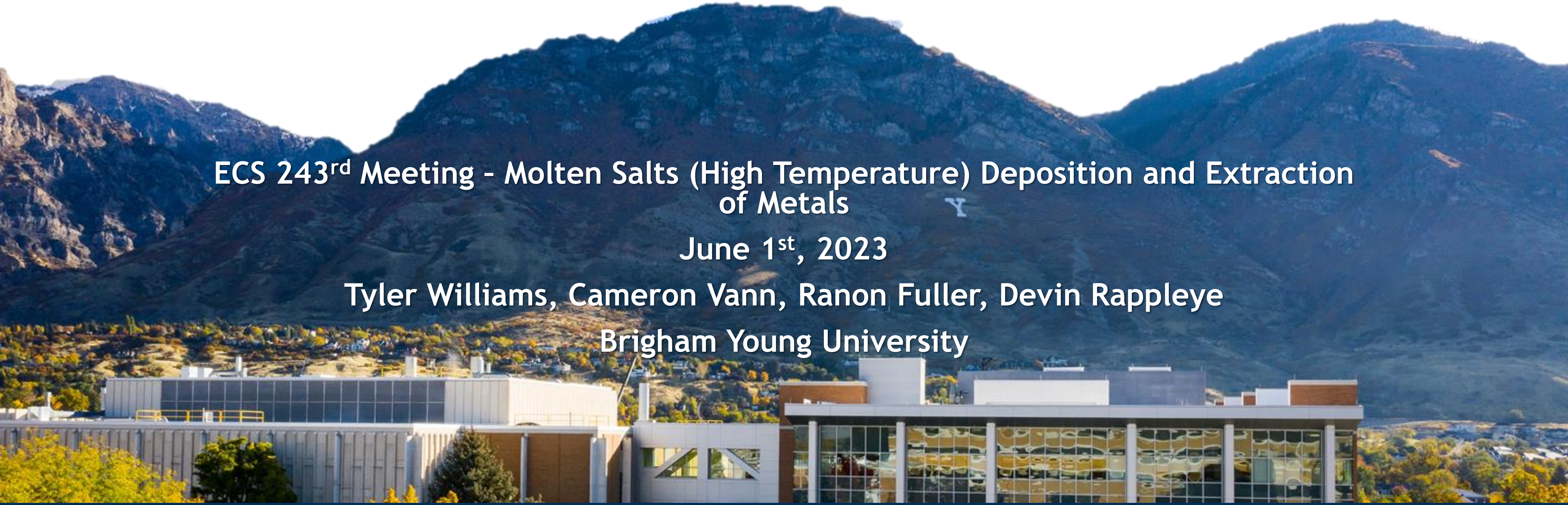
A Semi-Differentiated Model for the Potential-Sweep Voltammograms of Electrochemical Deposition Reactions



ECS 243rd Meeting - Molten Salts (High Temperature) Deposition and Extraction of Metals

June 1st, 2023

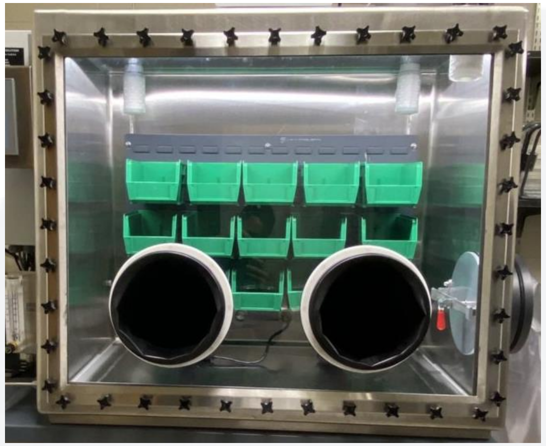
Tyler Williams, Cameron Vann, Ranon Fuller, Devin Rappleye

Brigham Young University

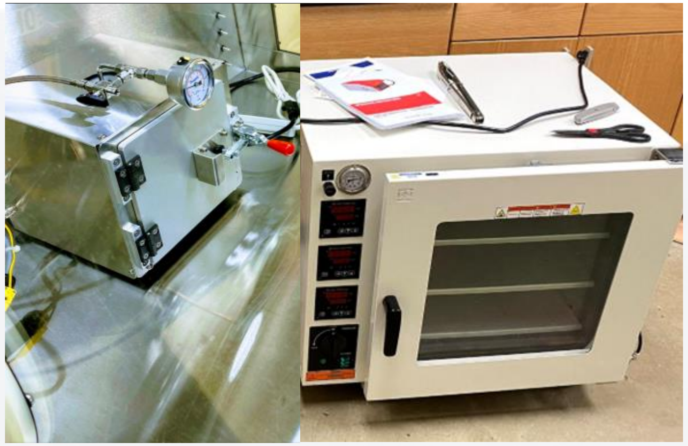
Acknowledgements

The PyRO Lab at BYU (pyro.byu.edu)

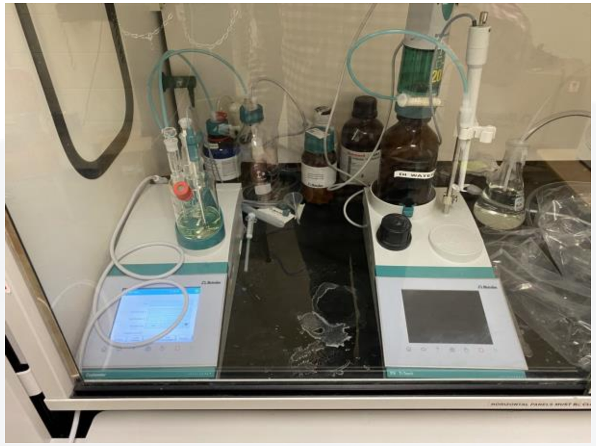
2 triple workstation inert atmosphere gloveboxes



Negative pressure workstation for transuranic compounds



Vacuum drying ovens in and out of glovebox (up to 300°C)

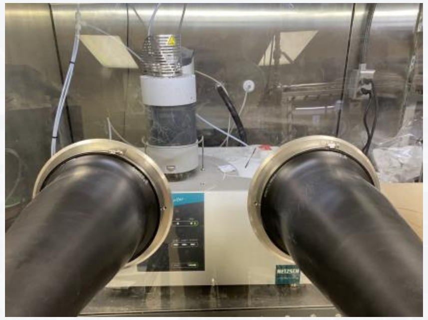


Autotitrator and KF titrator for oxide and moisture analysis

Furnaces & induction heater max. temp. 1000-2000°C

Potentiostats & power supplies (≤24 A)

Gas analyzer (≥100 ppb) plumbed to glovebox



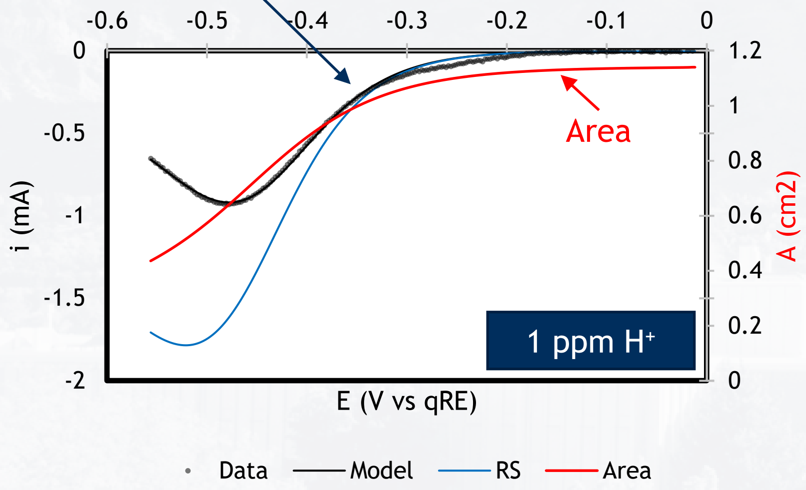
Simultaneous thermal analyzer in glovebox

Safe handling of Cl_2 and HCl gases

PyRO Lab

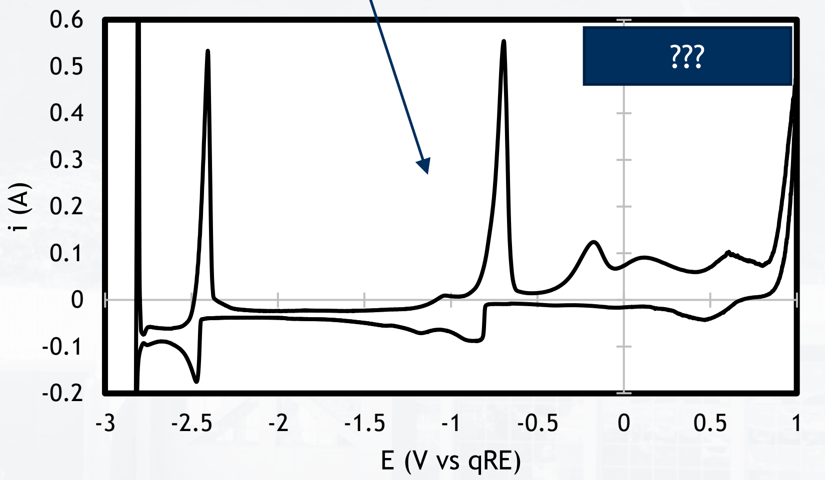
Develop sensors, models, and processes to support nuclear fuel processing, molten salt reactors, concentrated solar power, and other molten salt operations.

New Models:
Modified Randles-Ševcík for insulating, gaseous products



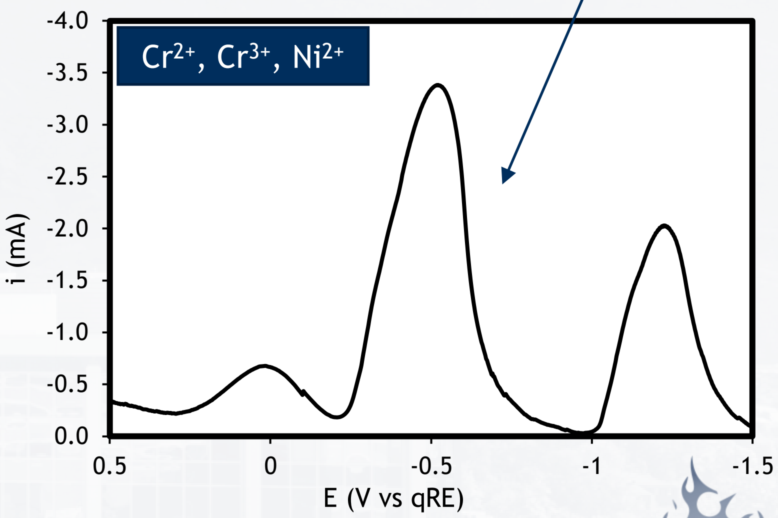
Low Concentrations

Semi-Differentiation:
Splitting overlapping peaks



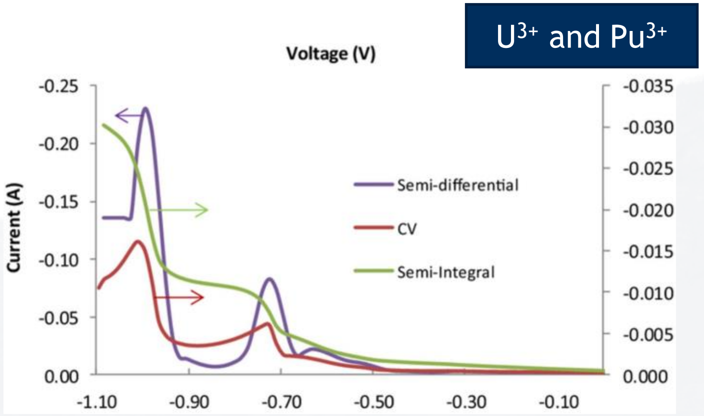
Multiple Species

Thin-layer Electrodes:
Bulk electrolysis

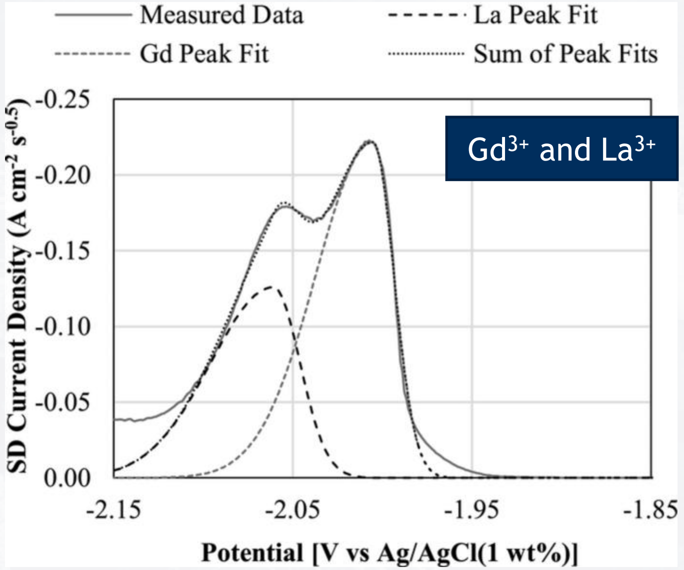


High Concentrations

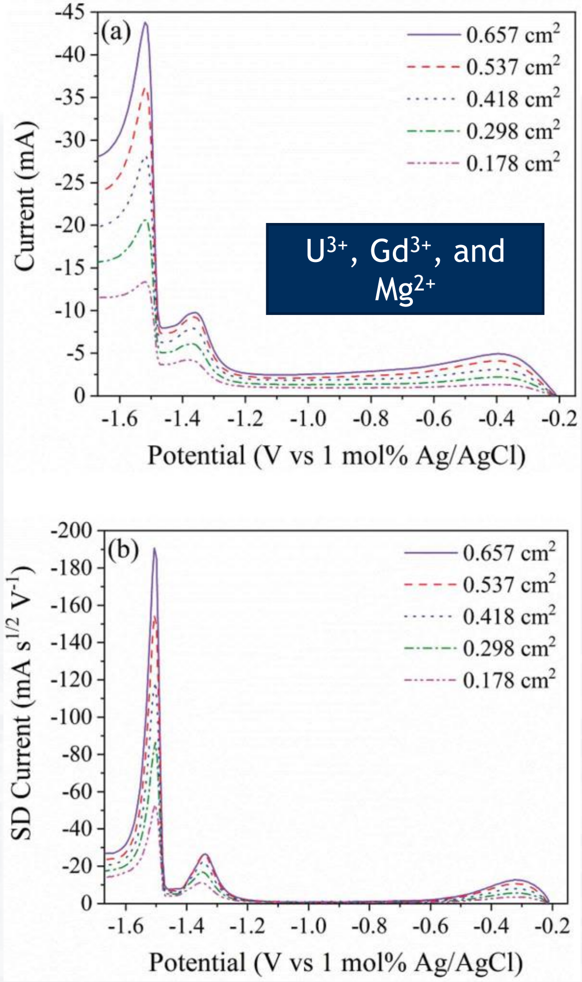
Motivation – Semi-Differentiation can Clarify



M. Tylka, J. Willit, J. Prakash, M. Williamson, *J. Electrochem. Soc.* **162**, H852 (2015)

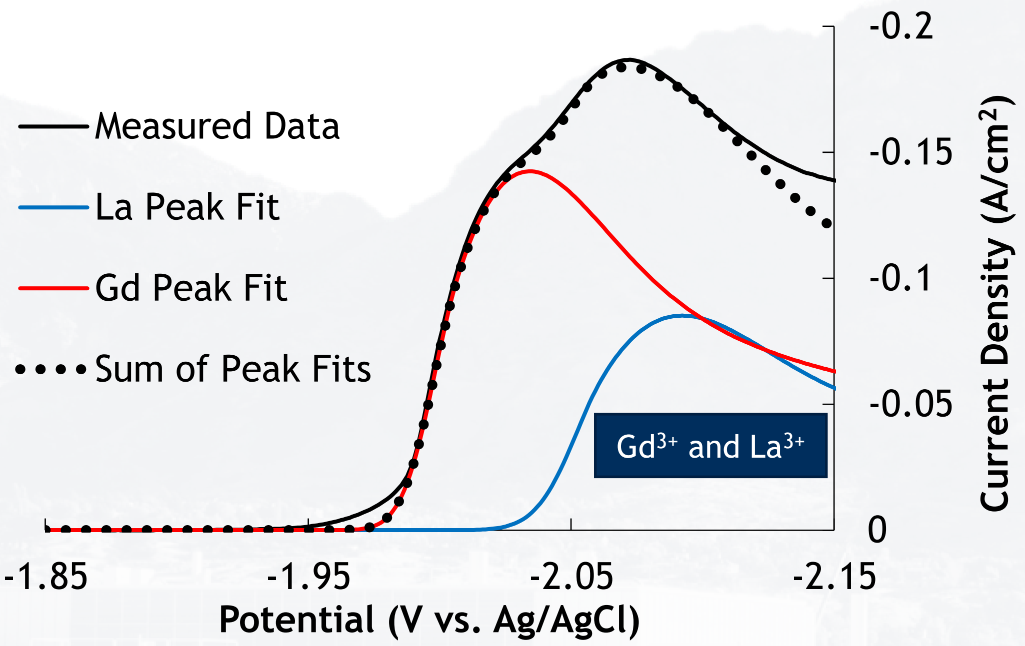


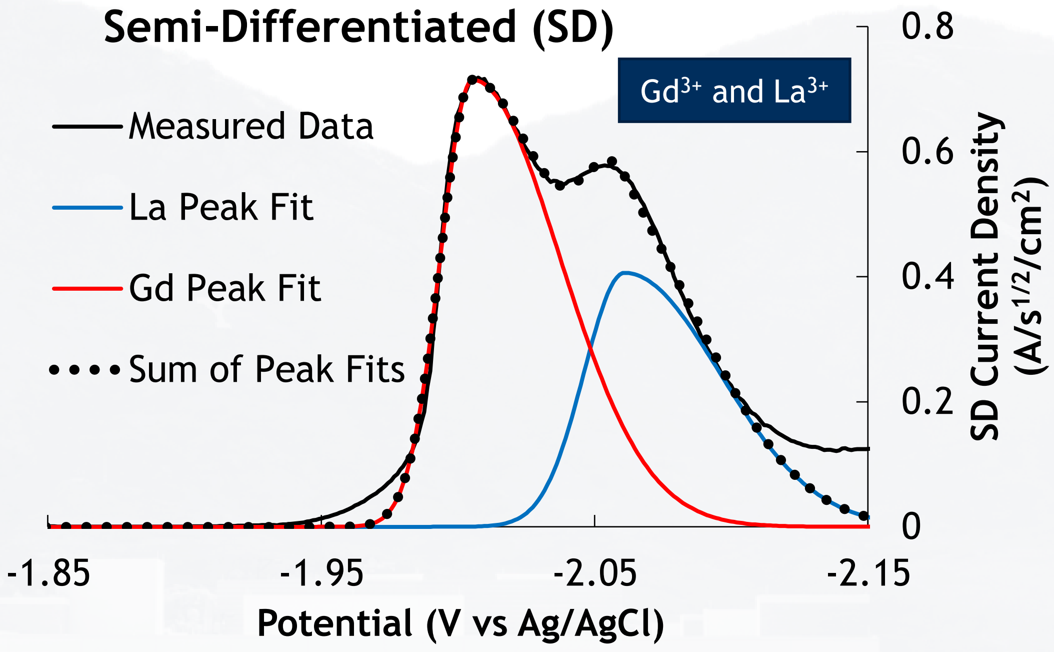
D. Rappleye, S.-M. Jeong, M. Simpson, *J. Electrochem. Soc.* **163**, B507 (2016)



H. Andrews & S. Phongikaroon, *Nucl. Tech.* **207**, 617-626 (2021)

Motivation – Peaks or Exponential Curves?





Rappleye, D., Jeong, S.-M., & Simpson, M. (2016). Electroanalytical Measurements of Binary-Analyte Mixtures in Molten LiCl-KCl Eutectic: Gadolinium(III)- and Lanthanum(III)-Chloride. *Journal of The Electrochemical Society*, *163*(9), B507. https://doi.org/10.1149/2.1011609jes

$$\mathcal{D}^{1/2}i(t) = \frac{n^2F^2A\sqrt{D_o}}{2RT}\nu C_o e^{\frac{nF}{RT}(E_{eq}-\nu t-E_{1/2})}$$

Tylka, M. M., Willit, J. L., Prakash, J., & Williamson, M. A. (2015). Application of Voltammetry for Quantitative Analysis of Actinides in Molten Salts. Journal of The Electrochemical Society, 162(12), H852–H859. https://doi.org/10.1149/2.0281512jes

An exponential function???

Theory - What is a Semi-Derivative?

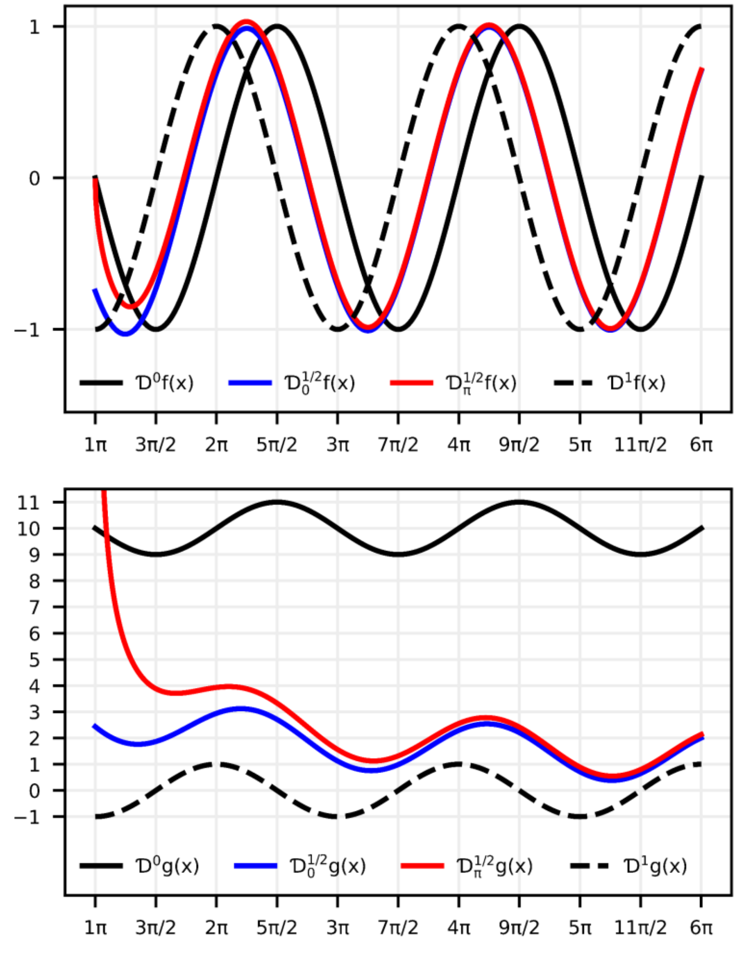
$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial f(x)}{\partial x}\right)$$

$$\frac{\partial f(x)}{\partial x}$$

$$f(x)$$

$$\frac{\partial^{-1} f(x)}{\partial x^{-1}} = \int f(x)dx$$

$$\frac{\partial^{-2} f(x)}{\partial x^{-2}} = \frac{\partial^{-1}}{\partial x^{-1}}\left(\frac{\partial^{-1} f(x)}{\partial x^{-1}}\right) = \int\int f(x)dxdx$$



T. Williams, C. Vann, R. Fuller, D. Rappleye, *J. Electrochem. Soc.* **170**, 042502 (2023)

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$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial f(x)}{\partial x}\right)$$

$$\frac{\partial f(x)}{\partial x}$$

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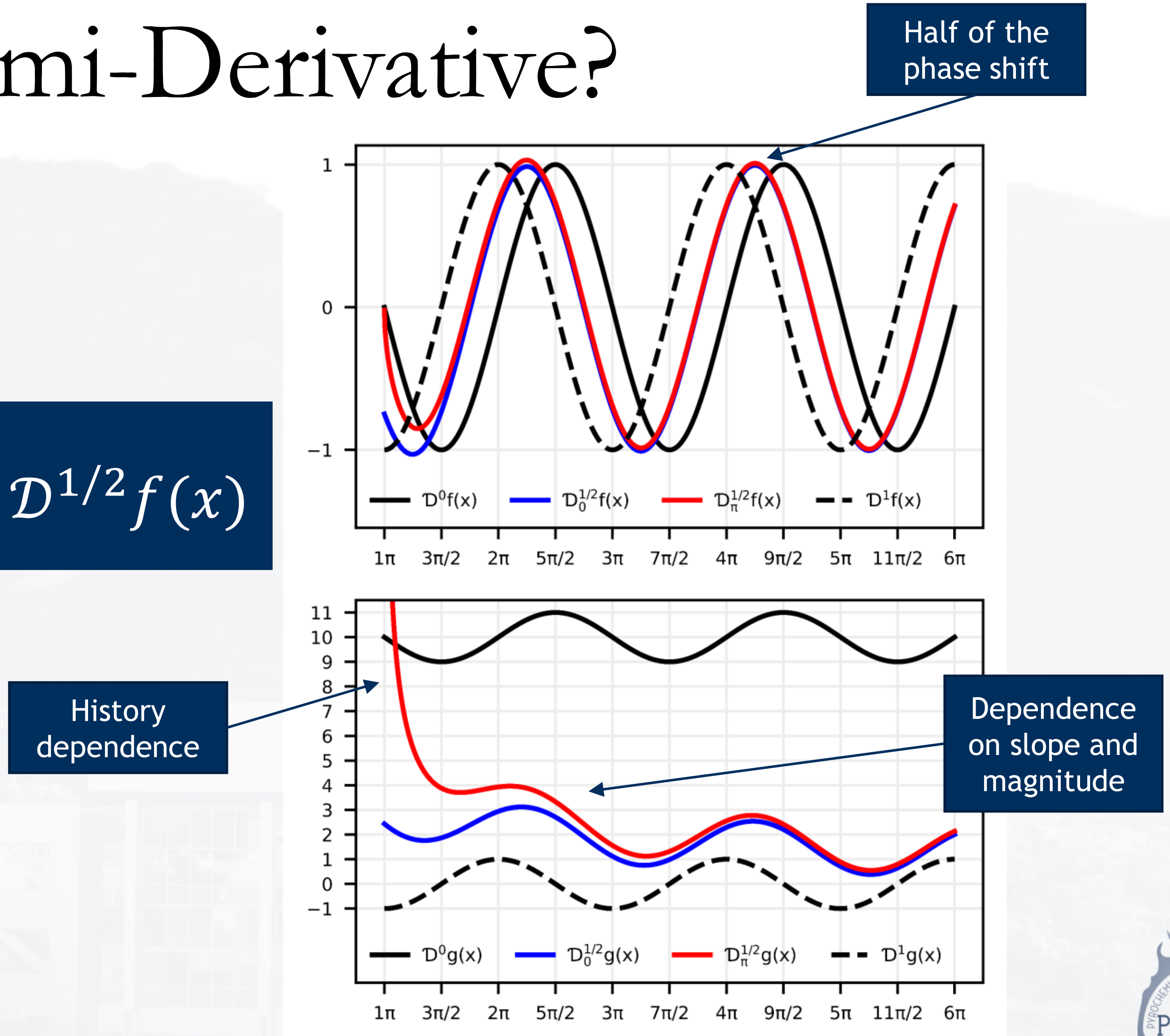
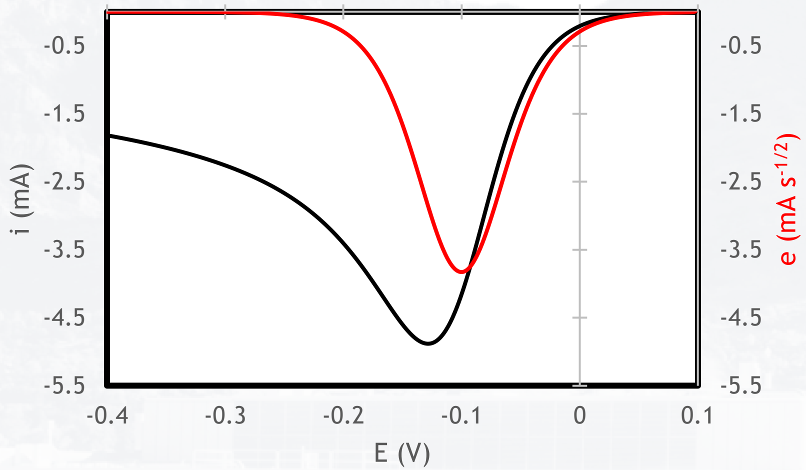
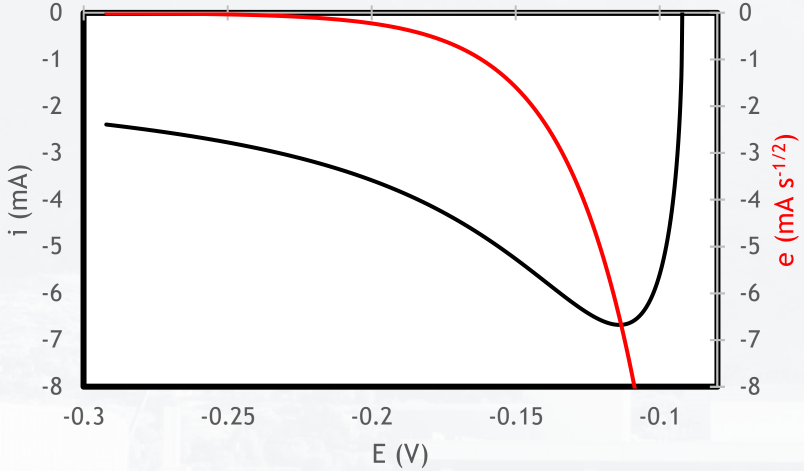


T. Williams, C. Vann, R. Fuller, D. Rappleye, *J. Electrochem. Soc.* **170**, 042502 (2023)

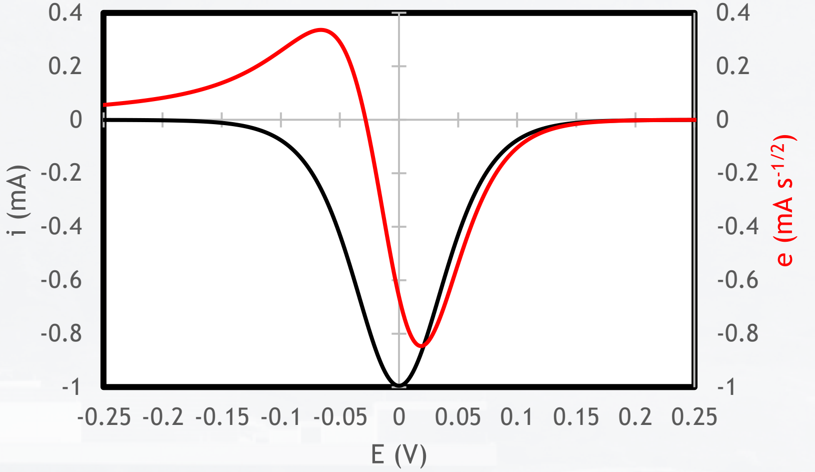
Theory – Semi-derivatives of Common Curves



Randles-Ševcík



Berzins-Delahay

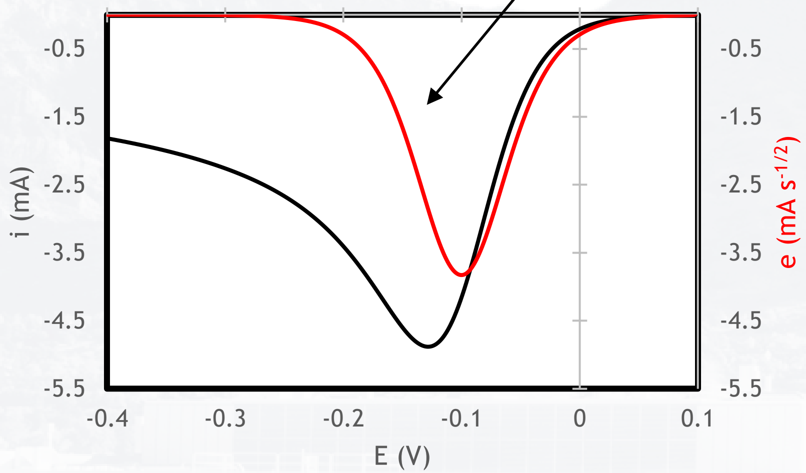


Thin-layer CV

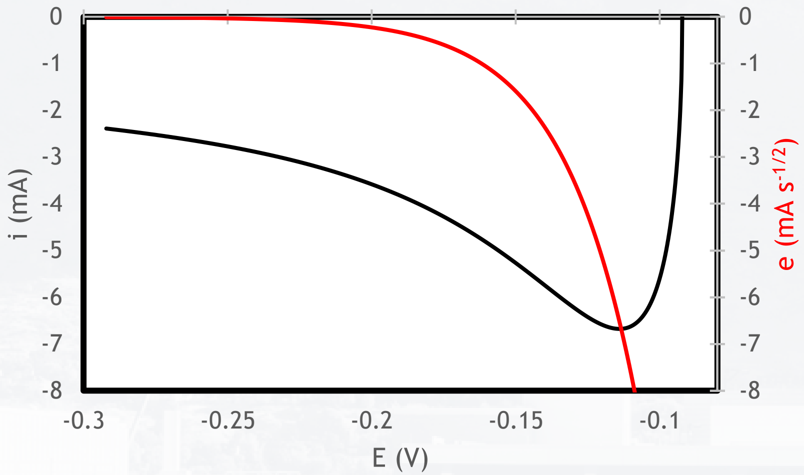
Hubbard and Anson, *Electroanalytical Chemistry, Vol. 4, pg 133*

Theory – Semi-derivatives of Common Curves

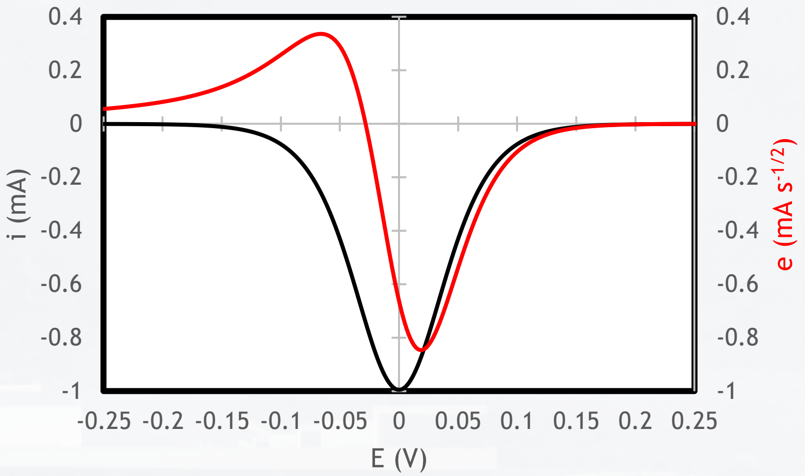
$$e(t) = -\frac{n^2F^2AC_O^*v}{4RT}D_O^{1/2}\,\mathrm{sech}^2\left(\frac{nF}{2RT}\left(E(t)-E_{1/2}\right)\right)$$



Randles-Ševcík



Berzins-Delahay



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Hubbard and Anson, *Electroanalytical Chemistry, Vol. 4, pg 133*

P. Dalrymple-Aford, M. Goto, K.B. Oldham, *J. Electroanal. Chem. Interfacial Electrochem.* **85**, 1 (1977) and T. Williams, R. Fuller, C. Vann, D. Rappleye, *J. Electrochem. Soc.*, **170**, 042502 (2023)

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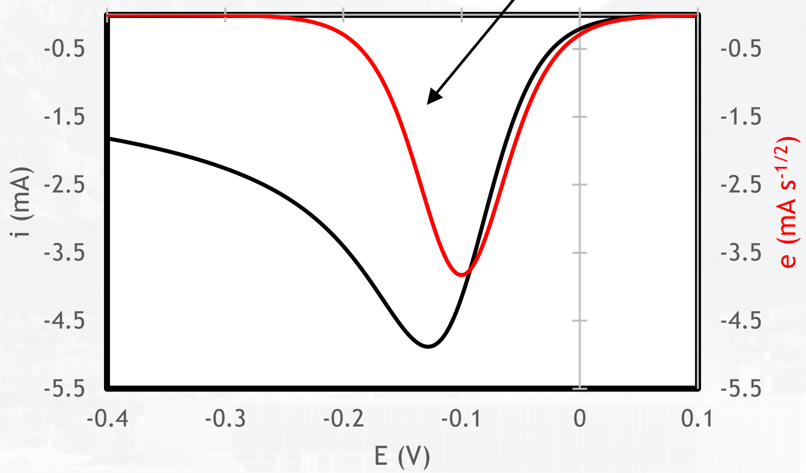
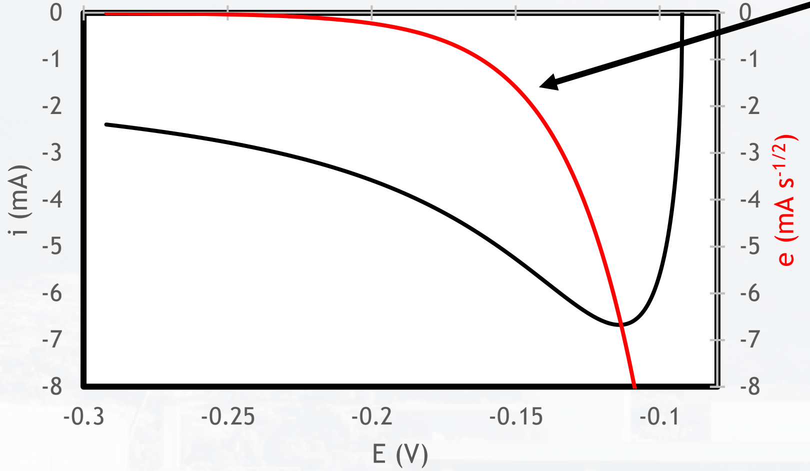
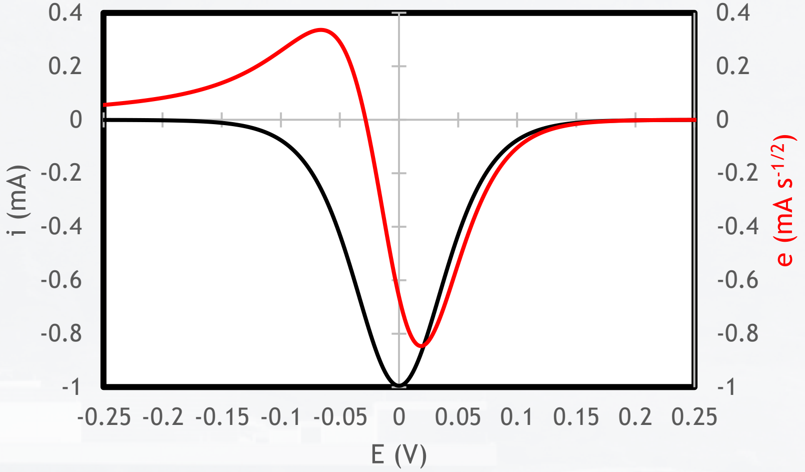
$$e(t) = -\frac{n^2F^2AC_O^*\nu}{RT}D_O^{1/2}\exp\left(\frac{nF}{RT}(-\nu t)\right)$$



Randles-Ševcík



Berzins-Delahay



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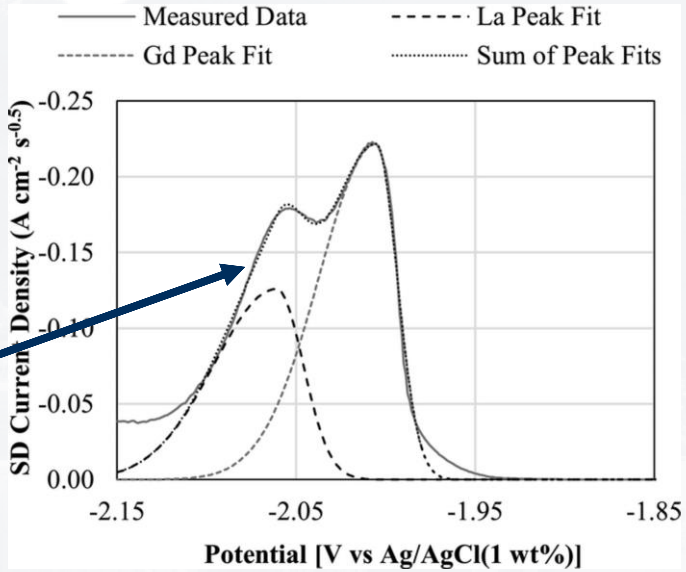
Results – Reconciling Peaks and Exponentials

$$e(E_p) = -0.4257\frac{n^2F^2AC_O^*\nu}{RT}D_O^{1/2}$$

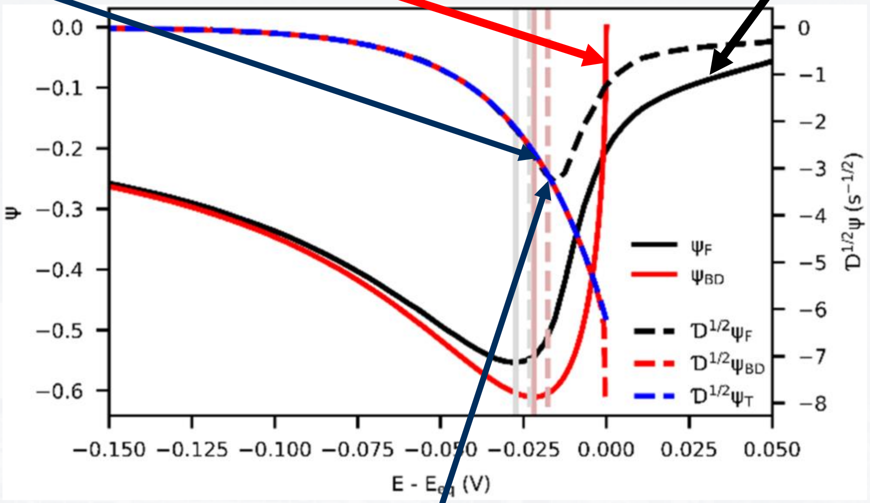
Theoretical ideal deposition model

Theoretical non-ideal deposition model

Deposition Rxns



D. Rappleye, S.-M. Jeong, M. Simpson, *J. Electrochem. Soc.* **163**, B507 (2016)



T. Williams, R. Fuller, C. Vann, D. Rappleye, *J. Electrochem. Soc.*, **170**, 042502 (2023)

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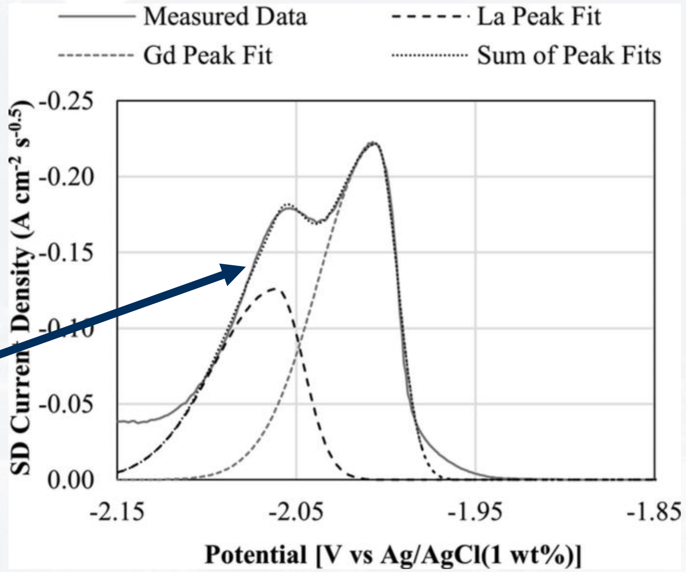

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Theoretical ideal deposition model

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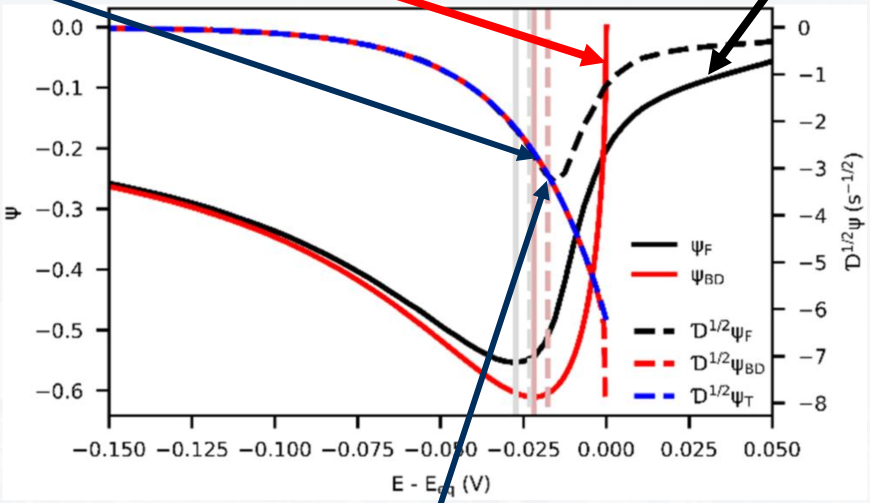
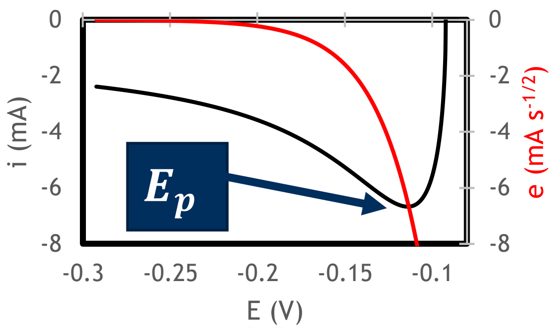


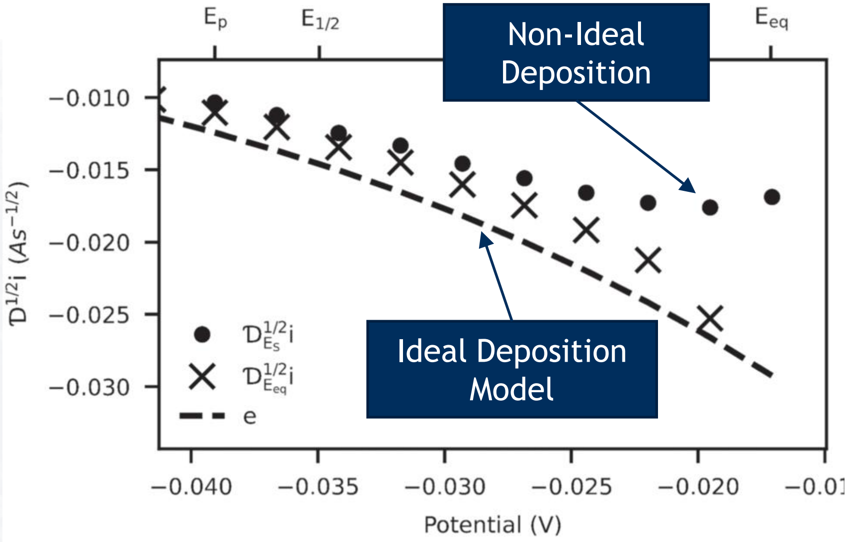
T. Williams, R. Fuller, C. Vann, D. Rappleye, *J. Electrochem. Soc.*, **170**, 042502 (2023)

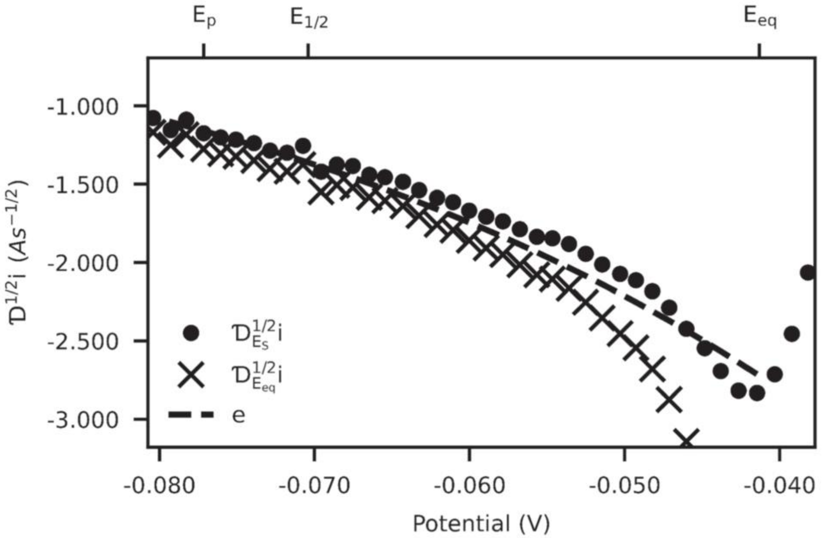
$$e(E_{1/2}) = -\frac{n^2F^2AC_O^*\nu}{2RT}D_O^{1/2}$$

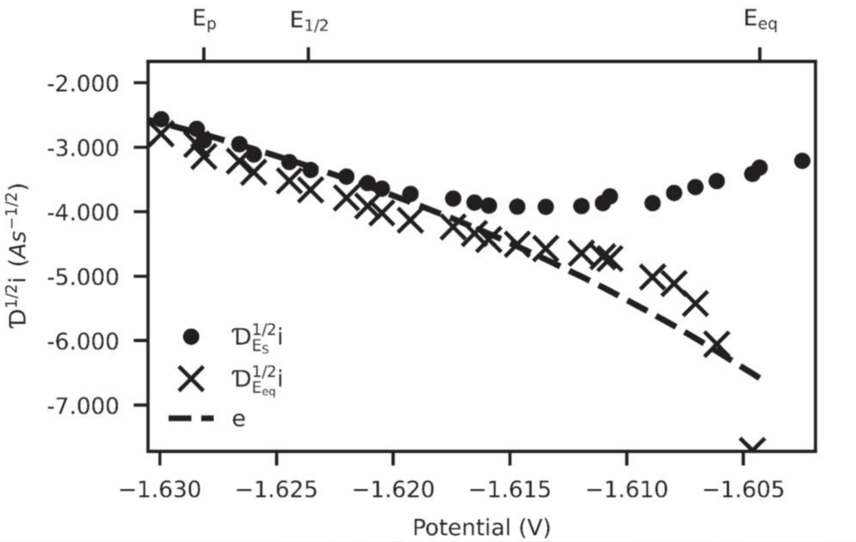
Non-ideal Deposition Model Needed

Results – Model vs Data (Curves)









0.027 M $AgNO_3$ in 1 M HNO_3
298 K
300 mV/s

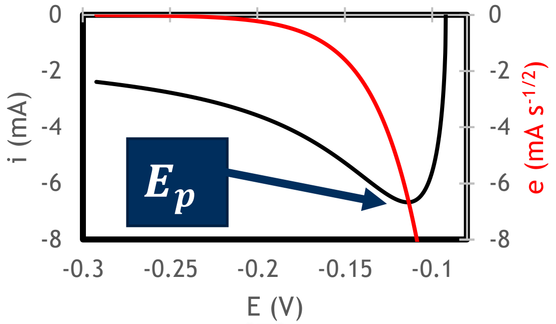
0.42 wt% $NiCl_2$ in LiCl
974 K
1000 mV/s

0.43 wt% $LaCl_3$ in LiCl
971 K
2000 mV/s

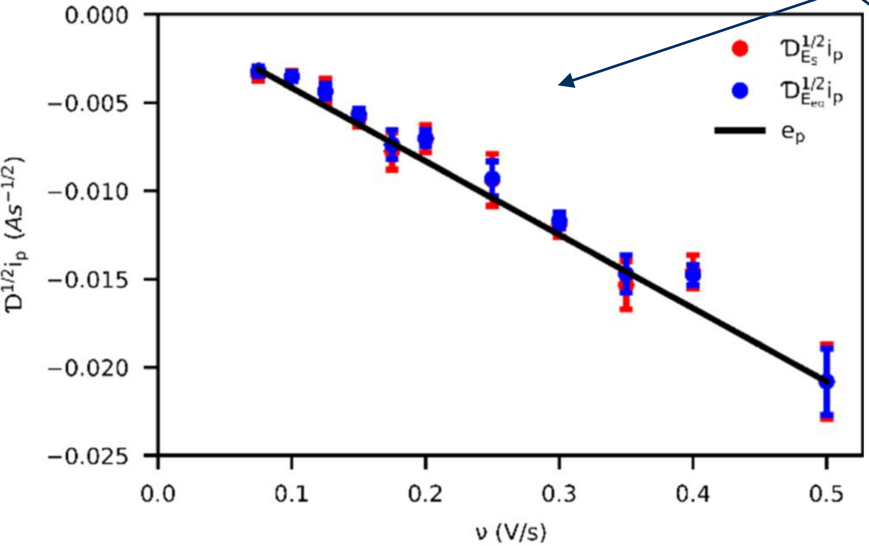
Theory and data converge at $E_{1/2}$, best at E_p

T. Williams, R. Fuller, C. Vann, D. Rappleye, *J. Electrochem. Soc.*, **170**, 042502 (2023)

Results – Model vs Data (E_p)



Linear i_p vs $v^{1/2}$



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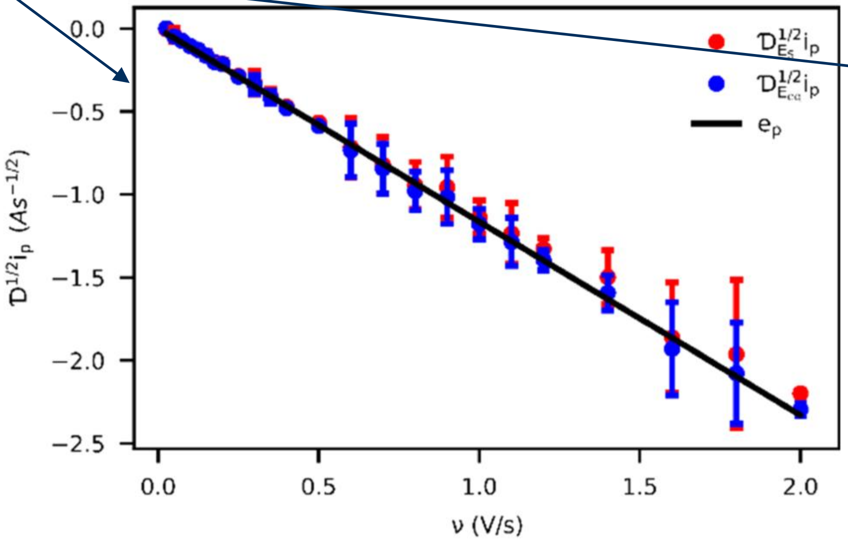

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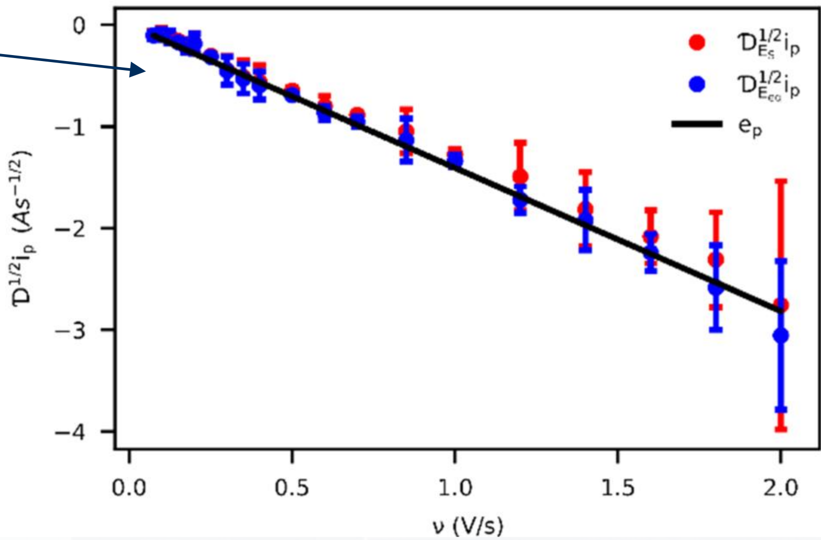

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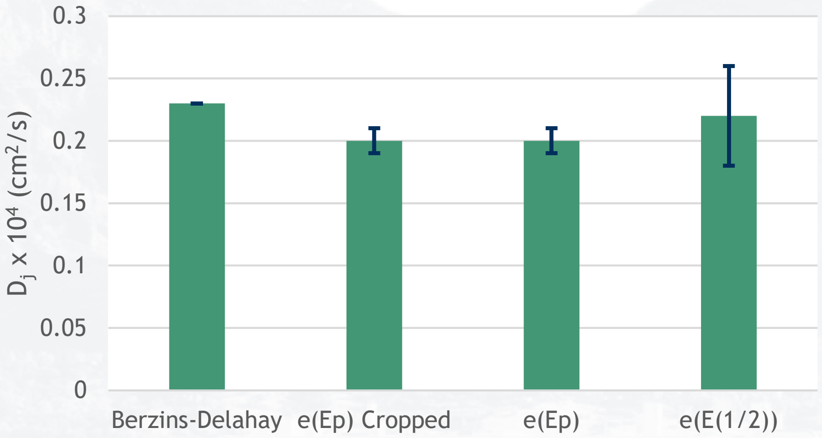
Results – Diffusion Coefficient Calculations

$$i(E_p) = -0.61AC_O^*\left(\frac{(nF)^3v}{RT}\right)^{1/2} D_O^{1/2}$$



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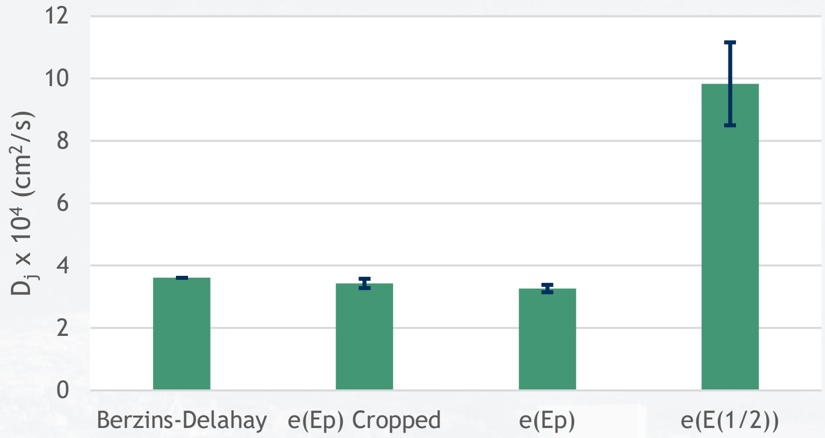

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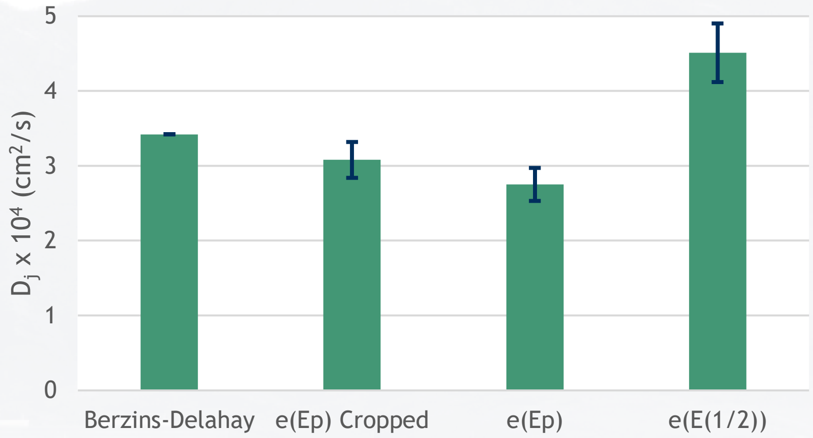

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T. Williams, R. Fuller, C. Vann, D. Rappleye, *J. Electrochem. Soc.*, **170**, 042502 (2023)

“Semi-Differentiation of Reversible, Soluble-Insoluble Potential Sweep Voltammograms”
J. Electrochem. Soc., **170**, 042502 (2023)

Conclusions & Next Steps

Conclusions:

- Semi-derivatives (SD) can help separate data.
- SD peaks are attributed to nucleation processes.
- The derived relations are as analytically useful as the Berzins-Delahay relations.

Next Steps:

- Develop non-ideal deposition models for cyclic voltammetry.
- Investigate the limits of how successful overlapping peaks can be separated.
- Optimize the fractional differentiation order. No reason why a semi-derivative would be necessarily best.

PYRO LAB

PYROCHEMICAL RESEARCH & OPERATIONS