Development of a Smart Signal Detection Method for Cyclic Voltammetry via Artificial Neural Intelligence

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ABSTRACT

The electrorefiner (ER) is the heart of pryoprocessing technology which is a high-temperature method for separating uranium from Used Nuclear Fuel (UNF). It is important to improve this technology with respect to nuclear materials detection and accountability. Artificial Neural Intelligence (ANI) is a novel data analysis and simulation method that can be applied to electrochemical data sets. This computational code, which has been performed using the commercial software *MATLAB*, can be trained to generalize adequate electrical current and potential simulated data sets for the unseen data with a high accuracy of prediction. For this purpose, a massive collection of cyclic voltammetry (CV) data sets by Hoover (2014), for 0.5, 1, 2.5, and 5 wt% of zirconium chloride in LiCl-KCl molten salt with different scan rates at 773K has been considered. The computer is trained via ANI to predict the unseen data after providing suitable hidden layers and validation numbers. In addition, this work can trace the CV plot for a blind condition by interpolating between two simulated data set. The different hidden layers with various neurons (from 5 to 30) at several validation numbers (from 5 to 30) has been studied and the average percent error between experimental and theoretical data for 0.5 wt% with 200 and 450 mV/s has been calculated. Preliminary results demonstrate that if the number of hidden layers increases from one to three, the average error falls down from 44% to around 8%. The best condition which gives a minimum average percent error has been discovered and the simulated CV graph has been compared with the experimental data.

INTRODUCTION

Pyroprocessing is one of the efficient methods for recycling Integral Fast Reactor (IFR) fuel which separates the actinide elements from fission products [1]. This process, recovery of uranium and plutonium from used nuclear fuel (UNF) through pyroprocessing at Argonne National Laboratory (ANL), can be implemented via electrorefinery [2]. One common method in electroanalytical chemistry, being proposed for signal detection and material accountability of the electrorefining process, is Cyclic Voltammetry (CV) due to its wide range applications from simple redox to multielectron-transfer [3].

An Artificial Neural Intelligence (ANI) is a computer simulation approach which is inspired by brain neural neurons [4,5]. It can be implemented to learn massive data sets through iterations and interrelationships among system variables such as scan rate, potential, current, process time, and weight percent [4-7]. It is compatible with non-linear, noisy, and uncertain data sets which is invaluable for modeling, prediction, and optimization towards detection and material accountability in nuclear safeguards [4-8]. Therefore, the main goal of this study is to apply ANI on the cyclic voltammetry (CV) to find a condition that provide a minimum error while predicting unseen data sets by focusing on 0.5 to 5 wt% of zirconium chloride in LiCl-KCl eutectic molten salt at 773 K under different scan rates [9]. The outcome is to provide a desired CV graph with a low error by determining the adequate numbers of hidden layers, neurons, and validation number.

SIMULATED PROCEDURE

Multi-Layered Perceptron (MLP) is the most useful feedforward model for ANI consists of input, hidden, and output layers [4]. The inputs are weighted and contrasted with the sum of inputs to the threshold value to produce the outputs. There are many algorithms for determining the network parameters such as weight values. The most well-known is Levenberg- Marquardt algorithm (LMA) which is more efficient due to its fast processing time [10, and 11]. It is important to mention that overfitting can occur when the system begins to memorize the training data set rather than learning. Therefore, overfitting happens when the training error is decreasing while validation error is increasing [12]. To avoid overfitting, the number of hidden layers, number of neurons, and number of training data sets can be increased [13]. Hoover's experimental data sets (77,000 points) from zirconium chloride in LiCl-KCl eutectic salt with different concentrations and scan rates were used in this simulating step [9]. The procedure is to run ANI at one to three hidden layers with various neurons at several validation numbers and calculate the average percent error between experimental and predicted data sets for 0.5 wt% with 200 and 450 mV/s. First for one hidden layer, the minimum error of each neuron at different validation number has been found. Therefore, the condition of both cases (200 and 450 mV/) with a minimum error percent was selected. Then, the number of hidden layer was increased to two and three layers with the same procedure.

RESULTS

The minimum error of one hidden layer for 0.5 wt% with 200 and 450 mV/s is related to 8 neurons (one layer with 8 neurons is denoted as {8}) with ~48% error. It is important to mention that with 25 neurons; the error is around 43% but because the process time increases significantly, it has not been considered as a good situation. Here, Figure 1 shows the minimum error at one hidden layer with 5 to 30 neurons.

Then, the second layer with 5 to 30 neurons and validation number has been added to the first layer with 8 neurons. That is, the first hidden layer has 8 neurons and the second hidden layer is considered with 5 to 30 neurons. The result has been demonstrated that the minimum error can happen at 13 neurons ({8 13}) with 23% error, 17 neurons ({8 17}) with 20%, and 30 neurons ({8 30}) with 14%. Fig. 2 shows the average minimum error for the second hidden layers. As mentioned before, this study does not work on the neurons larger than 25 due to its long process time. Therefore, the third layer is added to {8 13} and {8 17}. Fig. 3 demonstrates the effect of adding another hidden layers to {8 13} on the average error. Here, the minimum error occurs at {8 13 13} with 8% error. The validation numbers related to 200 and 450 mV/s yielding 8% error are related to 12 and 16, respectively. Summary of minimum average percent errors for this condition of 200 mV/s and 450 mV/s at 16 and 12 is given in Table I. The best condition that give less error with {8 13 13} is with 16 validation number. The ANI predicted CVs at this condition for both 200 and 450 mV/s are shown Figures 4 and 5, respectively.

Fig. 6 illustrates the minimum error for three hidden layers using up to 30 neurons with 5% error. However, overfitting happens after 18 neurons (with 10% error). The error for 200 mV/s (a trained data set) is decreasing while the test data set error for 450 mV/s is increasing significantly after 18 neurons. Therefore, the next situation that displays small different error between 200 and 450 mV/s is related to 16 neurons yielding ~8% error. Table II shows 200 and 450 mV/s at 28 and 23 validation number with 10% error. The 200 mV/s with 23 validation number provides 14% error and 450 mV/s with 28 validation number, gives 15% error. Therefore, the best condition for three layers providing the least error with the most adequate (less than 20 minutes) is related to {8 13 13}.

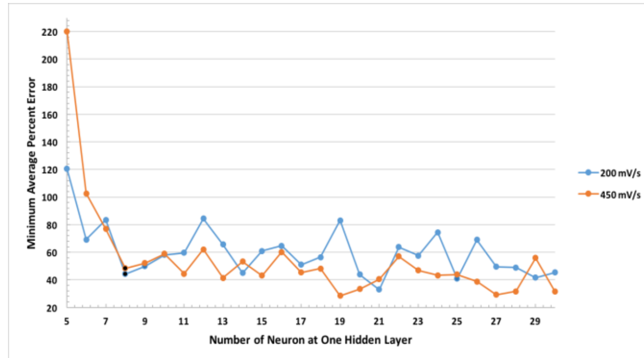

Fig. 1. Minimum average percent error of one hidden layer for 5 to 30 hidden layer for 0.5 wt% at 200 and 450 mV/s.

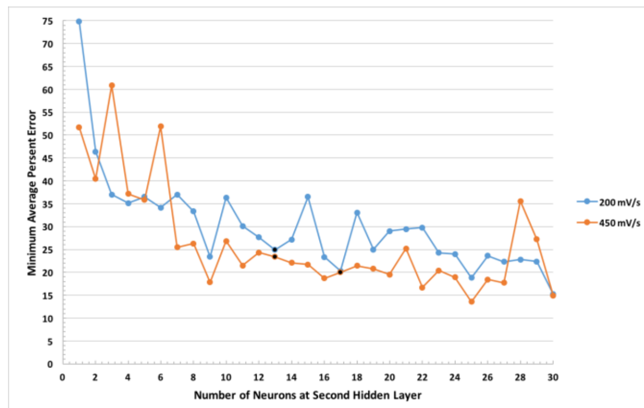

Fig. 2. Minimum average percent error of two hidden layers; first layer with 8 neurons and the second layer with 5 to 30 neurons for 0.5 wt% at 200 and 450 mV/s.

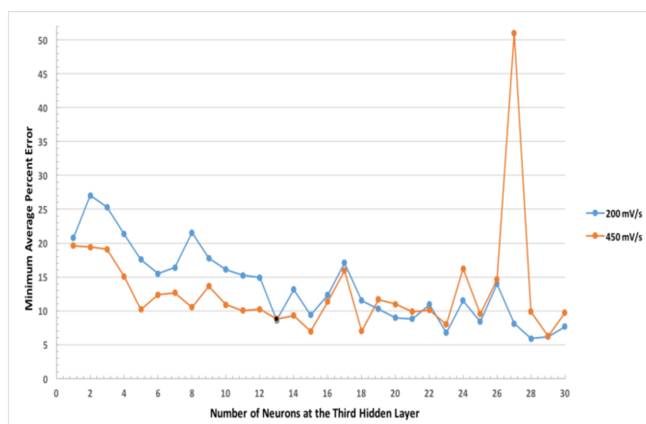

Fig. 3. Minimum average percent error of three hidden layers; first layer with 8 neurons, second layer with 13 neurons, and the third layer with 5 to 30 neurons for 0.5 wt% at 200 and 450 mV/s.

Table. I. Minimum average percent error for {8 13 13} with 12 and 16 validation number for 0.5 wt% at 200 mV/s and 450 mV/s.

	{8 13 13}	
	200 mV/S	450 mV/S
Validation Number	12	**16**
Average Error %	8%	8%
Validation Number	**16**	12
Average Error %	12%	30%

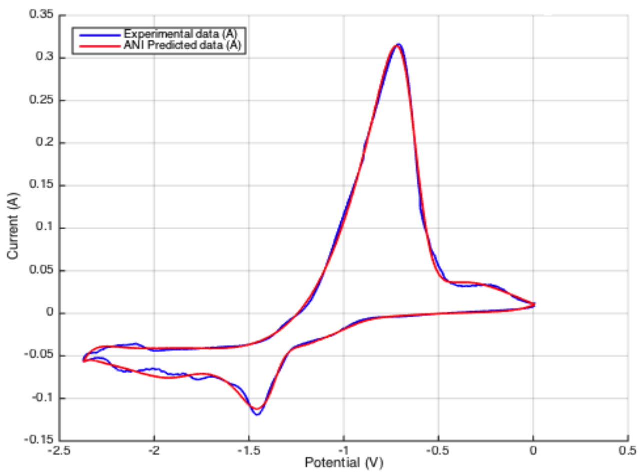

Fig. 4. Comparison of CV plot for ANI method for {8 13 13} with 16 validation number and experimental data for 0.5 wt% zirconium at 200 mV/s.

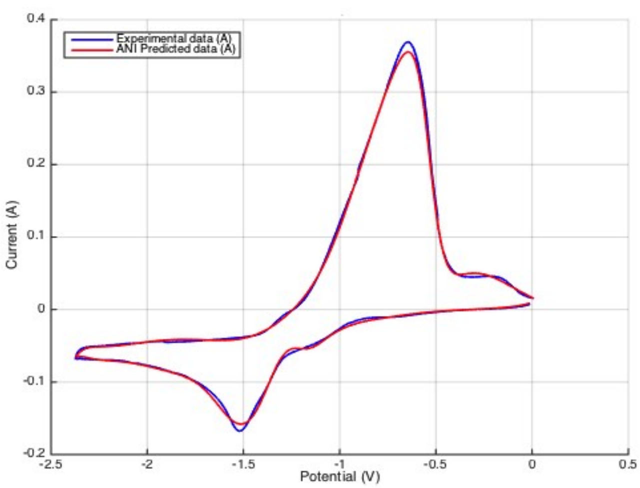

Fig. 5. Comparison of CV plot for ANI method for {8 13 13} with 16 validation number and experimental data for 0.5 wt% zirconium at 200 mV/s.

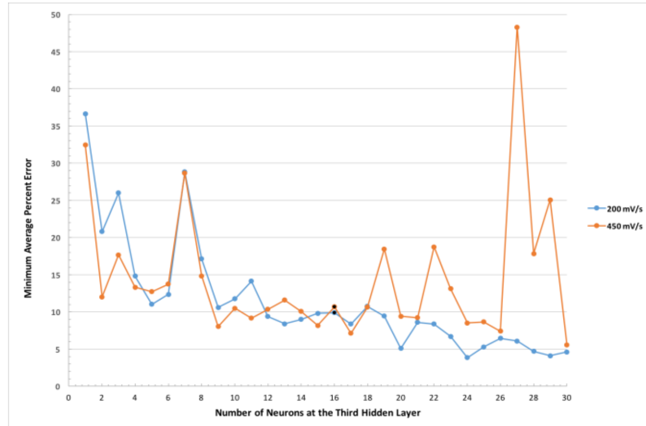

Fig. 6. Minimum average percent error of three hidden layers; first layer with 8 neurons, second layer with 17 neurons, and the third layer with 5 to 30 neurons for 0.5 wt% at 200 and 450 mV/s.

Table. II. Minimum average percent error for {8 17 7} with 16 and 27 validation number for 0.5 wt% at 200 mV/s and 450 mV/s.

	{8 17 16}	
	200 mV/S	450 mV/S
Validation Number	28	**23**
Average Error	10%	10%
Validation Number	**23**	28
Average Error	14%	15%

CONCLUSION

This work focused on zirconium chloride concentrations of 0.5, 1, 2.5, and 5 wt% at different scan rates at 773K based on the experimental data sets of Hoover [9]. One, two, and three hidden layers with neurons and validation numbers from 5 to 30 have been analyzed and the minimum average percent error for 0.5 wt% with 200 and 450 mV/s have been calculated. The results show that by increasing the number of hidden layers, the error for both cases decreases. The conditions that give a lower error for both 200 and 450 mV/s are related to {8 13 13} and {8 17 16} with 8% and 10%, respectively. Therefore, the {8 13 13} is the condition that provide CV plot with a less error in adequate time. The results indicate that the CV plots providing by ANI can possibly be used as an alternative method for signal detection towards safeguards application in electrochemical process.

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