thead>
<tr>
<th>Elements</th>
<th>Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>1.20 – 1.70</td>
</tr>
<tr>
<td>Fe</td>
<td>0.18 – 0.24</td>
</tr>
<tr>
<td>Cr</td>
<td>0.07 – 0.13</td>
</tr>
<tr>
<td>O</td>
<td>0.09 – 0.16</td>
</tr>
<tr>
<td>Zr</td>
<td>~ 98</td>
</tr>
</tbody>
</table>

- Irradiated claddings

Activity coming from:

- $\beta\gamma$ elements:
  - Fission products (FPs): $^3H$, $^{90}Sr$, $^{106}Ru$, $^{137}Cs$, $^{154}Eu$…
  - Activation products (APs): $^{55}Fe$, $^{60}Co$, $^{59}Ni$, $^{93}Zr$, $^{94}Nb$, $^{121}Sn$, $^{125}Sb$
- $\alpha$ elements: Actinides Am, Pu, Cm, U

Heterogeneity: distribution of radioelements, nature of elements (metal, oxide, hydrides)
Recycling Zr contained in Zircaloy cladding

- Spent fuel management in France (La Hague reprocessing plant)
  - pool storage
  - shearing in 3-5 cm section
  - dissolution of UO$_2$ pellet
- Treatment of remaining Zircaloy
- 25 wt.% of spent nuclear fuel

Aim of the study: investigation on potential recycling of Zr from irradiated Zircaloy

→ Re-use of Zr for zircaloy refabrication and/or easier storage

Identification of two promising routes
- Chemical attack at high temperature: chlorination (Collins et al. DOE, USA)
- Electrochemical processes in molten salts: electorefining

First step: fundamental comprehension of electrochemical behavior of Zr in salt
Experimental Setup

➢ Salt media
  ▫ Chlorides: several stable oxidation states (0, I, II, IV) of Zr reported in the literature → Not adapted
  ▫ Fluorides: should stabilise oxidation state → Eutectic LiF-NaF

➢ Equipment
  ▫ Inactive pyrochemistry lab in gloveboxes under Ar atmosphere (< 10 ppm H₂O and < 5 ppm O₂)

➢ Experimental conditions
  ▫ Temperature range 750 – 900°C
  ▫ ZrF₄ concentration: 0.2 – 1.5wt%

Electrochemical behavior and electocrystallisation process
  ▫ Working electrode: Ag wire (1mm Ø)
  ▫ Counter electrode: glassy carbon rod (3mm Ø)
  ▫ Quasi reference electrode: Pt wire (1mm Ø)

Electrodeposition
  ▫ Cathode: 3 different materials studied (Zr, Graphite, SS)
  ▫ Anode: Zr plates
  ▫ Quasi reference electrode: Pt wire

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Thermodynamic approach

Determination of Pourbaix diagram

- Using HSC® Chemistry database
- Considered species: Zr, ZrF₄, and ZrO₂
- ZrF₄ activity considered: 0.1
- Limits of the diagram: reduction of Na⁺ and oxidation of Ag working electrode

Influence of pO₂ on stability of Zr

Solubility limit: pKs = 24.5

→ pO₂⁻ = 11.7

Zr very sensitive to presence of O₂⁻ in the salt

Importance of preparation of the salt: avoiding maximum presence of oxide

<table>
<thead>
<tr>
<th>Couples</th>
<th>Redox reactions Inputs HSC Chemistry</th>
<th>ΔG⁰ (kJ/mol)</th>
<th>E⁰ (V/(F2/F⁻))</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrF₄/Zr</td>
<td>ZrF₄ + 4e⁻ ↔ Zr + 4F⁻</td>
<td>1574</td>
<td>-4.08</td>
<td>E = E⁰ + \frac{RT}{nF} \ln \left( \frac{a_{ZrF₄}}{a_{e⁻^4}} \right)</td>
</tr>
<tr>
<td>ZrO₂/Zr</td>
<td>ZrO₂ + 4e⁻ ↔ Zr + 2O²⁻</td>
<td>2053</td>
<td>-5.32</td>
<td>E = E⁰ + 2.3 \frac{RT}{nF} pO₂⁻</td>
</tr>
<tr>
<td>NaF/Na</td>
<td>NaF + e⁻ ↔ Na + F⁻</td>
<td>470</td>
<td>-4.87</td>
<td>E = E⁰ + \frac{RT}{nF} \ln \left( \frac{a_{NaF}}{a_{e⁻}} \right)</td>
</tr>
<tr>
<td>AgF/Ag</td>
<td>AgF + e⁻ ↔ Ag + F⁻</td>
<td>148</td>
<td>-1.53</td>
<td>E = E⁰ + \frac{RT}{nF} \ln \left( \frac{a_{AgF}}{a_{e⁻}} \right)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Couple</th>
<th>Solubility reaction input in HSC Chemistry</th>
<th>K</th>
<th>pO₂⁻ = f(K) Expression</th>
<th>pO₂⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂/ZrF₄</td>
<td>ZrO₂ + 4F⁻ ↔ ZrF₄ + 2O²⁻</td>
<td></td>
<td>\frac{1}{2} \log \left( \frac{K a_{e⁻^4}}{a_{ZrF₄}} \right)</td>
<td>11.7</td>
</tr>
</tbody>
</table>
Electrochemical behavior: cyclic voltammetry

Cyclic voltammograms of the LiF–NaF system at 100 mV.s\(^{-1}\) and 750 °C: without ZrF\(_4\) (grey) and with ZrF\(_4\) addition of 0.06 mol.kg\(^{-1}\) (black). Inset. Variation of the peak current density (\(\diamond\)) and the peak potential (\(\square\)) versus the square root of the potential scan rate.

Reduction of Zr(IV) occurs in one step
Reduction is controlled by diffusion of Zr(IV)
Quasi-reversible system

Variation of current density of the reduction peak as a function of ZrF\(_4\) molality, at 750°C and scan rate 100mV.s\(^{-1}\).

Diffusion coefficient
\[ j_p \propto \sqrt{v} \]
\[ D_{Zr(IV)} = 1.21 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \]

Arrhenius type law
\[ \ln D_{Zr(IV)} = -7.77 - \frac{3649}{T} \]
Electrochemical behavior: square wave voltammetry

Square wave voltammogram of the LiF–NaF–ZrF₄ (m₀ = 0.06 mol.kg⁻¹) at 16 Hz, pulse height: 20 mV, step potential: 2 mV and 750 °C.

Inset. Variation of the differential of the peak current density (◊) and the peak potential (□) versus the square root of the frequency.

Working electrode: Ag (S = 0.35 cm²); auxiliary electrode: glassy carbon; comparison electrode: Pt

Reduction of Zr(IV) in one step

Number of exchanged electrons

\[ W_{1/2} = 3.52 \frac{RT}{nF} = 2W_L \]

4 electrons exchange

Zr(IV) + 4e⁻ → Zr

Soluble/insoluble system
Electrocrystallisation process 1/2

Chronoamperometry → 3 areas:

■ **Part 1:** charging of the double layer and the formation of the first germs

■ **Part 2:** growth of the crystals

\[(t_m \; ; \; j_m) \rightarrow v_{\text{diffusion}} = v_{\text{growth crystals}}\]

■ **Part 3:** limitation of the reaction by the diffusion of Zr(IV) ions

Crossover on cyclic voltammograms observed: **Nucleation process evidenced**

Chronoamperogram on silver electrode at \(\eta = -0.969\) V vs Pt in LiF–NaF–ZrF\(_4\) (\(m_o = 0.17\) mol.kg\(^{-1}\)) at 690 °C. Working electrode: Ag (\(S = 0.35\) cm\(^2\)); auxiliary electrode: glassy carbon; comparison electrode: Pt

Non-dimensional models: 

\[\left(\frac{1}{i_m}\right)^2 = f\left(\frac{t}{t_m}\right)\]
Non-dimensional theoretical models → 2 nucleation modes (Scharifker et al. 1983)

- **Progressive nucleation** → \[ \left( \frac{I}{I_{m}} \right)^2 = 1.2254 \left( \frac{t}{t_{m}} \right) \left[ 1 - \exp \left\{ -2.3367 \left( \frac{t}{t_{m}} \right)^2 \right\} \right]^2 \]

- **Instantaneous nucleation** → \[ \left( \frac{I}{I_{m}} \right)^2 = 1.9542 \left( \frac{t}{t_{m}} \right) \left[ 1 - \exp \left\{ -1.2564 \left( \frac{t}{t_{m}} \right) \right\} \right]^2 \]

Comparison of the dimensionless experimental data obtained from the current-time transients at various overvoltages and temperature with the theoretical models for instantaneous and progressive nucleation in LiF–NaF–ZrF$_4$ ($m_0 = 0.17$ mol.kg$^{-1}$).

Working electrode: Ag; auxiliary electrode: glassy carbon; comparison electrode: Pt

Progressive nucleation mode whatever the overvoltage imposed and the working temperature Cristal growth in the three dimensions and limited by the diffusion of Zr(IV) ions

**Progressive nucleation**: high temperature, high concentration and high overvoltage → best deposit conditions

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Nuclear Energy Division - Marcoule
Research Department on Mining and Fuel Recycling Processes

2018 International Pyroprocessing Research Conference, October 24 - 26, 2018
Determination of the limiting current

- Fluoride media: No reference electrode
  → Galvanostatic electrodeposition
- System limited by Zr diffusion
  → Determination of the limiting current needed

**Linear Voltamperogram** on LiF-NaF-ZrF$_4$ (C = 7.46.10$^{-2}$mol/kg), scan range: 1mV/s at 750°C and polarisation plots.

**Chronoamperograms** on LiF-NaF-ZrF$_4$ (C = 7.46.10$^{-2}$mol/kg) at 750°C different applied potentials.

\[ i_{\text{lim}} = -0.097 \text{A.cm}^{-2} \]
\[ i_{\text{lim}} = -0.14 \text{A.cm}^{-2}.\text{wt}\%^{-1} \]

Higher applied current densities:

→ possible co-reduction of Na$^+$
Electrodeposition experimental results:

Deposit loss can be observed on several experiments.

Important faradic yields reached > 80%.

Difficulties to estimate it (salt remaining removal).

Feasibility of pur Zr metal deposition demonstrated in LiF-NaF.
ELECTRODEPOSITION OF ZR

XRD analysis:

- Confirmation of the SEM analysis
- Residual salt adhered onto the electrode
- Presence of oxygen: contamination of the deposit during sample preparation (*under air atmosphere*)

![XRD analysis plot]

- NaF
- LiF
- ZrO$_{334}$ Zirconium oxide
- Na$_3$ZrF$_7$ Sodium Zirconium Fluoride
- Zr $\alpha$-Zr
Influence of the operating parameters

**Substrate of cathodes**
- Zr
- C
- SS

- Dense, compact and adherent deposit on Zr and C cathodes

**Current density**
- a) Low density
- a) Medium density

- Strong effect of current density on the regularity
  - ↑ current density ⇒ ↑ nuclei formed

**ZrF$_4$ concentration**
- A
- B

- Moderate influence of concentration on the regularity
  - ↑ concentration ⇒ ↑ nuclei formed

In good agreement with the Zr nucleation study
Conclusions and prospects

- **Electrochemical behavior in fluoride salts**
  - Zr(IV) reduction in one step
    \[
    \text{Zr(IV)} + 4\text{e}^- \rightarrow \text{Zr}
    \]
  - Reduction is limited by diffusion of Zr(IV) ions → Arrhenius type law:
    \[
    \ln D_{\text{Zr(IV)}} = -7.77 - \frac{3649}{T}
    \]

- **Electrocrystallisation process**
  - Progressive nucleation mode
  - Crystal growth
    - in the three dimensions
    - limited by the diffusion of Zr(IV) ions

- **Electrodeposition**
  - Observations are in agreement with the Zr nucleation study
    \[
    \rightarrow \uparrow \text{current density or } \uparrow \text{concentration } \Rightarrow \uparrow \text{nuclei formed}
    \]

- **Next step**
  - Tests with non irradiated Zircaloy
Thank you for your attention

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