Analysis of Techniques for Determining the Number of Electrons Exchanged in Square-Wave Voltammetry

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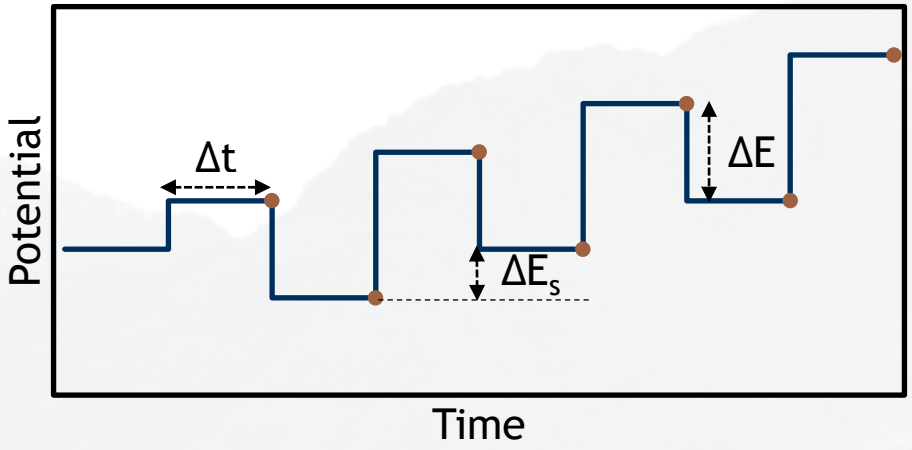
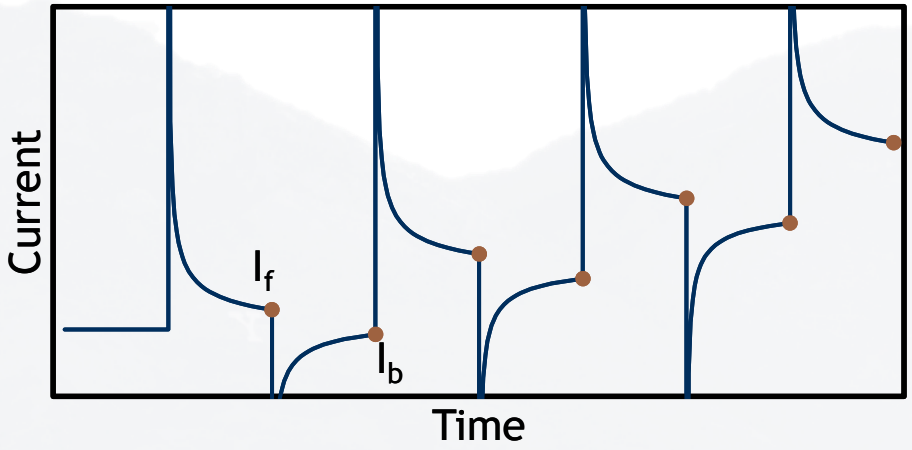
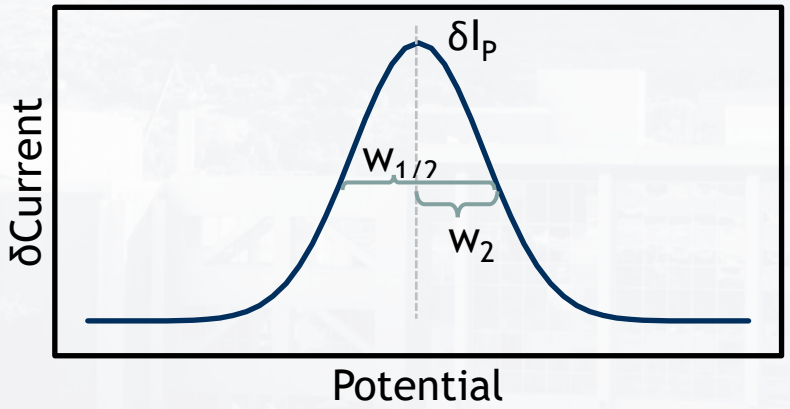
Introduction – About me

- PhD Student at Brigham Young University
- Part of the Pyrochemical Research and Operations (PyRO) lab
  - Focus on molten salt chemistry with an emphasis on electrochemical analytical techniques
- My advisor is Devin Rappleye

Introduction – Square-wave voltammetry



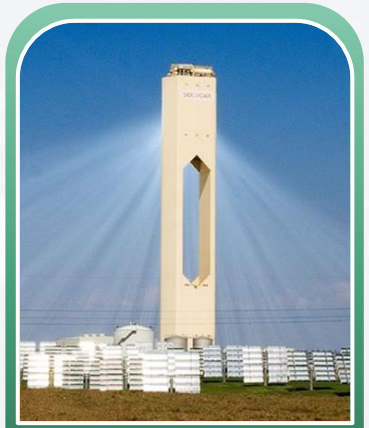




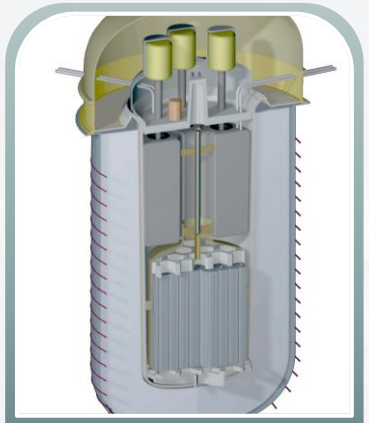
Introduction – Square-wave voltammetry

- Square-wave Voltammetry (SWV) can be used to identify the number of electrons exchanged in a redox couple
- Ideal for identifying contaminants in molten salts
- Such applications include:

Nuclear Material Processing



Solar Power & Energy Storage



Molten Salt Reactors

Critical Material Production

Introduction – Models for calculating n

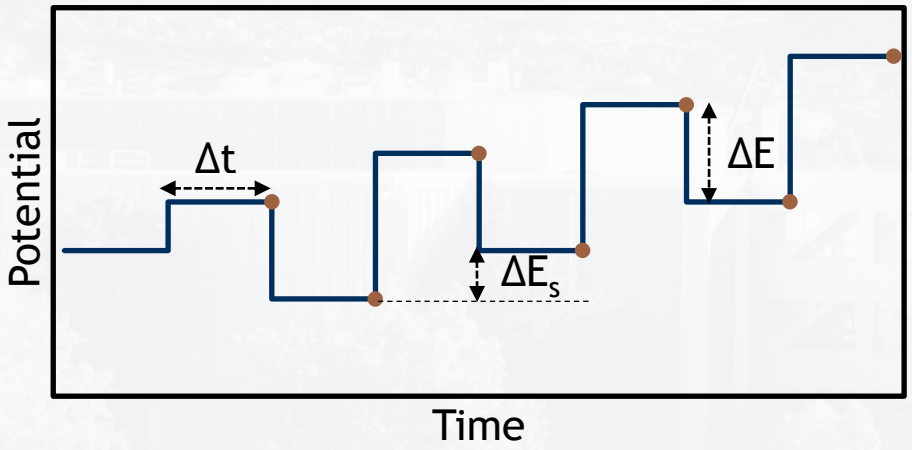
- Many recent publications have used soluble-soluble reaction models for calculating the number of electrons exchanged (n) in metal deposition[2-11]
  - Since metal deposition is a soluble-insoluble reaction, this application is fundamentally incorrect
- Fatouros and Krulic (2013) noticed this issue and attempted to resolve it by deriving their own SWV model for metal deposition[12]
- We at the PYRO Lab decided to compare the accuracy of each of these models in the cases of aqueous silver deposition and molten salt nickel and lanthanum deposition

Introduction – Models for calculating n

- Reversible, soluble-soluble reactions:

Barker (1965)[13]

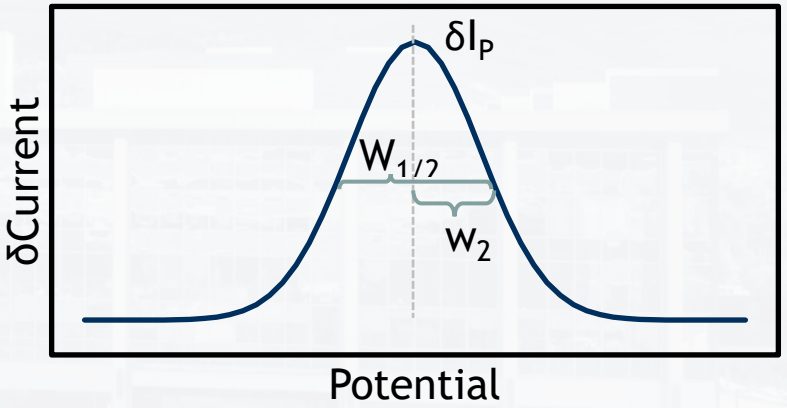
$$W_{1/2} = 3.52\frac{RT}{nF}$$



Aoki et al. (1986)[14]

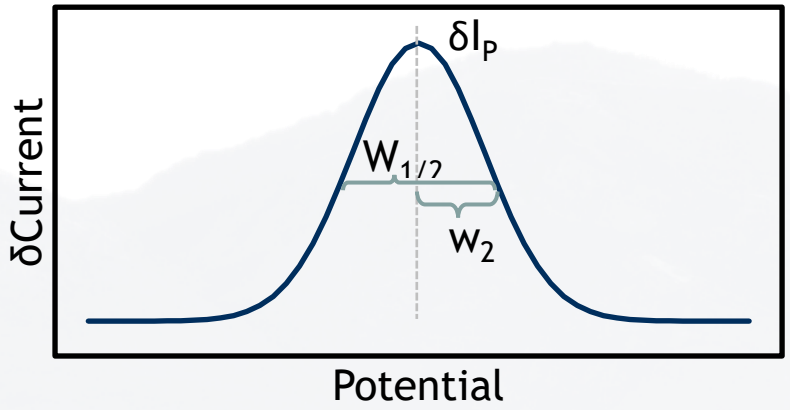
$$\xi_{SW} = \frac{nF\Delta E}{RT}$$

$$W_{1/2} = \left(\frac{RT}{nF}\right)\left(3.53 + 3.46\frac{\xi_{SW}^2}{\xi_{SW} + 8.1}\right)$$



Introduction – Models for calculating n

- Reversible, soluble-insoluble reactions:



Fatouros and Krulic (2013)[12]

$$w_2 = \frac{\mathcal{W}_2 RT}{nF}$$

$$\chi = \frac{C_{ox}^{*}\sqrt{D_{ox}\Delta t}}{\Gamma_1} \qquad \rho = \frac{n^2F^2AR_uC_{ox}^{*}\sqrt{D_{ox}}}{RT\sqrt{\Delta t}}$$

- Full model:

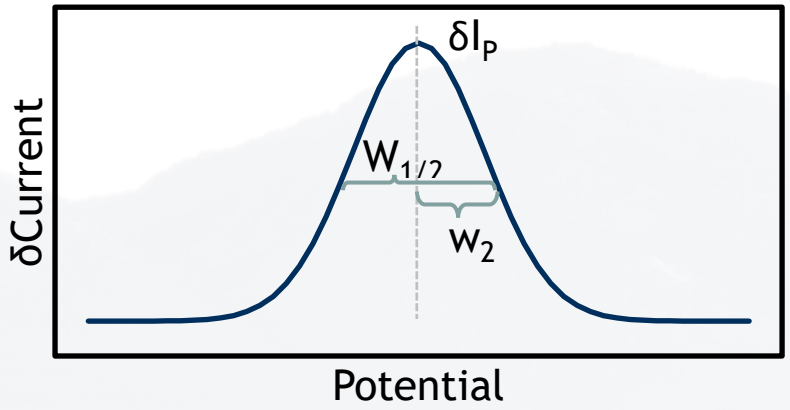
$$\mathcal{W}_2 = 0.37\chi^{-0.5} + 0.45\chi^{0.11} + (0.26 + 0.01\chi)\rho$$

Introduction – Models for calculating n

- Reversible, soluble-insoluble reactions:

Fatouros and Krulic (2013)[12]

$$w_2 = \frac{\mathcal{W}_2 RT}{nF}$$



$$\chi = \frac{C_{ox}^{*}\sqrt{D_{ox}\Delta t}}{\Gamma_1} \qquad \rho = \frac{n^2F^2AR_uC_{ox}^{*}\sqrt{D_{ox}}}{RT\sqrt{\Delta t}}$$

- F&K Truncated (for $\chi > 3.7$):

$$\mathcal{W}_2 = 0.7 + 0.3\rho$$

- IR-compensated Fatouros and Krulic model (IR-F&K):
  - For Low ρ:

$$\mathcal{W}_2 = 0.7$$

Experimental Methods

- Metals tested:

Depositing Metal	Ag^{+}	Ni^{2+}	La^{3+}
Solution	Aqueous HNO_3	Molten LiCl	Molten LiCl
Working Electrode (WE)	Pt	W	W
Reference Electrode (RE)	Pt-pseudo	W-pseudo	W-pseudo
Counter Electrode (CE)	Pt-coated Nb	W	W
Analyte Concentration	0.027 M	0.419 wt.%	0.433 wt.%
Temperature	23.1°C	701°C	698°C

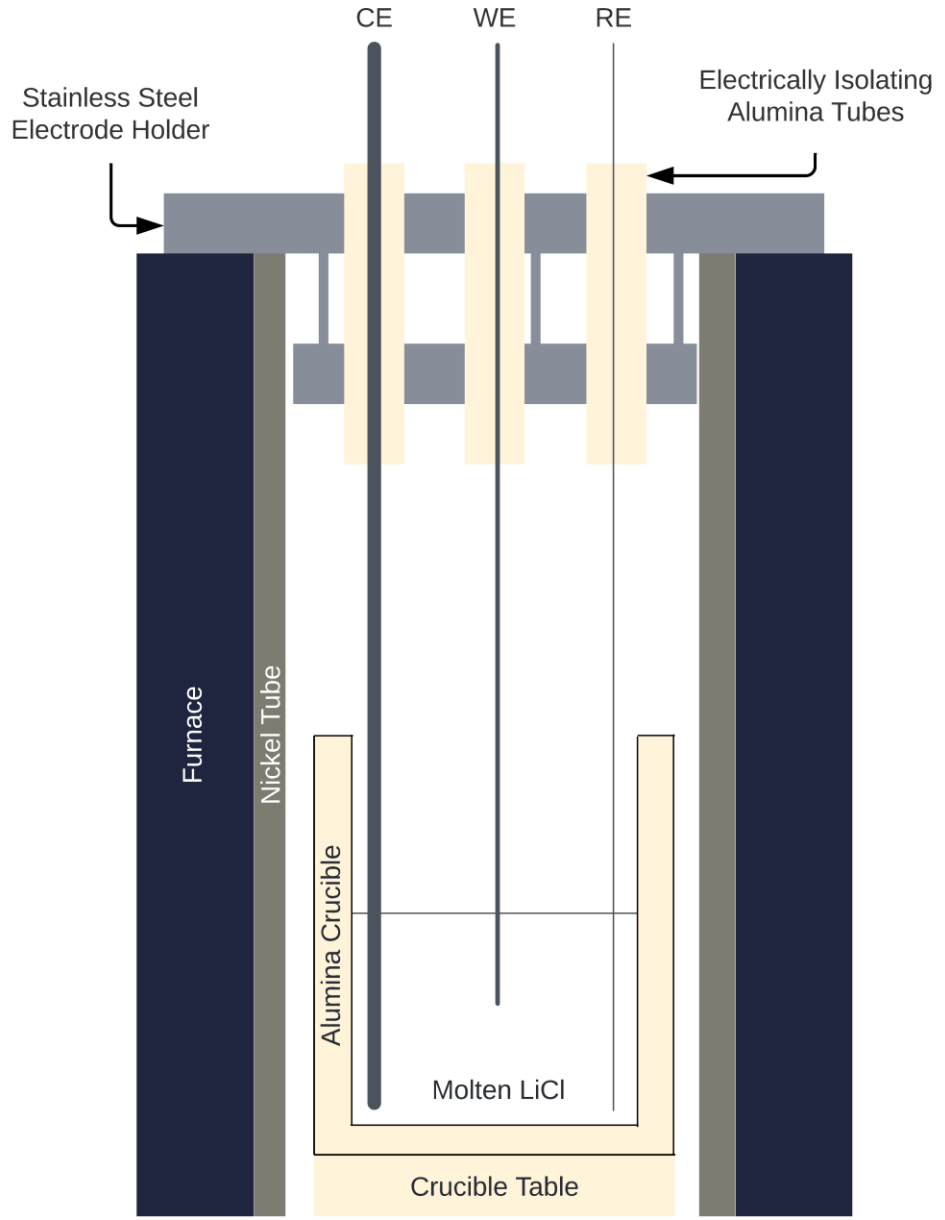


Figure taken from Fuller et al. (2022)[1]

Results – Ag deposition on Pt

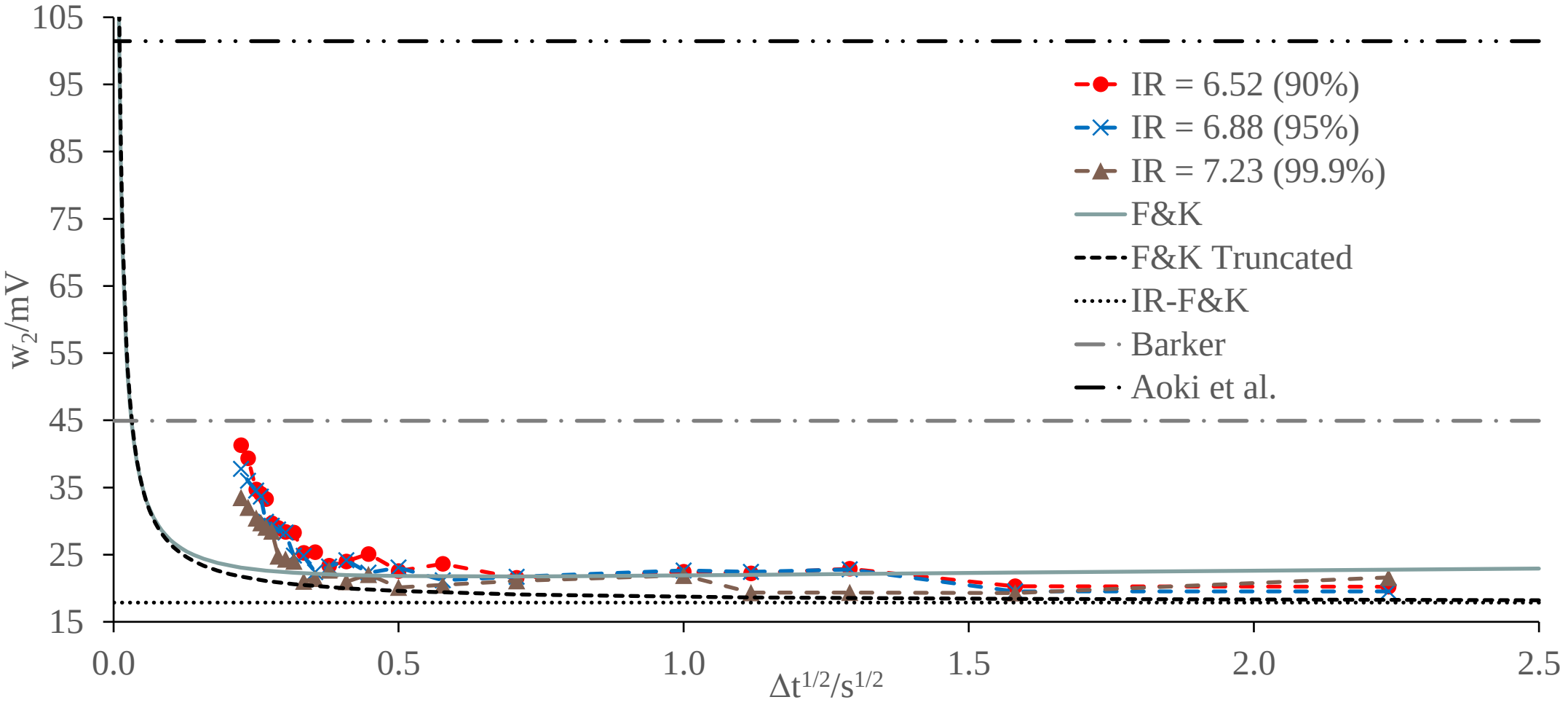
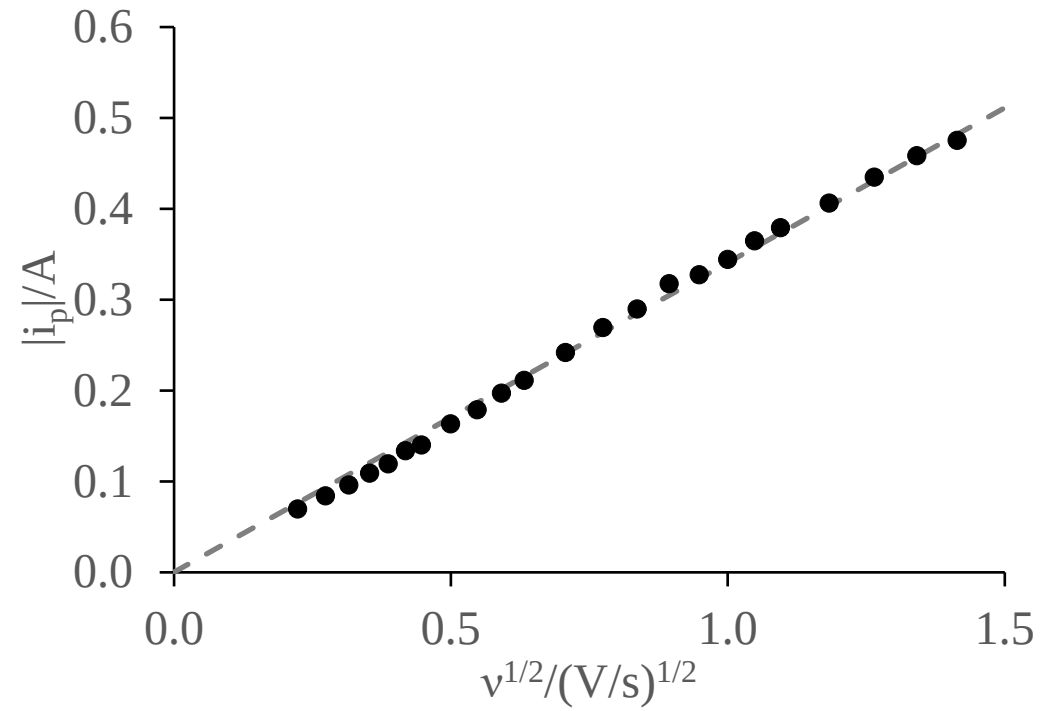


Figure taken from Fuller et al. (2022)[1]

Results – Diffusion coefficient of Ni^{2+}

- The region of reversibility in cyclic voltammetry was determined via the Berzins-Delahay relationship[15]:

$$i_p = 0.6105AC_{ox}^{*}\sqrt{\frac{(nF)^3 D_{ox}\nu}{RT}}$$



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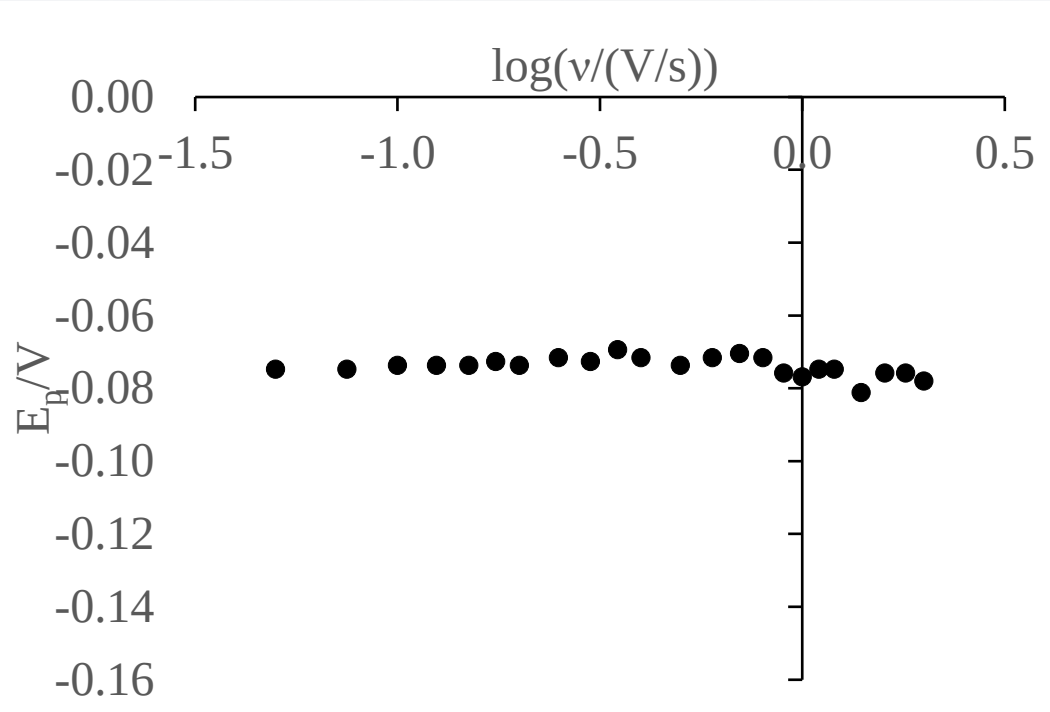

Figure taken from Fuller et al. (2022)[1]

Results – Diffusion coefficient of Ni^{2+}

- The slope was found to be 0.3408 A $s^{1/2}V^{-1/2}$
- The concentration of Ni^{2+} in solution was found to be 4.730×10^{-5} mol/cm^3 as measured by ICP-MS
- $D_{Ni^{2+}} = 3.612 \times 10^{-4} cm^2/s$

$$i_p = 0.6105 A C_{ox}^* \sqrt{\frac{(nF)^3 D_{ox} \nu}{RT}}$$

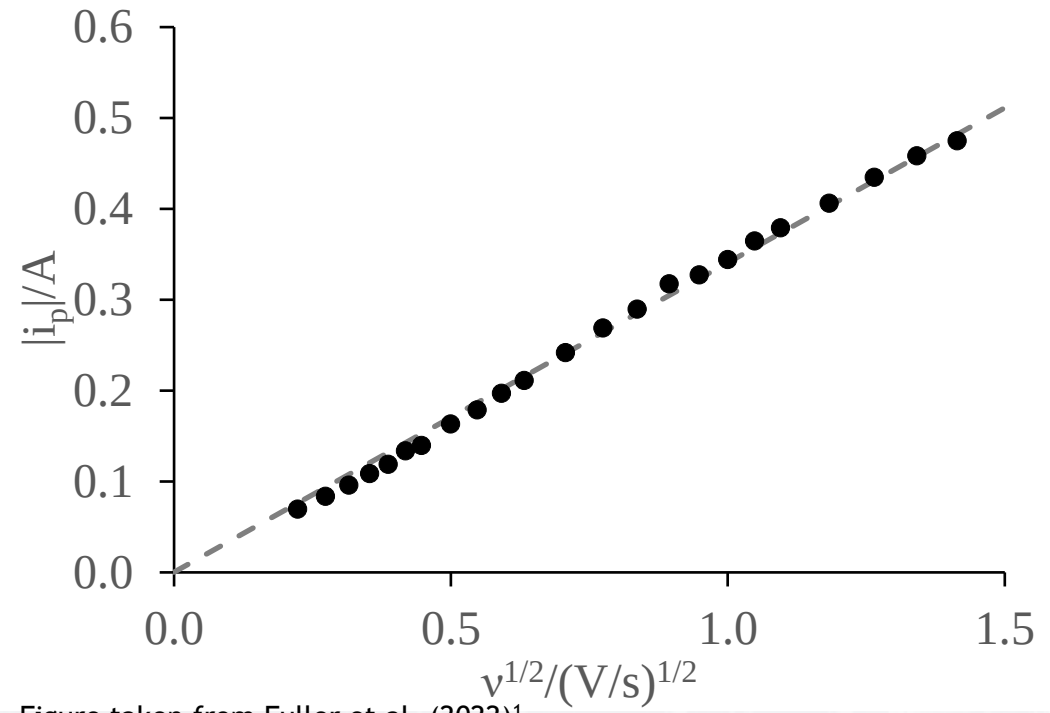

Figure taken from Fuller et al. (2022)[1]

Results – Ni deposition on W

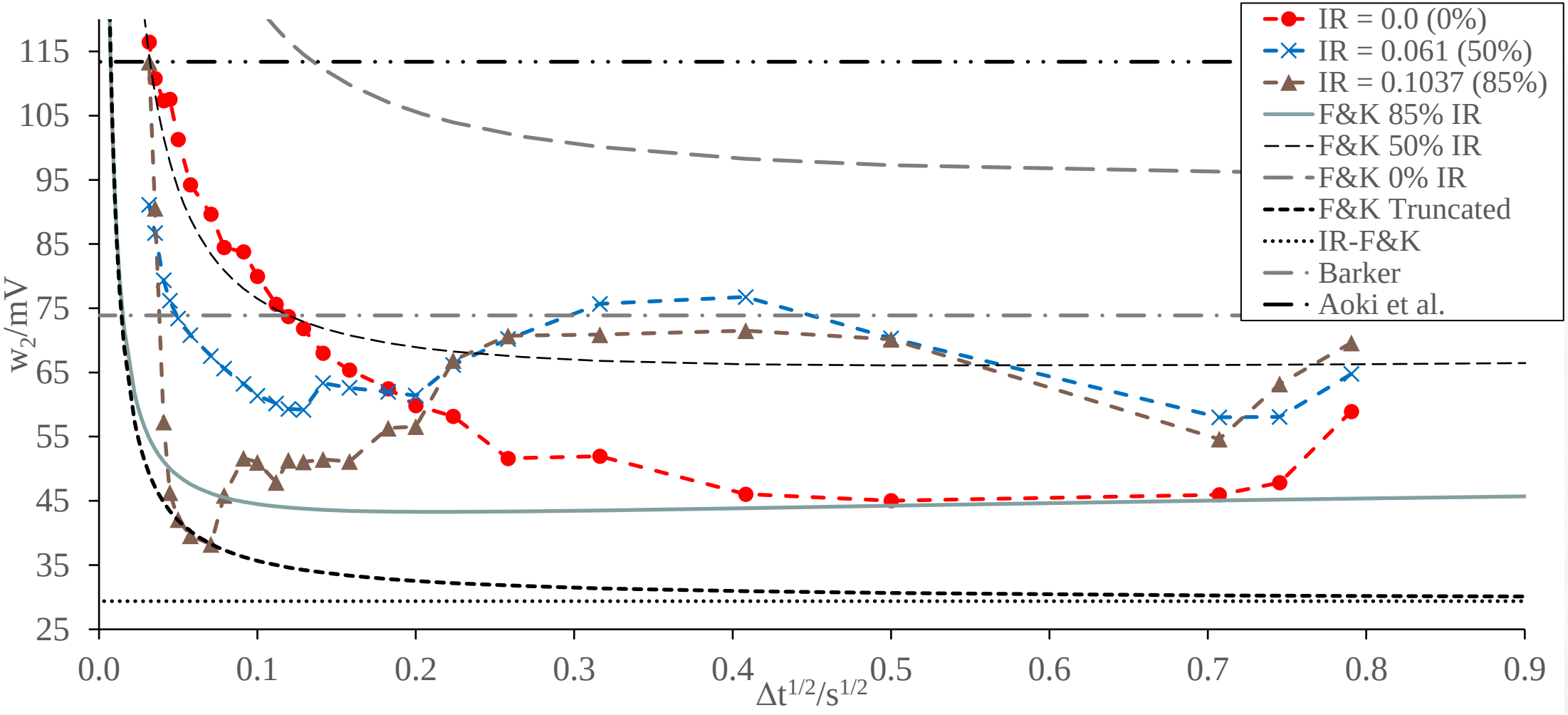

Figure taken from Fuller et al. (2022)[1]

Results – Diffusion coefficient of La^{3+}

- The region of reversibility in cyclic voltammetry was determined via the Berzins-Delahay relationship[15]:

$$i_p = 0.6105AC_{ox}^{*}\sqrt{\frac{(nF)^3 D_{ox}\nu}{RT}}$$

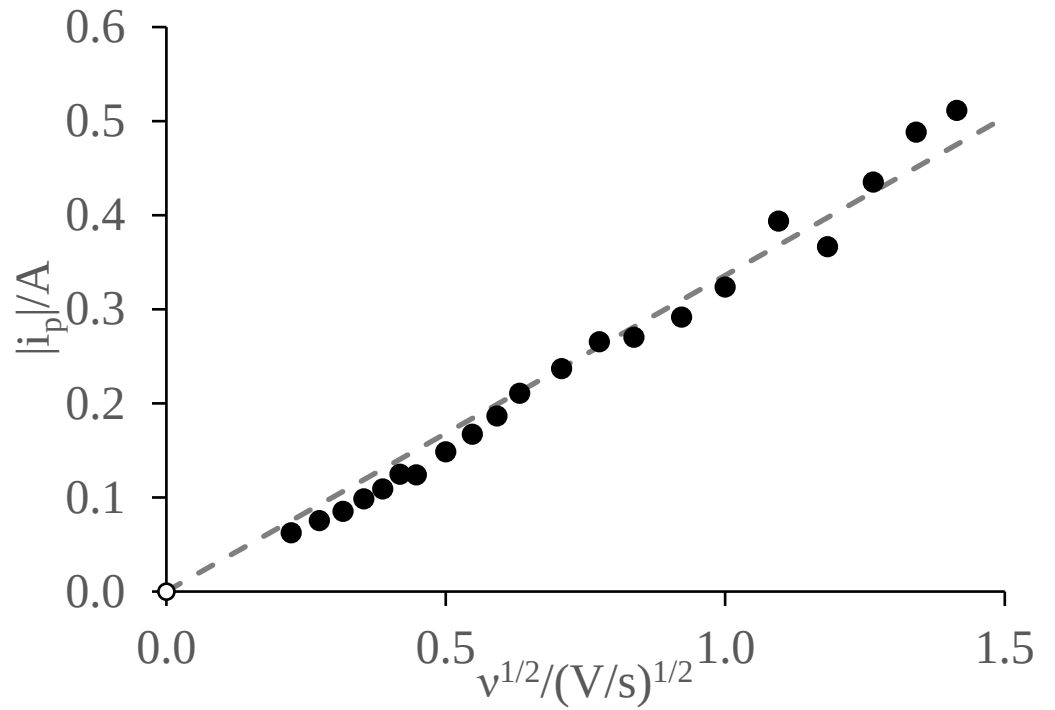

Figure taken from Fuller et al. (2022)[1]

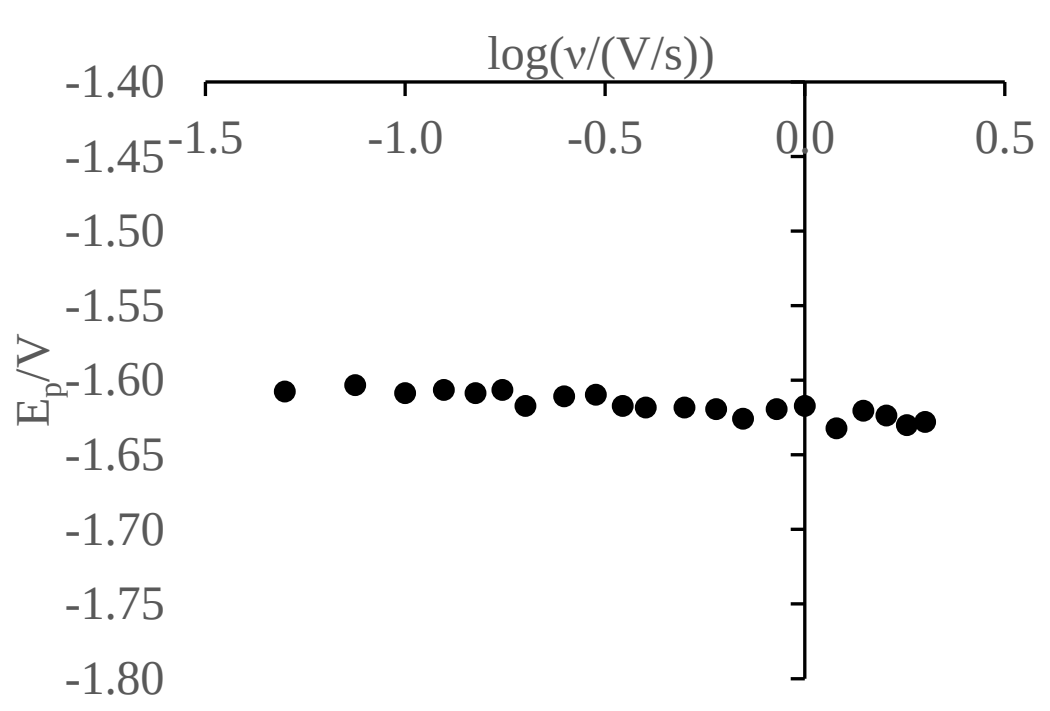

Figure taken from Fuller et al. (2022)[1]

Results – Diffusion coefficient of La^{3+}

- The slope was found to be 0.3358 A $s^{1/2}V^{-1/2}$
- The concentration of La^{3+} in solution was found to be 2.586×10^{-5} mol/cm^3 as measured by ICP-MS
- $D_{La^{3+}} = 3.42 \times 10^{-4} cm^2/s$

$$i_p = 0.6105 A C_{ox}^* \sqrt{\frac{(nF)^3 D_{ox} \nu}{RT}}$$

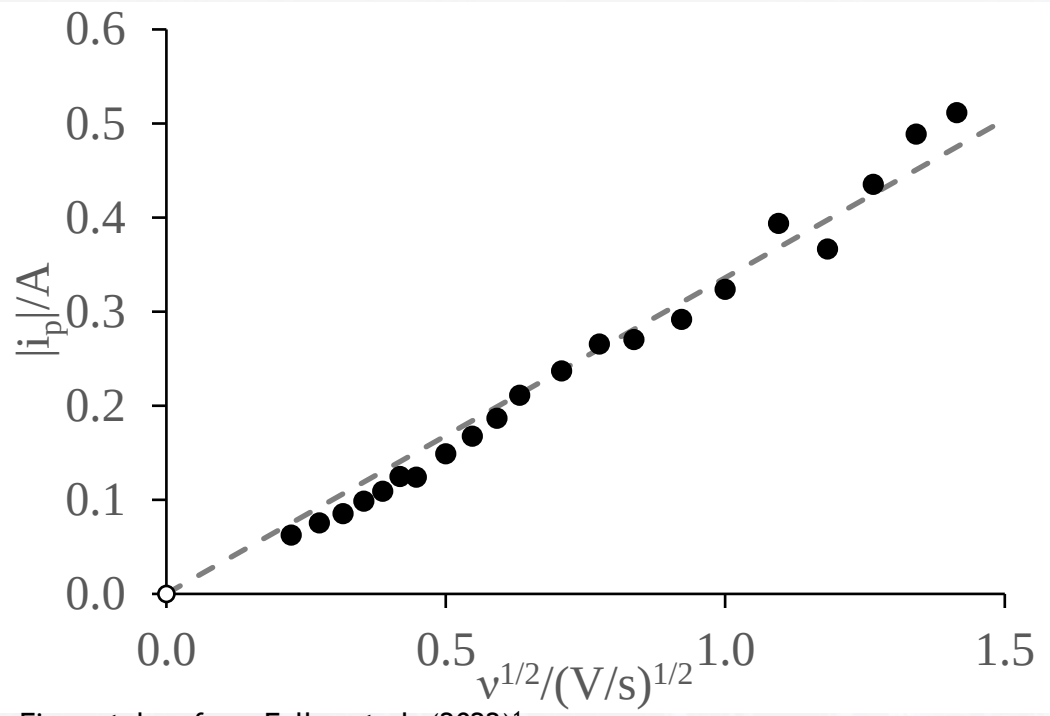

Figure taken from Fuller et al. (2022)[1]

Results – La deposition on W

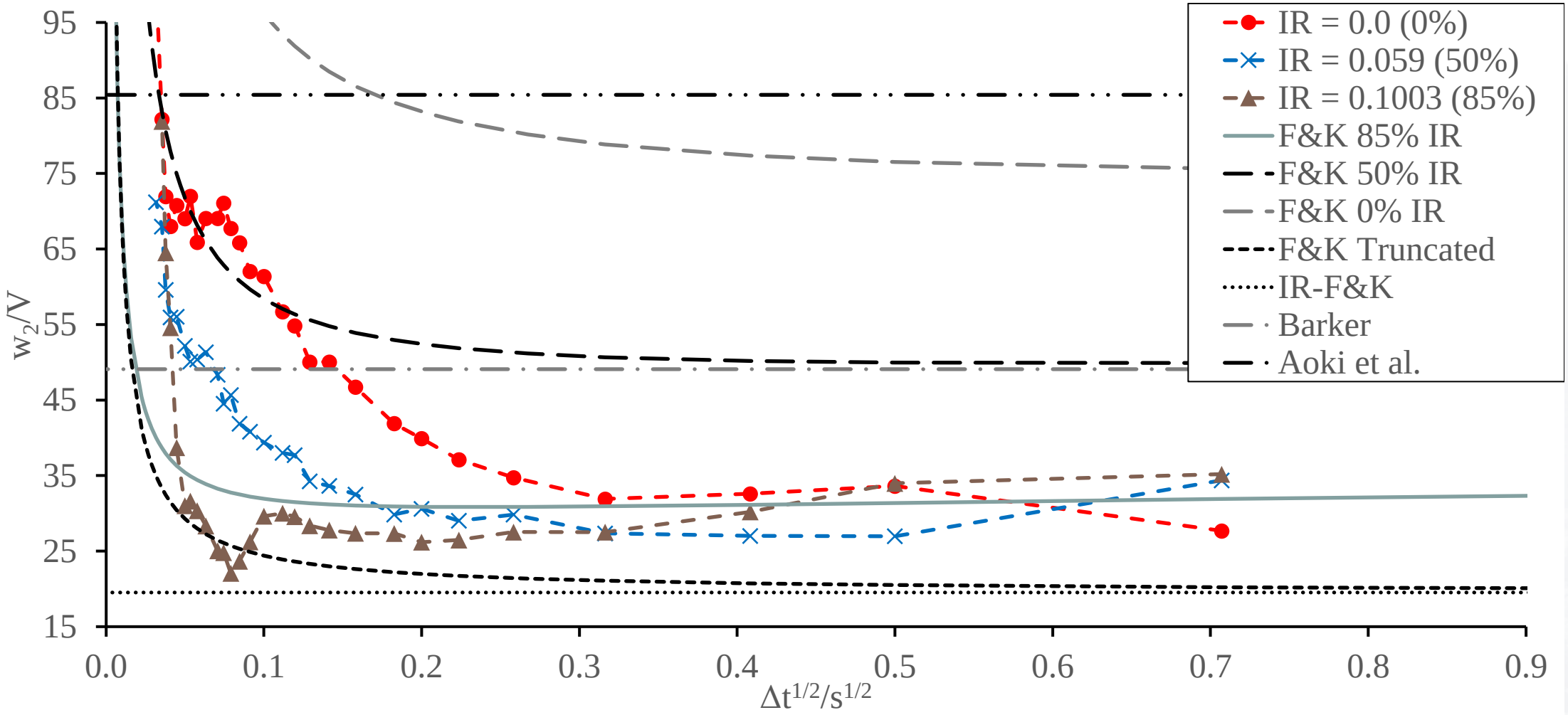

Figure taken from Fuller et al. (2022)[1]

Comparison of models for calculating n

	Barker		Aoki et al.		F&K		F&K Truncated		IR-F&K	
Trial	n	Error	n	Error	n	Error	n	Error	n	Error
Ag 90%	2.22	122%	1.14	14%	1.48	48%	0.92	8%	0.88	12%
Ni 85%	2.89	45%	3.74	87%	1.50	25%	1.21	40%	1.15	43%
La 85%	5.39	80%	4.66	55%	4.54	51%	2.32	23%	2.15	28%

Table adapted from Fuller et al. (2022)[1]

Limits of full Fatouros and Krulic model

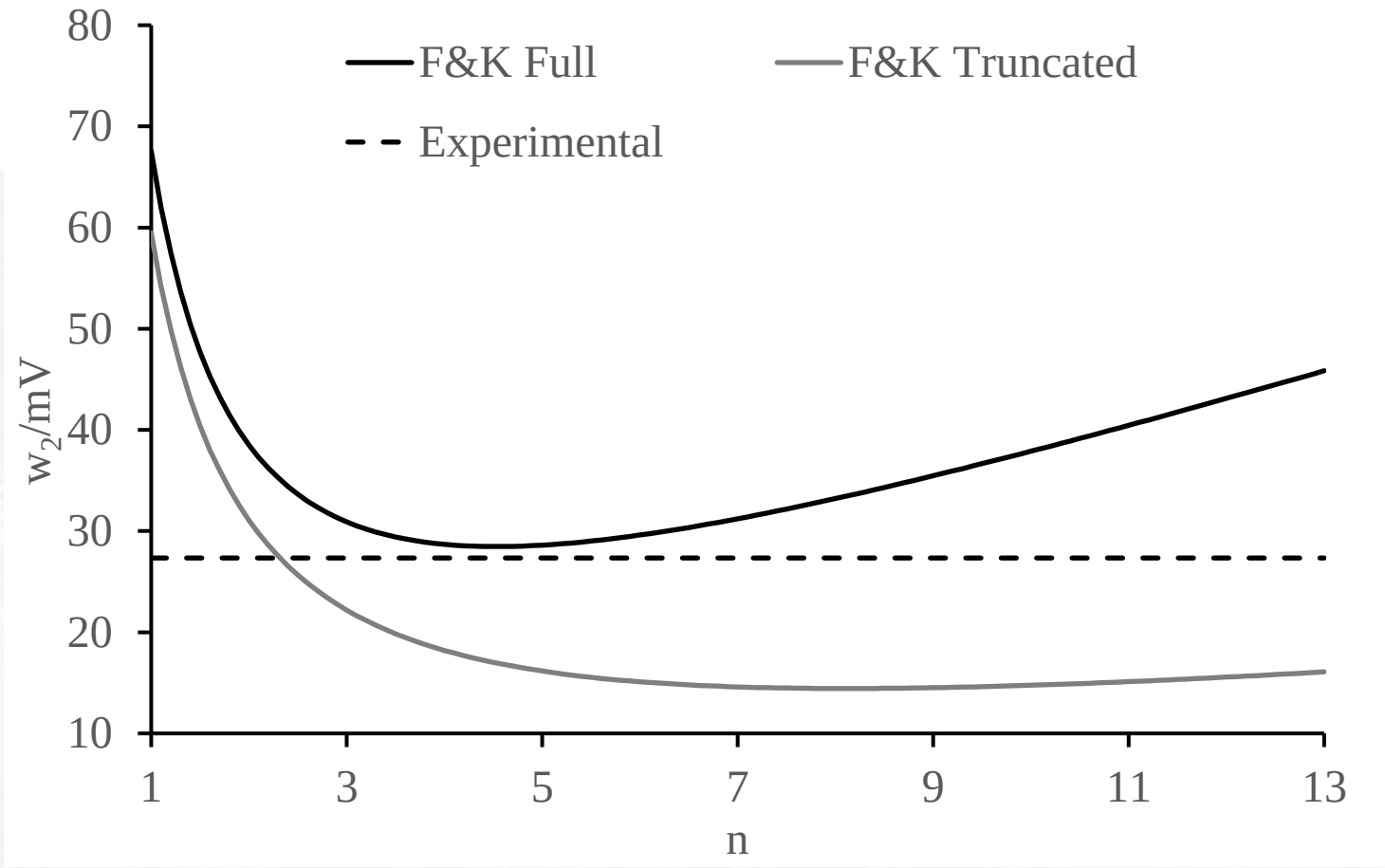

Figure taken from Fuller et al. (2022)[1]

Alternative linear fit

- New, experimentally observed linear fit

$$W_2 = 0.91 + 0.32\rho$$

- In the well-compensated case, this would simplify to:

$$W_2 = 0.91$$

  - Using this to calculate n results in:
    - $n = 1.06$ for Ag deposition at 90% IR compensation
    - $n = 1.49$ for Ni deposition at 85% IR compensation
    - $n = 2.79$ for La deposition at 85% IR compensation

Conclusion

- Soluble-soluble models are not consistently accurate for determining the number of electrons exchanged in metal deposition
- The IR-compensated Fatouros and Krulic model can be used to reliably predict the correct number of electrons exchanged for one, two, and three electron exchange, metal deposition reactions
- We suggest this method be used for rapid determination of n where concentrations and diffusion coefficients may be unknown

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Questions?

Methods – Ag deposition on Pt

- Three sets of SVW measurements were performed at different IR compensations:
  - 90% compensation (6.52 Ω)
  - 95% compensation (6.88 Ω)
  - 99.9% compensation (7.23 Ω)

Table 1: Experimental parameters compared to the range recommended by Fatouros and Krulic

	$\Delta E_s/\mathrm{V}$	$\Delta E/V$
Recommended Range	-0.0059 to -0.0010	0.020 to 0.120
Experimental Parameters	-0.003	0.1

Table adapted from Fuller et al. (2022)[1]

Table adapted from Fuller et al. (2022)[1]

Results – Ag deposition on Pt

Table 2: Representative w_2 and their associated χ values for silver deposition on platinum in aqueous HNO_3

	$\Delta t^{1/2}$ / $s^{1/2}$	f / Hz	w_2 / V	χ
IR = 6.52 Ω (90%)	2.24	0.1	0.0202	142
IR = 6.88 Ω (95%)	2.24	0.1	0.0195	142
IR = 7.23 Ω (99.9%)	1.58	0.2	0.0193	101

Table adapted from Fuller et al. (2022)[1]

Methods – Ni deposition on W

- Diffusion coefficients were calculated by the relationship derived by Berzins and Delahay (1953)
  - For a reversible soluble-insoluble reaction:

$$i_p = 0.6105AC_{ox}^{*}\sqrt{\frac{(nF)^3 D_{ox}\nu}{RT}}$$

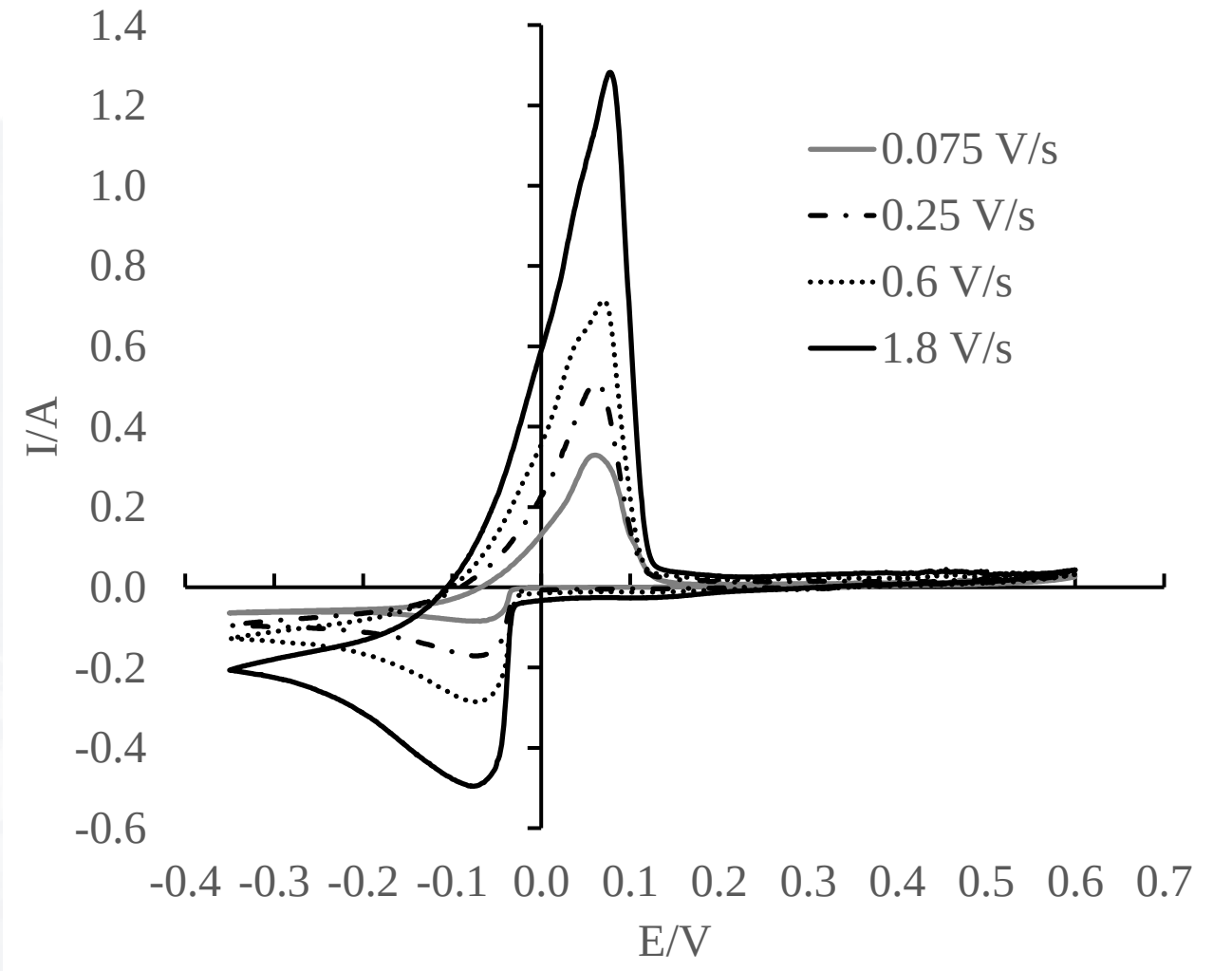

Figure taken from Fuller et al. (2022)[1]

Methods – Ni deposition on W

- SWV measurements were conducted at a range of frequencies and IR compensations:
  - 0.0% compensation
  - 50% compensation (0.061 Ω)
  - 85% compensation (0.1037 Ω)

Table 3: Experimental and recommended parameters for Ni deposition on W

	$\Delta E_s/V$	$\Delta E/V$
Recommended Range [13]	-0.00965 to -0.00168	0.034 to 0.197
Experimental Parameters	-0.005	0.1

Table adapted from Fuller et al. (2022)[1]

Results – Ni deposition on W

Table 4: Representative w_2 and their associated χ values for nickel deposition on tungsten in molten LiCl

	$\Delta t^{1/2}$ / $s^{1/2}$	f / Hz	w_2 / V	χ
IR = 0.0 Ω (0%)	0.158	20	0.0654	62.4
IR = 0.061 Ω (50%)	0.129	30	0.0592	50.9
IR = 0.1037 Ω (85%)	0.158	20	0.0511	62.4

Table adapted from Fuller et al. (2022)[1]

Methods – La deposition on W

- SWV measurements were conducted at a range of frequencies and IR compensations:
  - 0.0% compensation
  - 50% compensation (0.059 Ω)
  - 85% compensation (0.1003 Ω)

Table 5: Experimental and recommended parameters for La deposition on W

	$\Delta E_s/V$	$\Delta E/V$
Recommended Range [13]	-0.00642 to -0.00112	0.022 to 0.131
Experimental Parameters	-0.003	0.08

Table adapted from Fuller et al. (2022)[1]

Results – La deposition on W

Table 6: Representative w_2 and their associated χ values for Lanthanum deposition on tungsten in molten LiCl

	$\Delta t^{1/2}$ /s$^{1/2}$	f /Hz	w_2 /V	χ
IR = 0.0 Ω (0%)	0.183	15	0.0419	79.9
IR = 0.059 Ω (50%)	0.183	15	0.0299	79.9
IR = 0.1003 Ω (85%)	0.183	15	0.0273	79.9

Table adapted from Fuller et al. (2022)[1]

Comparison of models for calculating *n*

	Barker		Aoki et al.		F&K		F&K Truncated		IR-F&K	
Trial	n	Error	n	Error	n	Error	n	Error	n	Error
Ag 90%	2.22	122%	1.14	14%	1.48	48%	0.92	8%	0.88	12%
Ag 95%	2.30	130%	1.14	14%	1.22	22%	0.93	7%	0.92	8%
Ag 99%	2.33	133%	1.14	14%	1.04	4%	0.93	7%	0.93	7%
Ni 0%	2.26	13%	3.74	87%	1.27	37%	1.18	41%	0.90	55%
Ni 50%	2.50	25%	3.74	87%	1.73	13%	1.19	41%	0.99	50%
Ni 85%	2.89	45%	3.74	87%	1.50	25%	1.21	40%	1.15	43%
La 0%	3.52	17%	4.64	55%	1.75	42%	1.91	36%	1.40	53%
La 50%	4.93	64%	4.75	58%	2.48	17%	2.66	11%	1.96	35%
La 85%	5.39	80%	4.66	55%	4.54	51%	2.32	23%	2.15	28%

Table adapted from Fuller et al. (2022)[1]