Examining Cathodic Deposition Behavior to Improve Electrorefining Simulation Model

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1. Introduction

Pyroprocessing is a spent fuel recycling technology that uses a molten salt system. Because it produces a very impure plutonium composite, some authorities believe this technology has inherent proliferation resistance. However, several unique characteristics of pyroprocessing present a challenge to safeguards. A computer model-based simulation to augment the safeguards approaches to pyroprocessing has been suggested to overcome this challenge [1].

In pyroprocessing, electrorefining (ER) is a key process where uranium is selectively separated from spent fuel and deposited on a cathode. Tracking the uranium selectively separated is important to pyroporcessing safeguards. In the use of computer models to simulate ER and related mass transport, quantifying the uncertainty and improving the simulating capability of the model is essential. In previous work, we identified a major source of uncertainty in modeling the ER system. The uncertainty stemmed from the dynamic changes in the cathodic surface area during the reaction [2].

Based on those results, this study suggests an approach to improve the model's ability to simulate the ER.

2. Methods and Results

The objective of an ER model is to simulate the real system. For this, understanding the mass transfer and reaction rates of the system is essential. The ERAD [3] model was used in previous research to simulate ER with its ability to address anodic dissolution through considering an anodic passivation layer and the solubility limit near the anode. ERAD simulates reaction rate and mass transfer behavior through 'the Nernst equation and the Butler-Volmer equation' and 'the diffusion equation', respectively.

Like typical models, it assumes that the electrode surface area is constant because of the complexity of the ER process and the difficulty in expressing this dynamic change with theoretical methods. In the early phase, this assumption had little influence on the result. However, as the deposition continues, because the reaction area is increasing, the difference between the simulated results with the real result is also enlarged.

To describe the process more accurately, it is desirable to formulate a modeling equation which can describe the growth of electrode surface area as a function of time using an empirical approach.

2.1 Approach

The chronoamperometry (CA) is one electrochemical analysis method. It supplies a certain electric potential to the working electrode and records the current over time. The analysis results in a graph where the x-axis is time and y-axis is current. In the initial step, when the potential is suddenly supplied, the reactant around the electrode is consumed rapidly. As a result, the current increases steeply because of a lack of reactant. As the reactant around the electrode is recovered, the current is decreased. Ideally, the current should be maintained at a constant level. However, as the reaction continues, the signal is gradually increased because of growing surface area caused by deposition on the electrode. The growing surface area can be calculated by adapting the Cottrell equation. The Cottrell equation, which expresses the current as a function of time, could provide an insight into the relationship between current and reaction area. The Cottrell equation is as follows [4]

$$i(t) = \frac{nFADC_0}{\sqrt{\pi t}} \qquad (1)$$

where i is the diffusion limited current, n is the stoichiometric number of electrons involved in an electrode reaction, F is the Faraday constant, A is the surface area of the electrode, D is the diffusion coefficient, C_0 is the initial concentration of the target materials, and t is the duration time.

By integrating equation 1 with time, equation 2 is derived,

$$\Delta i(t) = \frac{2nFDC_0}{\sqrt{\pi}} A t^{1/2} \qquad (2)$$

It is possible to calculate the increased surface area because the fraction part, of equation 2, can be estimated as a constant.

2.2 Experimental set-up

In the experiment, because of the difficulty in using real process material like U and Pu, gadolinium (Gd) is to be used as a surrogate material since it has electrochemical properties similar to uranium.

Experiments will be performed in a glove box under argon atmosphere, where the concentration of both oxygen and moisture are less than 1 ppm. The furnace (SKUTT, KM-614, US) is located and operated inside the glove box. When compared to other typical electrochemical research, the size of the designed system (i.e., the diameter was 280 mm and the height was 380 mm.) is much larger than that of a typical electrochemical experiment. The operating temperature measured by a chromel-alumel thermocouple is expected to be 773 K. The electrolyte composed of 59-41 mol.% LiCl-KCl eutectic system with a bit of $GdCl_2$ is melted in an alumina crucible. A three electrode system is applied. Molybdenum wire, whose diameter is 1 mm, is used as a working electrode. The immersed length of working electrode is approximately 20 mm, but the exact length is recorded for accuracy. As a counter electrode, a stainless steel basket loading Gd metal is adapted. A Ag/AgCl electrode is used as the reference electrode. It is composed of a silver (Ag) wire, 0.5 mm in diameter, immersed in LiCl-KCl eutectic system with 1 wt.% AgCl,

contained in a mullite tube whose outer diameter is 6 mm and inner one is 4 mm. All electrodes are sheathed in an alumina tube to prevent contact with the stainless steel electrode supporter. A potentiostat/galvanostat (Biologic, SP-150) is employed along with EC-lab software for the electrochemical analysis and as a power supplier.

3. Conclusion

An empirical formula to model the varying surface area of the cathode is to be developed through experimental investigations using the chronoamperometry and the Cottrell equation. The experimental design was developed to enhance our understanding of the growth of uranium on the cathode through time. The resulting formula then is expected to improve the computational modeling capability for ER.

4. References

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