Diffusion Model and Artificial Neural Intelligence (ANI) Comparison for Cyclic Voltammetry Prediction of Uranium and Zirconium Chloride in LiCl-KCl Eutectic Salt

Samaneh Rakhshan Pouri, Supathorn Phongikaroon, Zeyun Wu

Department of Mechanical and Nuclear Engineering, Virginia Commonwealth University, Richmond, VA, USA.
rakhshanpous@vcu.edu

INTRODUCTION

Used nuclear fuel (UNF) reprocessing has been one of the main controversial issues related to the nuclear power production due to safeguard and proliferation concerns [1, 2]. Pyroprocessing technology is one of the proposed reprocessing routines to separate the uranium from UNF by using an electrorefiner (ER) [3]. Although there are some common methods to monitor behavior of ER contains such as inductively coupled plasma mass spectroscopy (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES), these techniques require sample preparation and result in long processing time (~ 3 - 4 weeks). The other alternative methods such as laser-induced breakdown spectroscopy (LIBS), ultraviolet-visible spectroscopy (UV-Vis) and electrochemistry experimental method (for examples, Cyclic Voltammetry (CV), chronopotentiometry (CP), and anodic stripping voltammetry (ASV)) have shown a promising trend in improving the processing time but they are still under development [4, 5]. This provides a motivation for this research to further explore one of the electrochemical technique, CV, to understand the composition material in ER, which can be beneficial to materials detection and accountability towards safeguards.

Here, the main goal of this study is to develop and assess proper computational methods—diffusion model versus artificial neutral intelligence (ANI)—for near real time monitoring to trace the trend of elemental compositions and predict the unseen situation. First, a diffusion model was developed to predict CV of uranium chloride in different concentrations and scan rates in a very short time (less than 2 minutes). Due to its limitation at high concentration and a complex species (e.g., zirconium chloride), an alternative technique, ANI, was developed in parallel to overcome this issue and assess its robustness in comparison to the diffusion model. It is anticipated that this outcome may provide significant path in improving the CV method towards safeguards in pyroprocessing technology.

COMPUTATIONAL METHODS AND PROCEDURES

A: DIFFUSION MODEL

In this part, data sets reported by Hoover [6] for the uranium chloride of 1, 2.5, 5, 7, and 10 wt% in LiCl-KCl eutectic salt with different scan rates were used for diffusion model. Based on the experimental data sets, diffusion coefficients for all species were calculated by using the Randles-Sevcik and Delahay equations [7-9]. In the numerical approach, two general form of current as a function of time for reversible and irreversible reactions were being considered, respectively:

$$i_{reversible} = nFAC_o^* \sqrt{\pi D_o \psi \chi(\psi t)} \quad (1)$$

$$i_{irreversible} = nFAC_R^* \sqrt{\pi D_R \psi \alpha \chi(\alpha \psi t)} \quad (2)$$

where $\psi = \frac{nF\upsilon}{RT} = (\frac{nF}{RT})(E_i - E)$, C_o^* and C_R^* are the bulk concentration of oxidant and reductant species (mol/cm^3), respectively, D_R and D_o are the diffusion coefficients of oxidant and reductant species (cm^2/s), respectively, E_i is the initial potential (V), n is the number of electron transferred per mole (eq/mol), F is the Faraday's constant (96485 C/eq), R is the universal gas constant (8.314 J/mol·K), T is the temperature (K), υ is the scan rate (V/s), and α is the transfer coefficient setting at 0.5.

To complete the computational routine, the Fick's law was being applied for the element. After applying the Laplace transform, convolution theorem, integration by part, and Riemann-Stieltjes integral, $\chi(\psi t)$ and $\chi(\alpha \psi t)$ were computed. The current, potential, and the concentration of each species could be computed from this approach [10, 11]. This work was written in *MATLAB* code, and conformed in a graphical user interface (GUI) environment. The details related to the numerical method, values of the diffusion coefficient, *MATLAB* and GUI codes can be found in Ref. 11.

B: ANI METHOD

ANI has a capability of learning by training data due to its similarity to human brain neural neurons [12, 13]. For this reason, ANI technique was applied on the electrochemical data sets to learn massive training data set through iterations and interpolations among system such as current, potential, concentration, scan rate, processing time, and weight percent [12-15].

ANI is consisted of one input layer, hidden layers, and one output layer which are interconnected by a number of nodes called neurons [12]. One simplest type of ANI is called perceptron that information goes in one node, in one direction with no loop [11]. In reality, the system is a complex network of perceptrons to make a suitable

decision (see Fig. 1) [14]. The input data using the MLP are weighted and added together with a bias value giving the output. The hidden layer comprises of neurons arrays that are received, and transferred the signal from the previous layer. The signals from the input and hidden layer to the output layer can be modeled by an activation function which is considered sigmoid in this study [16].

The whole experimental data sets can be divided into three groups: training, validation, and test data sets. Training data sets is a partial of the whole experimental data sets to adjust weight and bias. Validation data is an independent data and can be used to minimize the overtraining which happens when the system starts to memorize the training data set rather than learning [17]. The test data is leftover of training and validation data to assess the system performance. To avoid overfitting, validation checks have been considered which represent the numbers of consecutive iterations that system performance fails to reduce [18].

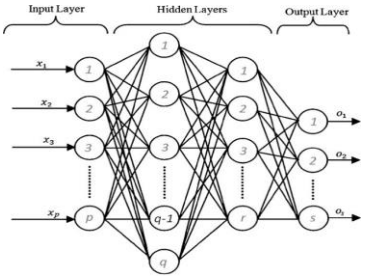

Fig. 1. Multi- layer perceptron schematic [14].

Here, the ANI was implemented on 43% of zirconium experimental data points (over 230,000) at different concentrations (0.5, 1, 2.5 and 5 wt%) and scan rates with a defined fixed train and test data set. One, two, and three hidden layers with 1-30 neurons at each layer and 1-30 validation checks were being considered. The structure that provided a minimum average error for both train and test sample condition was selected. In addition, this selected structure was applied to 49% of uranium experimental data (over 350,000 data points) with 5, 7.5, 10 wt% to prove capability of final structure and ANI prediction. Details of this approach can be found in Ref. 11.

RESULTS AND DISCUSSION

A: DIFFUSION MODEL

The CV of uranium chloride for 1 wt% has been illustrated in Fig. 2. There are two distinctive colors in this figure indicating the reversible side by blue dot and irreversible side by red asterisks. Fig. 2 shows the capability of anodic and cathodic peaks detection in this method while the root mean square error (RMS) for potential and current are around 0.01. However, the shape of CV predicted is not exactly the same as the experimental data set. This dissimilarity indicates that the Fick's law can only provide a proper outcome for a Gaussian trend. As shown in Fig. 3, this method cannot predict the irreversible cathodic side at high concentration. However, the main focus of this work is to capture the anodic and cathodic peak features in the absence of experimental data set; this is satisfactory with the shown results using the diffusion model. In addition to the CV tracing, this study can be used to calculate the concentration of each species with different concentrations of uranium chloride at various scan rates (see Fig. 4).

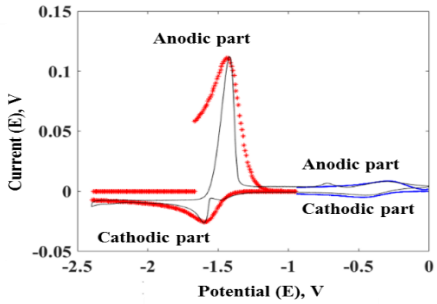

Fig. 2. Cyclic voltammetry of 1 wt% UCl_3 in LiCl-KCl eutectic at 773K with 100 mV/s.

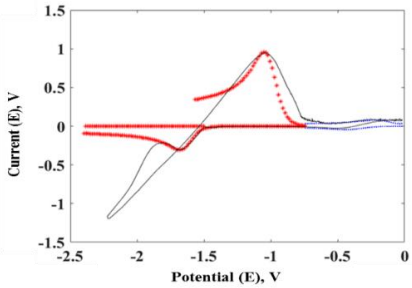

Fig. 3. CV of 10 wt% UCl_3 in LiCl-KCl eutectic at 773K with 200 mV/s.

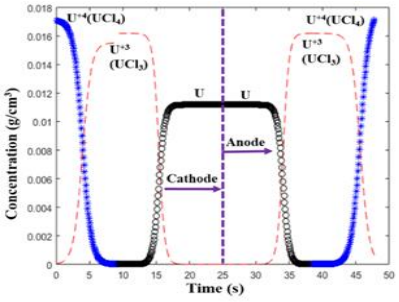

Fig. 4. Reduced and oxidized species for 1 wt% UCl_3 in LiCl-KCl eutectic at 773K with 100 mV/s.

Fig. 5 illustrates the diffusion model for the CV of zirconium chloride. The results show a complex feature (two reduction peaks) where the model fails to predict the trend of $ZrCl_4$ (see Fig. 5). This limitation will be explored by the ANI method and compared to the diffusion results later.

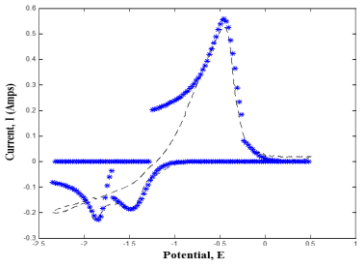

Fig. 5. Cyclic voltammetry of 1 wt% $ZrCl_4$ in LiCl-KCl eutectic at 773K with 300 mV/s.

B: ANI METHOD

The notation for the structure that will be used in the ANI discussion is '[a, b, c]-d', where a, b, and c are corresponding to the number of neurons in the first, second, and third hidden layers, respectively, and d is the number of validation checks. Here, [9, 15, 10]-18, [9, 21, 7]-27, [10, 11, 25]-19, and [10, 26, 7]-20 were selected after considering the following conditions: (i) applying one to three hidden layers using the number of neurons and validation checks from 1 to 30, and (ii) comparing the average error for the test and sample conditions [11]. These structures did not provide the same predicted results by repeating because of randomly selected weights and biases by the computer. Therefore, each selected structure was repeated 12 times to compare the predicted values errors for the test sample. The structure, [9, 15, 10]-18 (referring to as the 'final structure'), that provided a minimum RMS for CV prediction of zirconium chloride was ultimately selected for this discussion. Detailed discussion for each hidden layer and different number of neurons and validation check can be found in Ref. 11. The CV plot of 0.5 wt% $ZrCl_4$ at 450 mV/s with the final structure is compared with the experimental data set and shown in Fig. 6. The result shows ANI is able to predict the CV with a minimum RMS, around 0.02.

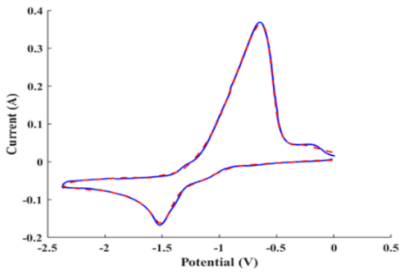

Fig. 6. Comparison of CV plot for 0.5 wt% $ZrCl_4$ in LiCl-KCl eutectic at 773K with 450 mV/s with [9, 15, 10]-18 implementation.

This final structure was also applied on UCl_3 to prove a capability of the final structure and ANI predictability. Fig. 7 shows the CV comparison for 7.5 wt% of UCl_3 at 450 mV/s and 10 wt% uranium chloride at 1700 mV/s with RMS of 0.0249 and 0.1586, respectively. This structure indicates a minimum RMS for different concentration of UCl_3 at various scan rates.

The results show that ANI simulation can capture the important features of the CV graph such as oxidation and reduction peaks (agreeing well with the experimental data sets); few deviations can be seen during the transition from the cathodic sweep to anodic sweep region. This final structure can be applied on any other CVs data sets of uranium and zirconium without going through all steps. The training and test data sets should be selected and the final structure can predict the CV in less than 10 minutes.

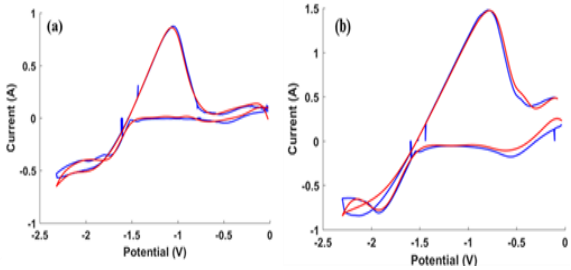

Fig. 7. Comparison of CV plot for (a): 7.5 wt% UCl_3 at 450 mV/s, (b): 10 wt% at 1700 mV/s.

C: DIFFUSION MODEL VERSUS ANI METHOD

To have a better comparison between the diffusion model and ANI, Fig. 8 compares a CV of 5 wt% UCl_3 at 400 mV/s with diffusion model and ANI method.

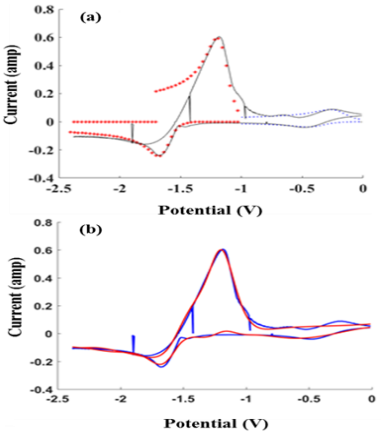

Fig. 8. Cyclic voltammetry of 5wt% UCl_3 in LiCl-KCl eutectic at 773 K with 400 mV/s, (a): diffusion mode, (b): ANI method.

Here, the average RMS of current for 5 wt% UCl_3 at 400 mV/s with diffusion model and ANI method are approximately 0.091 and 0.014, respectively. The results shows that ANI can be used to trace CV curve well whereas the diffusion model can only predict the reduction and oxidation peaks failing to obtain the remaining trends. This implies that for safeguards detection, if the cathodic and anodic reactions are of concern, then diffusion can provide a robust result. And ANI is better at providing the predictive trends for fine detailed characters.

SUMMARY

Diffusion model and ANI technique were applied to the CV experimental data sets to show their capabilities in predicting cathodic and anodic reactions of UCl_3 and $ZrCl_4$ in replicating the ER conditions for Pyroprocessing technology. The diffusion model was able to capture the oxidation and reduction peaks of experimental data sets. The diffusion model could be used to calculate the concentration of reduced and oxidized species as a function of time. However, the CV profiles predicted by diffusion model showed a dissimilarity and had several limitations at high concentration of UCl_3. Moreover, this model could not fully predict a complex CV of $ZrCl_4$. Thus, an ANI methodology was developed as an alternative electro-chemical method. Different hidden layers (1 to 3) with various neurons (1 to 30) at several validation checks (1 to 30) and compared the minimum RMS for a selected test and train sample. The structure that provides a minimum error (around 0.02) is [9, 15, 10]-18. This final structure was also applied on the 5 to 10 wt% UCl_3. The results reveal that ANI is able to predict the CV without any dissimilarity and does not show any limitation in high concentration or in a complex CV. In addition, ANI can predict the CV in less than 10 minutes. These results suggest that with further ANI study and development, this methodology can possibly be used for safeguards on pyroprocessing facility.

REFERENCES

[1]. D. YOON, "Electrochemical Studies of Cerium and Uranium in LiCl-KCl Eutectic for Fundamentals of Pyroprocessing Technology," Ph.D. Dissertation, Mechanical and Nuclear Engineering Department, Virginia Commonwealth University (2017).

[2]. Nuclear Technology Review 2016, Reported by Director General, GC (60)/INF/2.

[3]. J. L. WILLIT et al., "Electrorefining of Uranium and Plutonium- A Literature Review", Journal of Nuclear Materials, 195, 229-249 (1992).

[4]. AMMON N. WILLIAMS, "Measurement of Rare Earth and Uranium Elements Using Laser-induced Breakdown Spectroscopy (LIBS) in an Aerosol System for Nuclear Safeguards Applications", Ph.D. Dissertation, Mechanical and Nuclear Engineering Department, Virginia Commonwealth University (2016).

[5]. J. HEINZE, "Cyclic Voltammetry- Electrochemical Spectroscopy", Angewandte Chemie International Edition, **23**(11), 831-918 (1984).

[6]. R. O. HOOVER, "Uranium and Zirconium Electrochemical Studies in LiCl-KCl Eutentic for Fundamental Applications in Used Nuclear Fuel Reprocessing", Ph.D. Dissertation, Mechanical and Nuclear Engineering Department, Virginia Commonwealth University (2014).

[7]. R. O. HOOVER et al., "Electrochemical studies and analysis of 1–10 wt% UCl_3 concentrations in molten LiCl–KCl eutectic," *Journal of Nuclear Material*, **452** (1-3), 389-396 (2014).

[8]. A. J. BARD and L. R. FAULKNER, *Electrochemical Methods: Fundamentals and Applications*, Second Edition, Wiley (2000).

[9]. S. A. KUZNETSOV et al., "Electrochemical Behavior and Some Thermodynamic Properties of UCl_4 and UCl_3 Dissolved in a LiCl-KCl Eutectic Melt," *Journal of the Electrochemical Society*, **152**(4), C203-C212 (2005).

[10]. R. S. NICHOLSON, "Theory and Application of Cyclic Voltammetry for Measurement of Electrode Reaction Kinetics," *Journal of Analytical Chemistry*, **37**(11), 1351-1355 (1965).

[11]. SAMANEH RAKHSHAN POURI, "Comparative Studies of Diffusion Model and Artificial Neural Intelligence on Electrochemical process of U and Zr Dissolution in LiCl-KCl Eutectic Salts," PhD Dissertation, Mechanical and Nuclear Engineering Depatment, Virgnia Commonwealth University (2017).

[12]. S. LAHIRI AND K. C. GHANTA, "Artificial Neural Network Model with Parameter Tuning Assisted by Agentic Algorithm Technique: Study of Critical Velocity of Slurry Flow in Pipeline," *Asia-Pacific Journal of Chemical Engineering*, **15**(2), 763-777 (2010).

[13]. D. KRIESEL, "A Brief Introduction to Neural Networks," 2007, Available at http://www.dkriesel.com/_media/science/neuronalenetze-en-zeta2-2col-dkrieselcom.pdf.

[14]. D. WIJAYASEKARA et al., "Optimal Artificial Neural Network Architecture Selection for Performance Prediction of Compact Heat Exchanger with the EBaLM-OTR Technique," *Nuclear Engineering and Design*, **241**(7), 2549-2557 (2011).

[15]. A. RIDLUAN, et al., "EBaLM-THP-a Neural Network Thermo hydraulic Prediction model of Advanced Nuclear System Components," *Nuclear Engineering and Design*, **239**(2), 308-319 (2009).

[16]. A. S. PLANCHE and N. D. S. CORDEIRO, "A General ANN-Based Multitasking Model for the Discovery of Potent and Safer Antibacterial Agents," *Methods in Molecular Biology*, **1260**, 45- 64 (2015).

[17]. P. SIRIPHALA, "Controlling Artificial Neural Networks Overtraining When Data Is Scarce," Ph.D. Dissertation, Department of Industrial and Manufacturing Engineering, Wichita State University (2000).

[18]. B. TAYLOR, et al., "Verification and Validation of Neural Networks: a Sampling of Research in Progress," *Proceeding in the International Society for Optical Engineering (SPIE)*, Intelligent Computing: Theory and Applications, **5103** (8), August 7 (2003).