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


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**Location:** Franklin
**Date and Time:** Tuesday, June 19, 2018, 10:00 AM


VCU Virginia Commonwealth University
Department of Mechanical & Nuclear Engineering

# Presentation Outline

- **Background**
  - Motivation
  - Objective
  - Approach
- **Diffusion Model**
  - Computational Method and Procedure
  - Results and Discussion
- **Artificial Neural Intelligence (ANI)**
  - Computational Method and Procedure
  - Results and Discussion
- **Comparison Between Diffusion Model and ANI Method**

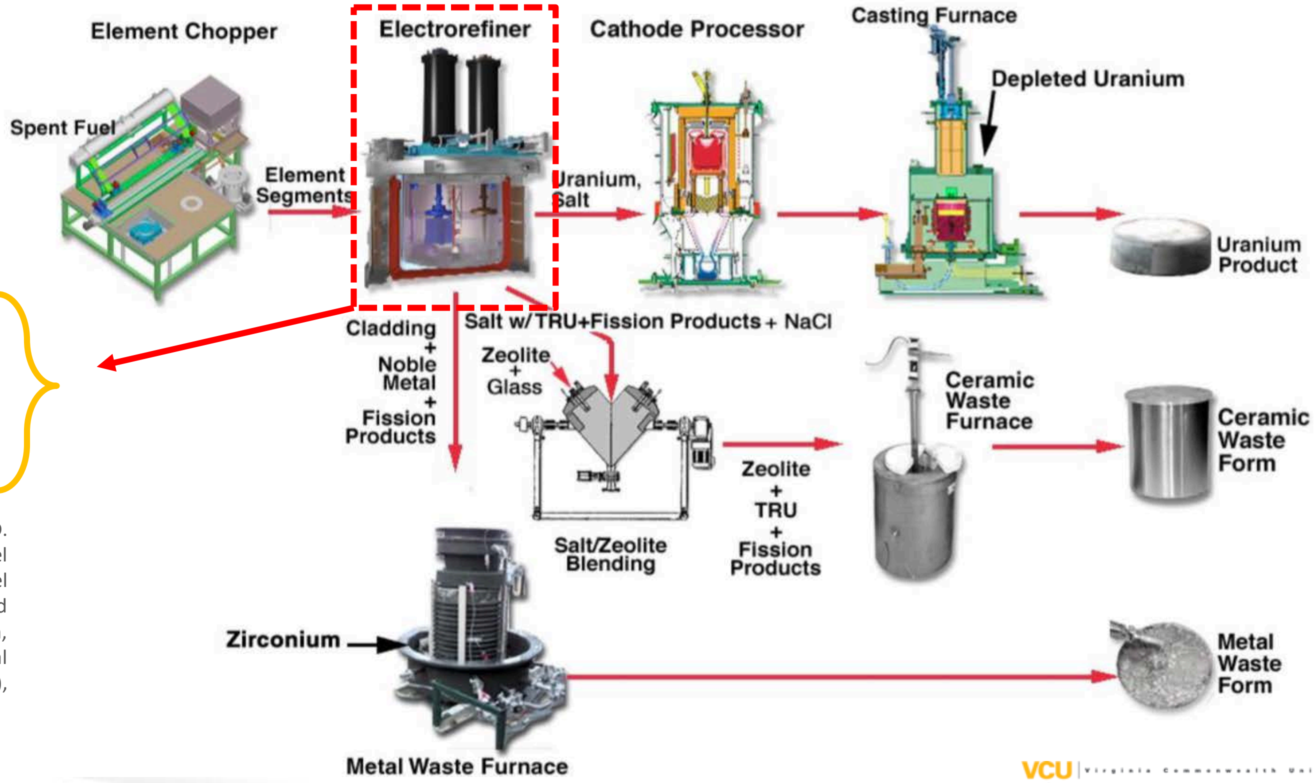
# Pyroprocessing Technology

## Oxidation and Reduction Reactions

$$U\ (anode) \rightarrow U^{+3}(salt) + 3e^{-}$$

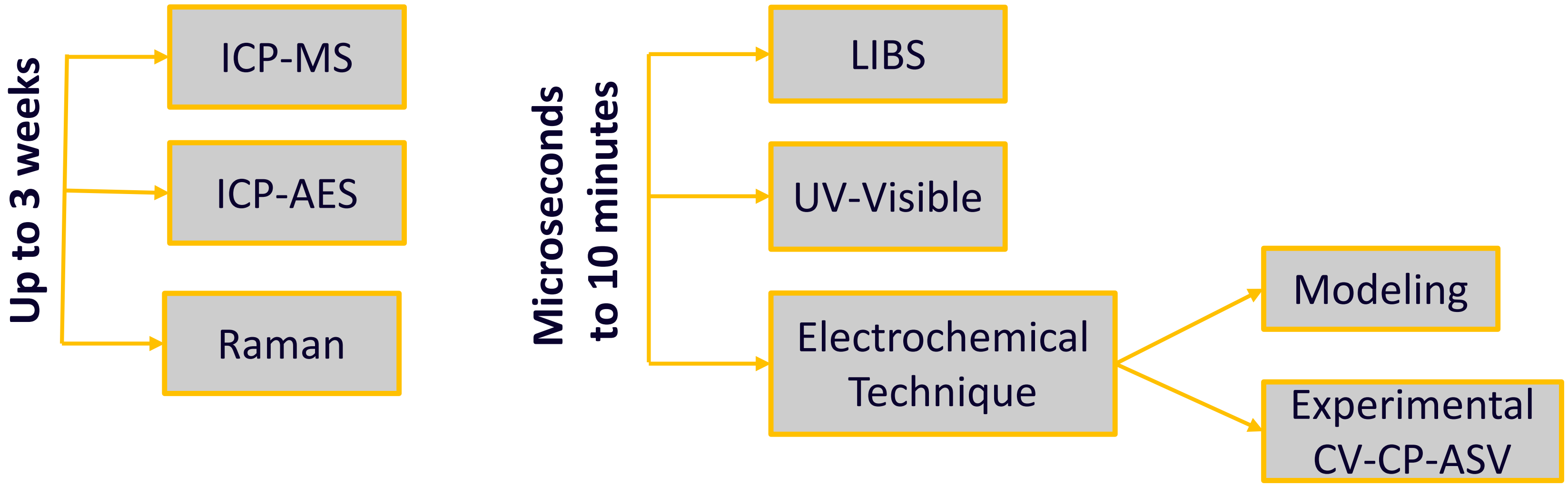
$$U^{3+}(salt) + 3e^{-} \rightarrow U(cathode)$$

M. F. Simpson, J. D. Law, "Nuclear Fuel Reprocessing", Fuel Cycle Science and technology Division, Idaho National Laboratory (2010), INL/EXT-10-17753.



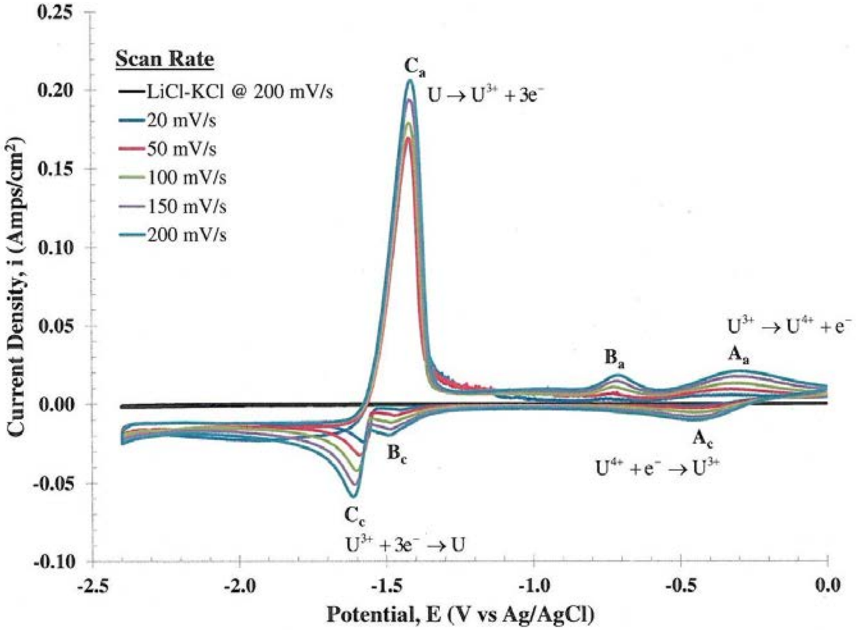
# Analytical Method for Material Analysis

**Common Practice** | **Proposed Other Method**



# Experimental Uranium Cyclic Voltammogram (CV)

## CV of 1 wt% $UCl_3$ in LiCl-KCl at Various Scan Rates




R. O. Hoover, M. R. Shaltry, S. Martin, K. Sridharan, and S. Phongikaroon, "Electrochemical studies and analysis of 1–10 wt% $UCl_3$ concentrations in molten LiCl–KCl eutectic", *Journal of Nuclear Material*, **452** (1-3), pp. 389-396 (2014).

# Motivation

➢ There are diverse software package, which can provide the current versus potential diagram within ER for CV method. However, predicting the trace of species without experimental data sets in a short time has become a huge concern and a great need in nuclear material detection and accountancy.

# Objective

- Develop a modified computational model (diffusion model) to predict less complex CV data sets in a short time (less than 2 minutes), such as uranium chloride;
- Implement ANI on massive experimental data sets of more complex CV, such as zirconium chloride;
- Verify the ANI's concept by considering the uranium chloride data sets;
- Compare the effectiveness of both methods to deliver the best methodology for rapid concentration detection and measurement for CV graphs.

# Approach

## ➢ Diffusion Model

- Tracing the trend of each element in the absent of experimental data through the current versus potential;
- Calculating the concentration of each species at each time step; and
- Predicting the CV plot with a blind input information.

## ➢ Artificial Neural Intelligence

- Implementing ANI through iterations and interrelationships among system variables such as scan rate, potential, current, process time, and weight percent for complex CV systems; and
- Determining the adequate number of neurons (1 to 30), hidden layers (one to three), and validation checks (1 to 30) to find the minimum average percent error between experimental and predicted data.

# (a) Diffusion Model (1/2)

## Computational Methods and Procedures:

### Diffusion Coefficient and Current Calculation

## ❑ Randles- Sevcik Equation:

$$D = \frac{I_{PC}^2 RT}{(0.446nFAC)^2 \upsilon nF\alpha} \qquad (1)$$

## ❑ Delahay Equation:

$$D = \frac{I_{PC}^2 RT}{(0.496nFAC)^2 \upsilon nF\alpha} \qquad (2)$$

- **A:** Working electrode surface area ($cm^2$)
- **C:** Initial concentration ($mol/cm^3$)
- **D:** Diffusion coefficient ($cm^2/s$)
- **$I_{pc}$:** Current od cathodic peak (amp)
- **n:** Number of electron (eq/mol)
- **F :** Faraday's constant (96485 C/eq)
- **R :** Universal gas constant (8.314 J/mol.K)
- **T :** Temperature (K)
- **$\upsilon$ :** Scan rate (V/s)
- **$\alpha$ :** Transfer coefficient (0.5)

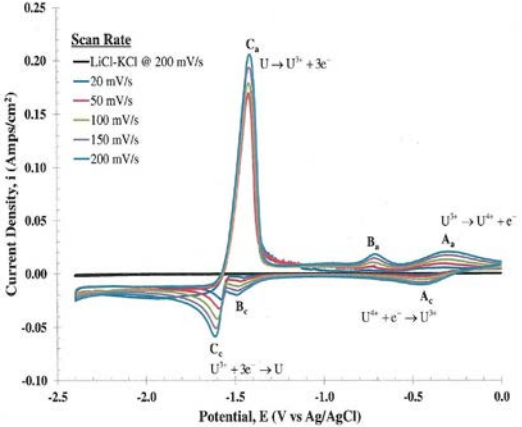
## ❑ Current Calculation:

$$i = nFAC_R^* \sqrt{\pi D_R \alpha \psi}\, \chi(\alpha\delta j) \quad \text{Irreversible} \qquad (3)$$

$$i = nFAC_O^* \sqrt{\pi D_O \psi}\, \chi(\delta j) \quad \text{Reversible} \qquad (4)$$

$$\psi = \frac{nF\upsilon}{RT} = \left(\frac{nF}{RT}\right)(E_i - E) \qquad (5)$$

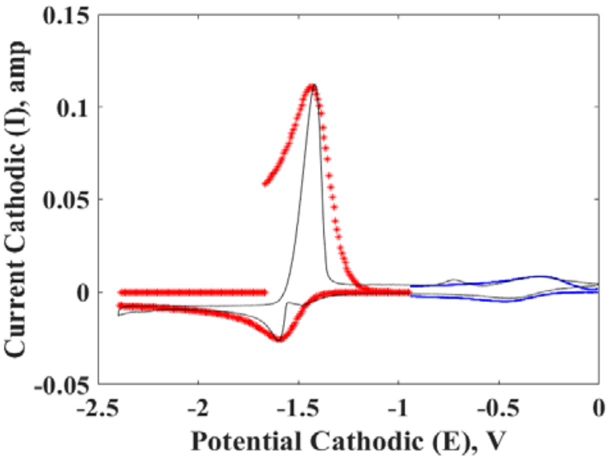
- **$C^*_o$ and $C^*_R$ :** Bulk Concentration of oxidant and reductant ($mol/cm^3$)
- **$D_R$ and $D_o$ :** Diffusion coefficient of oxidant and reductant ($cm^2/s$)
- **$E_i$ :** Initial potential (V)



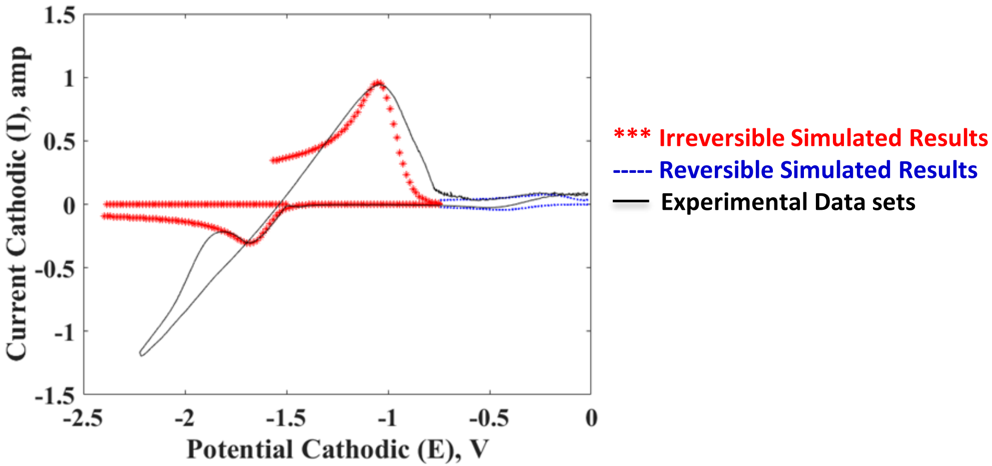
# (a) Diffusion Model (2/2)

## Results and Discussion

CV of 1 wt% $UCl_3$ in LiCl-KCl at 100 mV/s




CV of 10 wt% $UCl_3$ in LiCl-KCl at 200 mV/s




❑ **The Average Root Mean Square Error (RMSE) for 100 mV/s**

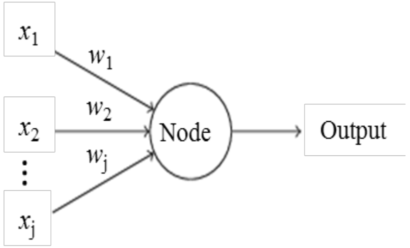
- ➢ **Potential**: 0.00764
- ➢ **Current**: 0.01780

$$RMSE = \sqrt{\frac{\sum_{t=1}^{n} (Forcast\ Value_t - Actual\ Value_t)^2}{n}}$$

# (b) ANI (1/6)

## Computational Methods and Procedures

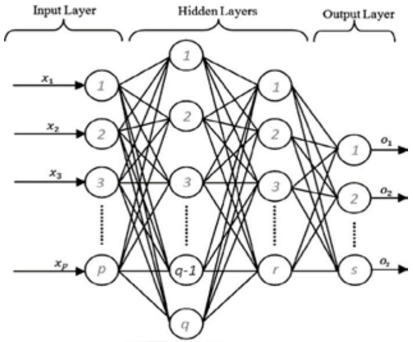
### Perceptron

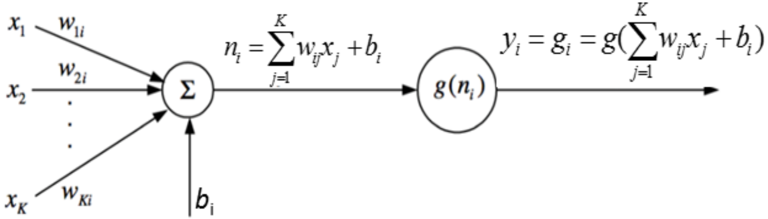


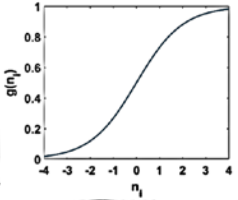

$$
\begin{cases} \sum_j w_j x_j \le threshold \rightarrow 0 \\ \sum w_j x_j > threshold \rightarrow 1 \end{cases}
$$

$$
\begin{cases} \sum_j w_j x_j + b \le 0 \rightarrow 0 \\ \sum_j w_j x_j + b > 0 \rightarrow 1 \end{cases}
$$

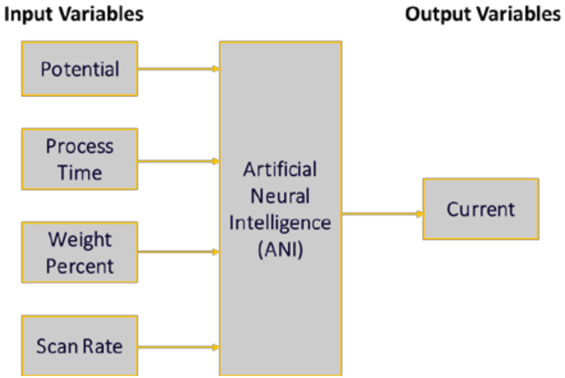
### Multi Layer Perceptron (MLP)




$$
g(n_i) = \frac{1}{1+e^{-n_i}} = \frac{1}{1+\exp(\sum_{j=1}^{K} w_{ij} x_j + b_i)}
$$



# (b) ANI (2/6)

## Computational Methods and Procedures: Experimental Data Set for $ZrCl_4$

| Concentration (mol/cm³) | Scan Rate (mV/s) | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.5 wt% | **200 Train** | 250 Test | 300 Train | 350 Test | 400 Train | **450 Test** | 500 Train | | | | | | |
| 1 wt% | 150 Train | 150 Test | 200 Train | 200 Test | 250 Train | 250 Test | 300 Test | 300 Test | 350 Train | 350 Test | | | |
| 2.5 wt% | 100 Train | 100 Test | 150 Test | 200 Test | 250 Train | 300 Train | 300 Test | 400 Test | 500 Train | | | | |
| 5 wt% | 50 Train | 50 Test | 100 Train | 100 Test | 150 Train | 150 Test | 200 Train | 200 Test | 200 Test | 250 Test | 250 Test | 300 Train | 300 Test |

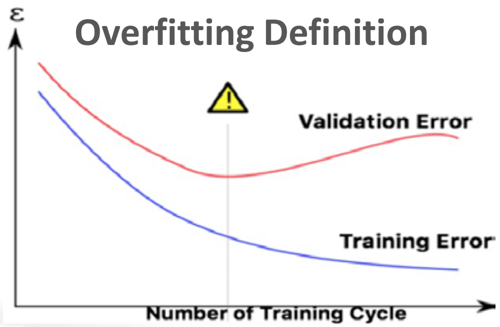
**Red** = Focus of This presentation

Training data sets

Test data sets

- **Total Experimental Data sets: 231,765**
- **Total training data set: 43%**

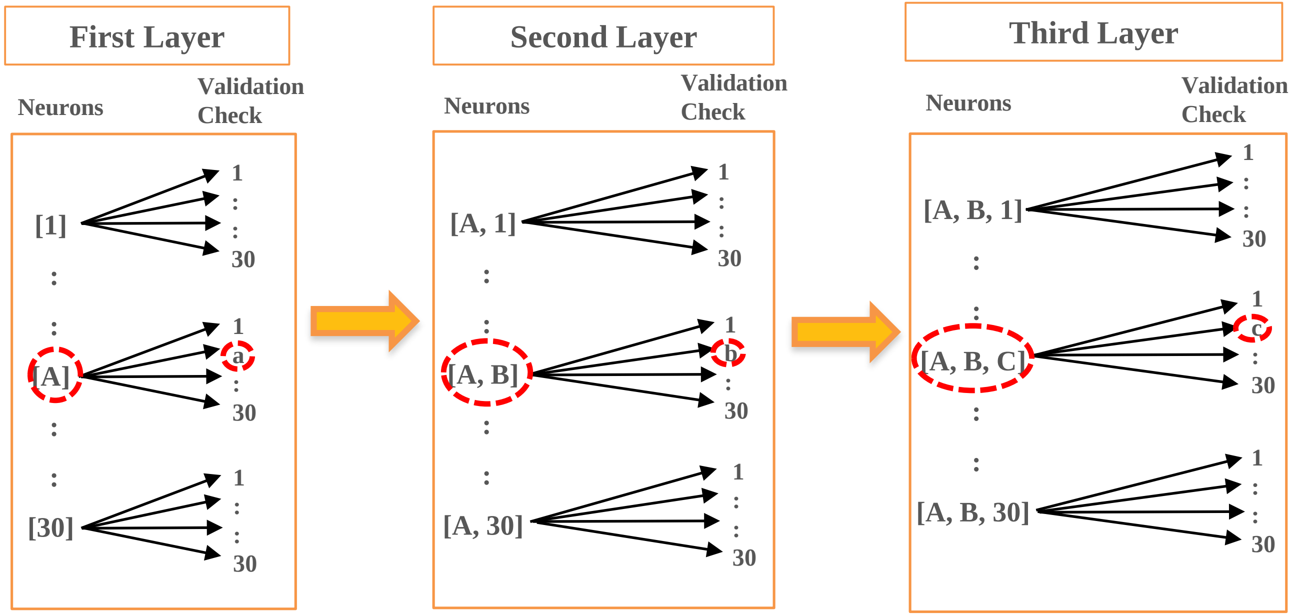
- **Training Data Set:** Partial of whole experimental data sets for adjusting the weights and bias.
- **Validation Data Set:** Independent data sets from training sample to minimize the overfitting.




- **Test Data Set:** The left over data sets that being simulated to assess the system performance.
- **Validation Checks (numbers):** The number of consecutive iterations that system performance fails to decrease.

# (b) ANI (3/6)

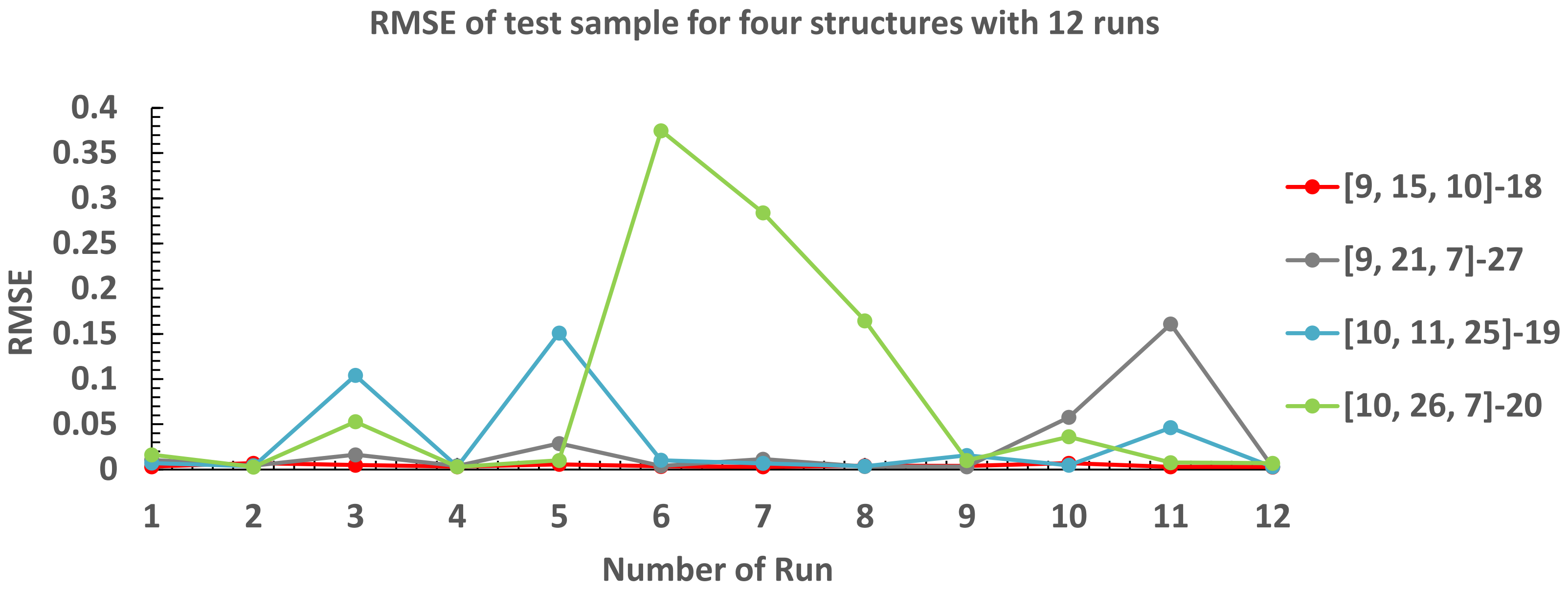
## Computational Methods and Procedures




$$\text{Mean Average Percentage Error }(MAPE) = \frac{100}{n}\sum_{t=1}^{n}\left|\frac{Actual\ Value_t - Forecast\ Value_t}{Actual\ Value_t}\right|$$

# (b) ANI (4/6)

## Computational Methods and Procedures



# (b) ANI (5/6)

## Computational Methods and Procedures

### Experimental Data Set for $UCl_3$

| Concentration (mol/cm³) | Scan Rate (mV/s) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 5 wt% | 100 Train | 150 Test | 200 Train | 250 Test | 300 Test | 350 Train | 400 Test | 450 Test | 500 Train | 600 Test |
| | 700 Test | 800 Train | 900 Test | 1000 Train | 2000 Train | | | | | |
| 7.5 wt% | 200 Train | 250 Test | 300 Train | 350 Test | 400 Test | 450 Test | 500 Train | 600 Test | 700 Train | 800 Test |
| | 900 Train | 1000 Test | 1100 Test | 1200 Train | 1300 Test | 1400 Test | 1500 Train | 1600 Test | 1800 Train | 2000 Train |
| 10 wt% | 200 Train | 450 Train | 500 Train | 600 Test | 700 Test | 800 Test | 900 Train | 900 Test | 1000 Test | 1100 Train |
| | 1200 Test | 1300 Test | 1400 Test | 1500 Train | 1600 Test | 1700 Test | 1800 Train | 1900 Test | 2000 Train | 2500 Train |
| | 2500 Test | 3000 Train | 3500 Test | 4000 Train | | | | | | |

- **Total Experimental Data sets: 353,823**
- **Total training data set: 49%**

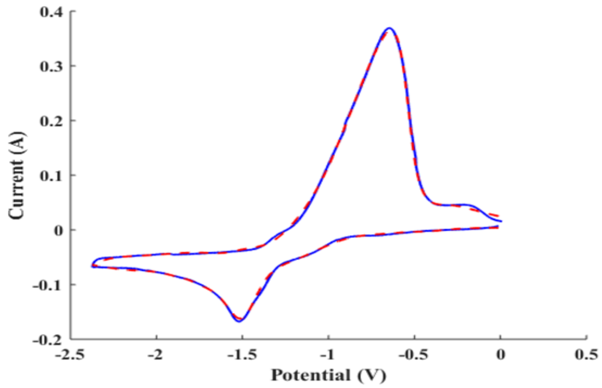
# (b) ANI (6/6)

## Results and Discussion:

### CV Plot for $ZrCl_4$ and $UCl_3$ in LiCl-KCl Eutectic at 773 K with Final Structure

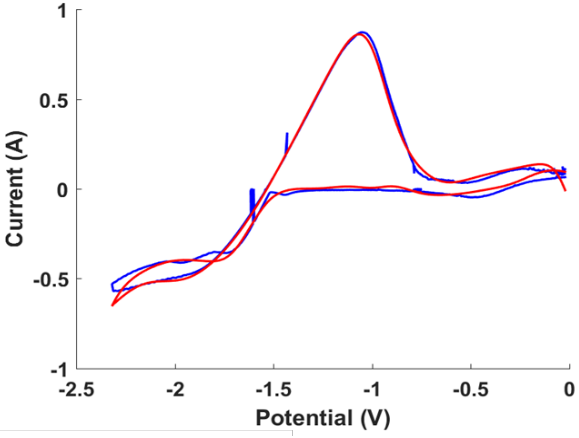
### [9, 15, 10]-18

0.5 wt% $ZrCl_4$ at 450 mV/s



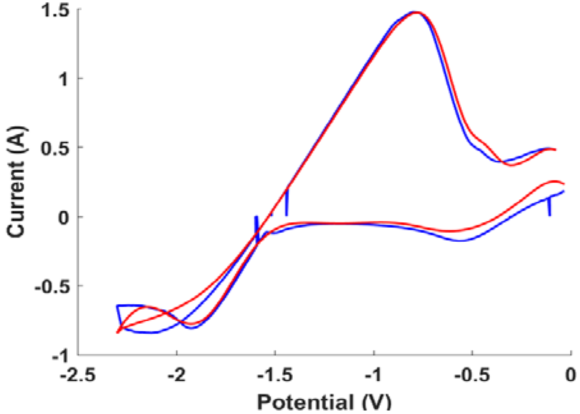

- RMSE: 0.003

7.5 wt% $UCl_3$ at 450 mV/s




- RMSE: 0.0249

10 wt% $UCl_3$ at 1700 mV/s

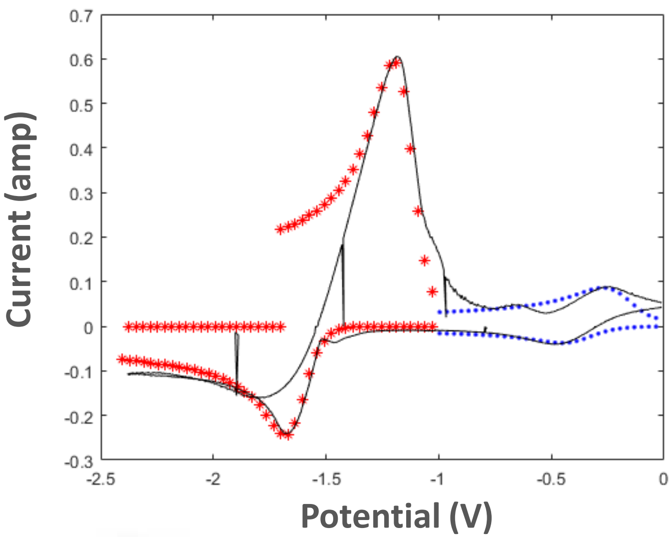



- RMSE: 0.1586

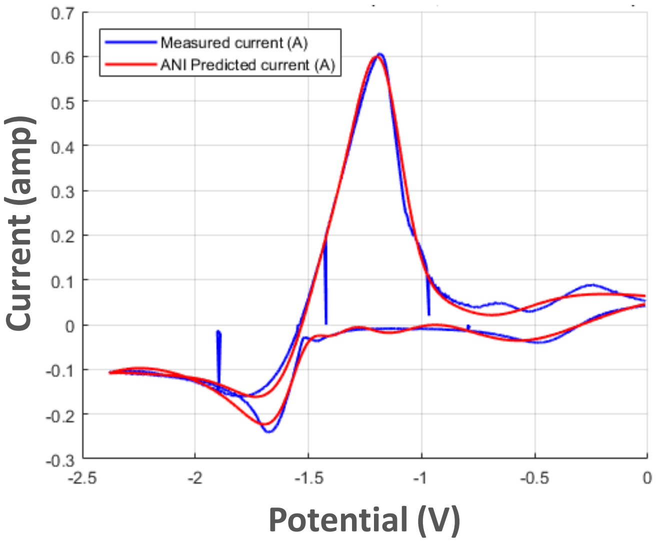
# (c) Comparison between Diffusion Model and ANI Method

5 wt% $UCl_3$ at 400 mV/s

(a) Diffusion Model



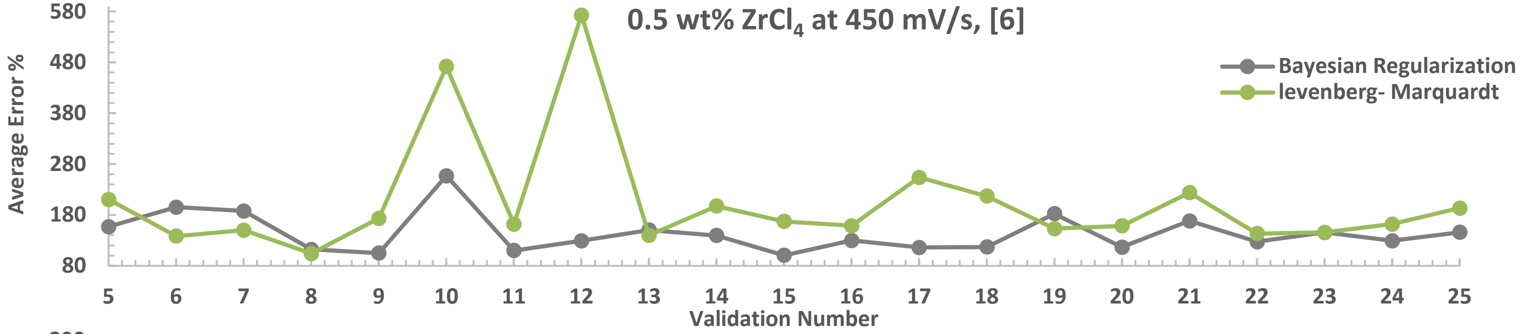

(b) ANI

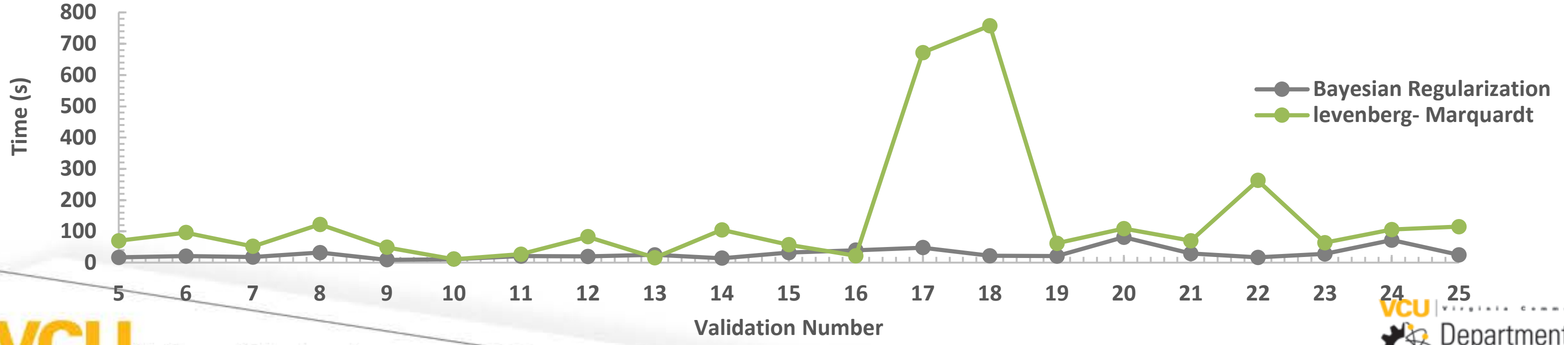



- **(a) RMSE:** 0.091
  - **Time:** 00:04
- **(b) RMSE:** 0.014
  - **Time:** 03:18

# Future Work

- ➢ Repeat the framework from first step on the other experimental data sets such as cerium chloride to compare the final ANI structure; and
- ➢ Comparative between Bayesian Regularization and Levenberg-Marquardt algorithms.



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- Funding support from the NRC Faculty and Development.
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- My Postdoctoral advisor: Dr. Zeyun Wu.
- Colleague: Ammon Williams, Dalsung Yoon, Dumidu Shanika Wijayasekara, Hunter Andrews, Michael Woods, and Riyadh Monty.


# Deliverables and Outcomes


- Samaneh Rakhshan Pouri, Supathorn Phongikaroon, "An Interactive Reverse-Engineering Cyclic Voltammetry for Uranium Electrochemical Studies in LiCl-KCl Eutectic Salt", ***Nuclear Technology***, Vol. 197, No. 3, pp.308-319 (2017).
- Samaneh Rakhshan Pouri, Supathorn Phongikaroon, Milos Manic, "A Novel Framework for Intelligent Signal Detection via Artificial Neural Networks for Cyclic Voltammetry in Pyroprocessing Technology", ***Annals of Nuclear Energy*****,** Vol. 111, pp.242-254 (2017).

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Thank you so much for your attention ☺

Any Question?

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