# Examination of Uncertainty in Modeling Mass Transfer and Electrodeposition from Electrorefining Simulation

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## 1. Introduction

As the use of nuclear energy continues to expand internationally, the issue of spent nuclear fuel management becomes increasingly significant. As part of spent fuel management, recycling based on pyroprocessing has been proposed. Although debates on the pros and cons of the pyroprocessing technology continue, research and development (R&D) efforts for the technology are underway in a number of countries. Various computer models are utilized as part of this R&D effort for process simulation, design optimization, and scale up analysis.

A number of computer models have been developed since the 1970s as part of this effort. Initial modeling work focused on examining fundamental electrochemical properties such as thermodynamics. As time went on, the developed models became more versatile by simulating various phenomena including electrolyte resistance, diffusion, kinetics etc. However, compared to the level of effort in model development, the related model validation work was given less attention in the open literature.

In numerous cases, the validation work was limited by the nature of existing experiment data. In this study, a partial validation work was conducted for the ERAD code [1,2] (a 1-dimensional ER computational model) to examine the code's mass transfer analysis capability. The experiments were performed by using Lanthanum as a surrogate material to avoid complications associated with the use of actual process materials.

As part of the validation work, data on electrochemical properties at specific operating conditions were developed through experiments. To confirm the reliability of the results, the extracted values (experimental data) of the electrochemical properties were compared with the published data. A mass transfer study was performed through electro-deposition experiments and computer model simulations using the developed input data.

## 2. ERAD

### 2.1 ERAD Description

ERAD, a one-dimensional electrochemical kinetics and transport analysis code, was developed based on a previous model, REFIN [3]. The ERAD simulates not only major phenomena (i.e. thermodynamics, kinetics, and diffusion) but also secondary phenomena; an anodic passivation layer and a solubility limit. These are important when the anode is SNF (containing a variety of impurities), and the solubility of the anode limits current density.

ERAD uses three major equations to simulate the system. Each of the three equations simulates a specific phenomenon: the Nernst equation defines the equilibrium potential; the Butler-Volmer equation addresses the reaction rate at the electrode surface; and finally, the diffusion equation, with a migration term, evaluates mass transfer near each electrode.

It is important to note that ERAD focuses on describing rate-limiting steps in mass transport, during electrorefining operations. Therefore, ERAD does not model adsorption, pseudo-capacitance, ohmic drop, or dendrite formation. Additionally, ERAD does not simulate electrolyte fluid flow or current flow in more than one dimension.

### 2.2 Input Parameters of ERAD

To validate the credibility of a computer model, it is important to understand which input parameters are needed to appropriately run the computer model. Input parameters required to operate the ERAD code can be categorized into six groups based on their function: the electrochemical property section, the operating condition section, the cell design/geometry section, the solver pack (LSODE) section, the output setting section, and the element property section. Of these six categories, only the electrochemical property group and the operating condition group are determined through experimentation.

The electrochemical property group consists of four parameters: apparent standard potential, exchange current density, diffusion coefficient, and charge transfer coefficient. The standard potential gives basic information on the reaction. It can define the equilibrium where the reaction begins. The exchange current density governs the rate of reaction occurring on the electrode surfaces. The diffusion coefficient is a factor related to mass transfer in the electrolyte, while the charge transfer coefficient determines the preferred reaction between oxidation and reduction. These parameters can be calculated using the results of electrochemical analysis from the experiments. However, the input values for all elements, except the target material (La), were based on published data.

The operating condition group includes all parameters that are adjustable by changing the settings of the experiment conditions (i.e. temperature, electrode area, electrolyte composition etc.). Theses have a considerable effect on the electrochemical properties.

## 3. Experiment

### 3.1 Electrochemical Study

Experiments were performed in a glove box under an argon atmosphere, which has less than 1 ppm of both oxygen and moisture. The furnace (SKUTT, KM-614, US) was located and operated inside the glove box. In comparison with other systems in related studies, the size of the furnace in this study was designed to be relatively large (i.e., the diameter was 280 mm and the height was 380 mm.) to study mass transfer in the cell.

The operating temperature measured by a chromel-alumel thermocouple was 773 K. The electrolyte, composed of 59-41 mol.% LiCl-KCl eutectic with 2.5 wt.% of Lanthanum chloride, was melted in the alumina crucible. All reagents were ACS grade and purchased from Alfa-Aesar except the Lanthanum chloride, which was purchased from Sigma-Aldrich.

The electrochemical cell consists of three components: a working electrode, a counter electrode, and a reference electrode. The working electrode is a 1 mm diameter Molybdenum (Mo) wire. The immersed length of the working electrode is 2 ($\pm$ 0.1) cm. The counter electrode consists of a La rod (6.35 mm diameter and 25.4 mm length) located in a stainless steel basket. An Ag/AgCl electrode was used as the reference electrode. It is composed of a silver (Ag) wire (0.5 mm in diameter), immersed in 1 wt.% AgCl in LiCl-KCl eutectic. The eutectic is in a mullite tube whose outer and inner diameters are 6 mm and 4 mm, respectively. All electrodes were sheathed in alumina tubes to prevent electrical conduction between materials. A schematic of the electrochemical cell is shown in Fig. 1.

A potentiostat/galvanostat (Biologic, SP-150) with EC-lab software were used for electrochemical analysis.
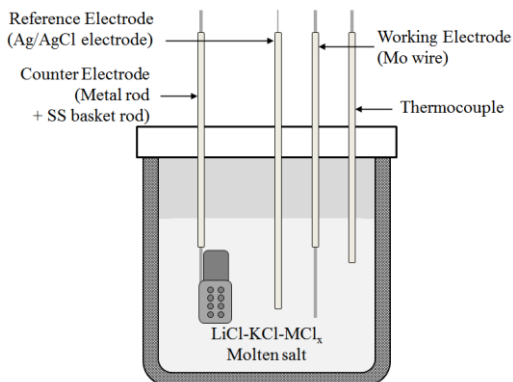


Fig. 1. The electrochemical cell design for experiment.

### 3.2 Mass Transfer Study

To investigate the sensitivity of the computation model, a mass transfer study was conducted by using five test cases, as shown in Table I. Since the electric current and duration time ($T_D$) are the adjustable parameters in ERAD, a galvanostatic mode (control current) was employed for electro-deposition experiments.

In the table, the "standard" of retained current was obtained in the following manner: First, the cathode peak potential was attained by using Cyclic Voltammetry (CV). Next, the Chrono-amperometry (CA) method was used to find the constant current level that corresponds to the standard of the retained current. This was done by applying a more negative potential (about - 0.1 V) than the cathode peak potential, to the working electrode. "$T_D$" indicates the duration time of supplying power. The experiment was stopped before the dendrite formation prohibited the ability to vertically remove the cathode (with deposits) from the cell's narrow hole (1.4 cm diameter).

After deposition, Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES; Agilent, Agilent ICP-OES 720) was employed to measure the amount of deposition and composition of electrolyte. The samples were prepared by cutting a 3 cm segment from the bottom of Mo electrode including the immersed portion, and dissolving it in aqua regia (HCl : HNO$_3$ = 3 : 1). This acid solution was diluted 100 times.

Table I: Test cases for mass transfer study

| Case | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Retained Current [mA] | Standard | | | Half | Double |
| Duration [hr] | $T_D$ | $2T_D$ | $T_D/2$ | $T_D$ | $T_D$ |

## 4. Result

### 4.1 Electrochemical Analysis

In this study, three electrochemical analysis methods were employed: CV, Chrono-potentiometry (CP), and Linear Polarization (LP).

CV detects current movement as a function of electric potential shift. When the potential shifts between the maximum and the minimum value repeatedly at a constant rate (scan rate), peaks appear in the flow of current as a response to the oxidation and reduction reaction. The equilibrium potential can be calculated as the arithmetic mean of the anodic peak potential and cathodic peak potential, which is obtained from the oxidation and reduction peak. The diffusion coefficient can be determined by the Berzins-Delahay equation which assumes the activity of metal deposits is a constant (one). It describes the processes of metal deposition on solid electrodes in eutectic systems.

In CP, controlled current is supplied to the system and the potential is recorded as the response. When the current is supplied, the reactant around the electrode is rapidly consumed and exhausted by the reduction reaction. The time required until the concentration of reactant at the electrode surface reaches zero is defined as the transition time, $\tau$. Since the system is reversible, the diffusion coefficient was determined by substituting the transition time with the Sand's equation.

LP measures the response of current by polarizing the electrode. The purpose of this method is to draw the Tafel plot which defines the exchange current density and the charge transfer coefficient. This graph can be plotted by setting the over-potential and the logarithmic current on the x-axis and y-axis, respectively. The Tafel equation can be extracted by simplifying the Butler-Volmer equation when the over-potential consists of large values. The exchange current density and the charge transfer coefficient can be calculated by using the y-intercept and the slope, respectively.

The electrochemical properties of La determined through electrochemical analysis are summarized in Table II.

Table II: Electrochemical properties of La from experimentations

| | | La |
|---|---|---|
| Apparent standard potential [V] | vs $Ag^+/Ag$ | -1.854 |
| | vs $Cl^-/Cl_2$ | -3.089 |
| Diffusion coefficient [$10^5$ cm$^2$/s] | CV | 1.468 |
| | CP | 2.585 |
| Exchange current density [mA/cm$^2$] | | 42.13 |
| Charge transfer coefficient | | 0.484 |

*4.2 Mass Transfer Study*

To validate the mass transfer modeling capability of ERAD, a comparison between experiment results and
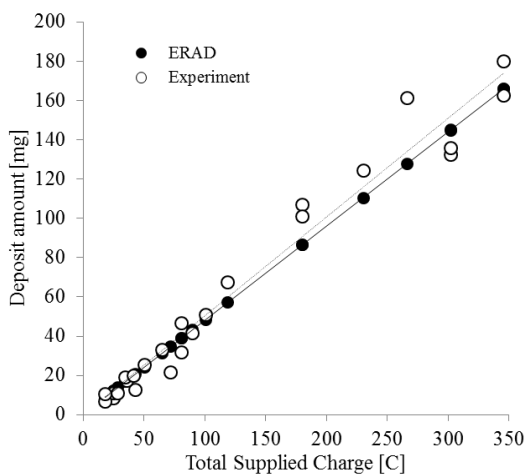


Fig. 2. Amount of La deposited as a function of the total supplied charge

computation output was conducted. The ERAD code used the results of electrochemical studies as the assigned values for the input parameters. Based on the test cases in Table I, the conditions of the electrodeposition experiments and the corresponding ERAD simulations were determined. Fig. 2 shows the results of this comparison for the amount of La deposited as a function of the total supplied charge (in Coulomb).

**5. Discussion**

According to the results, the amount of deposition increases as a function of time and current. Due to the deterministic nature of the computational model, the amount of deposition on the cathode increased linearly ($R^2 = 1$). The simulation result shows that as the total supplied charge increases to 1 C, the deposit increases by 0.480 mg. In the "experiment", the slope (0.503) is slightly more rapid than the computation results and the $R^2$ value is less than 0.97.

The comparison results show that ERAD estimates the tendency of deposition amount, reasonably well. However, further studies on the effect of electrochemical properties are required in a multispecies system. Though the results show the predictability of ERAD as reasonable, the deposit amount is still small. A larger scale experiment would be beneficial to confirm the applicability of the code.

Considering the limitations of ERAD, including the issue of ignoring several important phenomena occurring in the system, the discrepancy between the code predictions and experimental results is expected. The discrepancy would continue to increase as the deposit grows. For instance, in ERAD, the cathode is considered as a point. Therefore, the growth of dendrite and the resulting geometrical complications are not considered. However, in a real system, because of dendrite formation, over-potential distribution is expected. Further study is needed to examine the validity of the code in a larger scale experiment.

Issues to be examined in future studies include: 1) Using a multi-species system to study the effect of electrochemical property inputs. 2) Conducting larger scale experiments to confirm the code's applicability to a large throughput facility.

**6. Conclusion**

In an effort to validate the ERAD code (a one-dimensional computer model for ER in pyroprocessing) electrochemical analyses and mass transfer analyses were conducted in this study. Based on the use of La as a surrogate metal, the electrochemical properties of La in LiCl-KCl eutectic salt were investigated. The extracted results were used as input data in computer model-based simulations. The simulation results were compared with the results obtained from electrodeposition experiments.

This study indicates that the current version of ERAD is adequate in estimating the tendency of mass transfer in electrorefining. However, further studies are needed to confirm the use of the code for a large throughput facility.

## ACKNOWLEDGMENTS

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