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Investigation of Electrochemical Recovery of Zirconium from Spent Nuclear Fuels

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Research Objectives

This project uses both modeling and experimental studies to design optimal electrochemical technology methods for recovery of zirconium from used nuclear fuel rods for more effective waste management. The objectives are to provide a means of efficiently separating zirconium into metallic high-level waste forms and to support development of a process for decontamination of zircaloy hulls to enable their disposal as low- and intermediate-level waste. Modeling work includes extension of a 3D model previously developed by Seoul National University for uranium electrorefining by adding the ability to predict zirconium behavior. Experimental validation activities include tests for recovery of zirconium from molten salt solutions and aqueous tests using surrogate materials.

Research Progress

To investigate dissolution and deposition behavior of zirconium in molten salt, cyclic voltammetry, chronopotentiometry, and anodic stripping voltammetry were conducted with molten salts consisting of LiCl-KCl-ZrCl₄, LiCl-KCl-UCl₃, and LiCl-KCl-UCl₃-ZrCl₄ at 500°C. Details of the oxidation and reduction reactions for each peak were defined based on an electrolysis experiment and previous cyclic voltammetry results from literature. For the zirconium reduction, Zr(IV), is reduced to ZrCl rather than Zr metal when cathode potential is not negative enough. Therefore, to directly recover zirconium metal, the cathode potential should be maintained at less than -1.5V (vs. Ag/AgCl). From the electrochemical tests performed, key physical properties (diffusion coefficient, standard reduction potential, and activity coefficient) were measured. Table 1 summarized the values for these properties measured for U(IV), U(III), Zr(IV), and Zr(II).

Table 1. Summary of Electrochemical and thermodynamic properties of UCl_3 and ZrCl_4 in LiCl-KCl .

	Diffusion coefficient, D (cm^2/s)			Apparent standard reduction potential, E^* (V vs Cl_2/Cl^-)			Activity coefficient, γ
	450 °C	500 °C	550 °C	450 °C	500 °C	550 °C	500 °C
U(IV)	---	6.72×10^{-6}	---	---	-1.448	---	0.00236 – 0.0109
U(III)	---	1.04×10^{-5}	---	---	-2.568	---	4.86×10^{-5} – 4.42×10^{-4}
Zr(IV)	5.85×10^{-6}	5.05×10^{-6}	7.88×10^{-6}	-2.012	-1.972	-1.914	---
Zr(II)	4.73×10^{-5}	6.87×10^{-5}	6.33×10^{-5}	-2.234	-2.190	-2.138	---

Cobalt is the impurity of interest in the zircaloy cladding. Cyclic voltammetry for cobalt was conducted, and it was revealed that oxidation and reduction reactions of cobalt are much simpler than zirconium. Cobalt is also more reductive than zirconium. In addition, lab-scale electrorefining of Zircaloy-4 was performed and results are summarized in Table 2. Anode potential was controlled to prevent dissolution of all elements except zirconium. Composition of cathode deposits was evaluated by ICP-MS analysis. Zirconium of 99.7 wt% was recovered on the cathode with Fe and Cr impurities. Since Fe and Cr came from the initial molten salt, it is speculated that pre-purification of the molten salt could lead to achieving almost 100% Zr purity on the cathode.

Table 2. Composition of Zircaloy-4 specimen and cathode deposits.

Zircaloy-4 specimen		Deposits with LiCl-KCl		Deposits except LiCl-KCl	
Element	wt%	Element	wt%	Element	wt%
Zr	98.6	Zr	79.1	Zr	99.7
Sn	1.104	Sn	0	Sn	0
Fe	0.1595	Fe	0.1	Fe	0.2
Cr	0.0830	Cr	0.1	Cr	0.1
Co	0.0016	Co	0	Co	0
Li	N/D	Li	1.2	Li	-
K	N/D	K	19.4	K	-

Two pilot scale Zircaloy cladding electrorefiners were designed. One is an electrorefiner including auxiliary electrode, and another is a rotating drum cell electrorefiner. Characteristics of each electrorefiner were simulated via a three-dimensional multi-species electrodeposition model. It was predicted that a very high purity zirconium can be deposited on the main cathode, and most of the other elements can be dissolved from the anode and deposited on an auxiliary cathode. Furthermore, it is expected that zirconium metal rather than ZrCl can be obtained on the cathode, since its potential can be controlled to be more negative than -1.5V (vs. Ag/AgCl). For the rotating drum cell electrorefiner, uniform contacting of cladding hulls with the molten salt can be achieved, and chlorine gas can be readily collected from the anode.

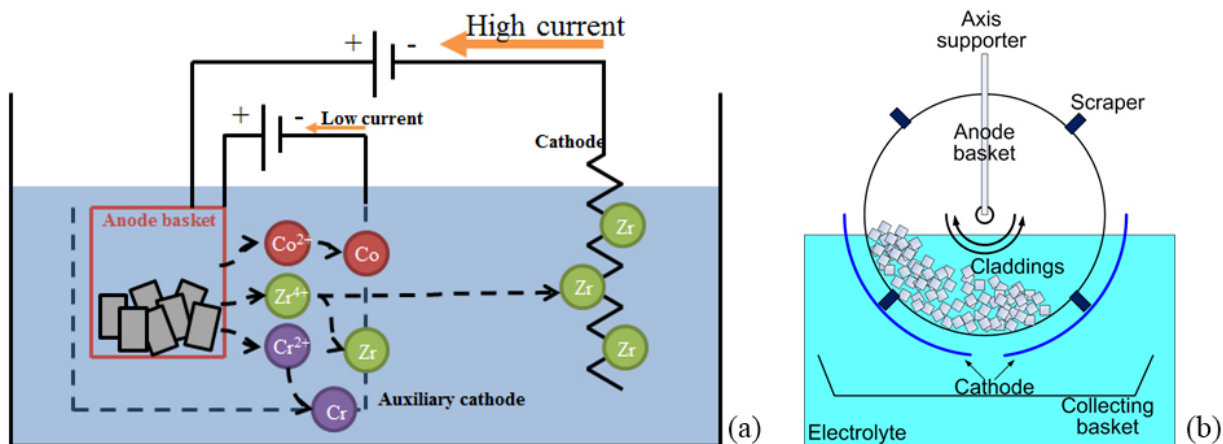


Figure 1. Schematic diagrams of designed electrorefiner with (a) auxiliary cathode and (b) rotating drum cell.

A process has also been designed with the objective of selectively recovering zirconium from the Mark-IV ER. It involves electrorefining excess U metal followed by oxidizing residual U metal to UCl_3 . Then further oxidation would occur to convert a fraction of the Zr metal to ZrCl_4 . Then it is hypothetically possible to electrorefine purified Zr from the cadmium pool to the cathode. Two models were run to assess the viability of this process. They both predicted that high purity Zr cathode deposits could be achieved even with relatively high UCl_3 concentrations in the salt, provided that no U metal is in contact with the salt.

Planned Activities

None. The project has been completed.