

For a one-step reaction, the peak potential follows the following equation¹:

$$E_p = E^O - \frac{RT}{\alpha F} \left[0.780 + \ln \left(\frac{D_0^{\frac{1}{2}}}{k^0} \right) + \frac{1}{2} \ln(v) + \frac{1}{2} \ln \left(\frac{\alpha F}{RT} \right) \right] \quad (\text{S1})$$

Where E_p is the peak potential, E^O is the standard potential, R is the ideal gas constant, F is Faraday's constant, α is the transfer coefficient, D_0 is the diffusion coefficient, v is the scan rate, and k^0 is the kinetic rate constant.

Equation S1 can be simplified to:

$$E_p - E^O = -\frac{RT}{2\alpha F} \ln(v) + C \quad (\text{S2})$$

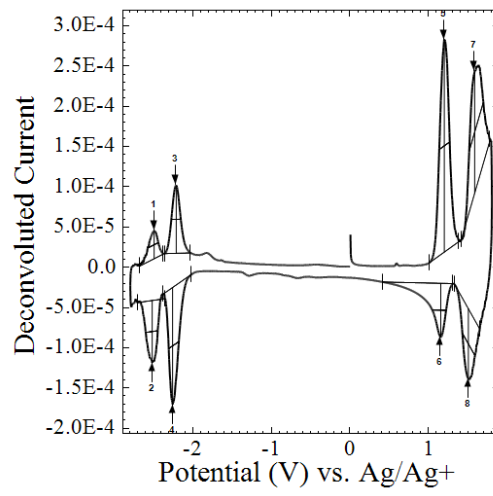
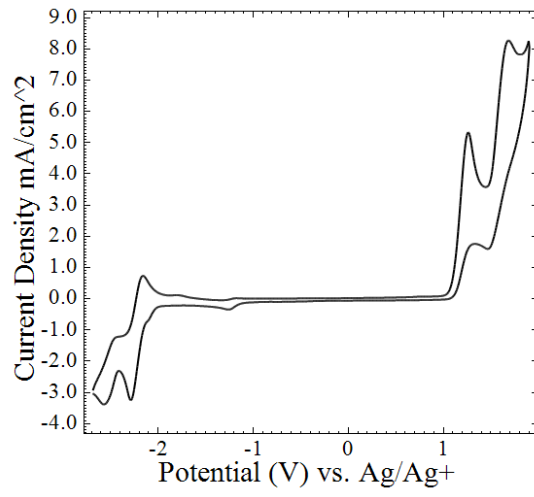
Where C is a constant. Plots of $E_p - E^O$ versus $\ln(v)$ were used to determine α .

For quasireversible reactions, the Nicholson method was used to determine the kinetic rate constants, which utilizes a dimensionless parameter defined as ²:

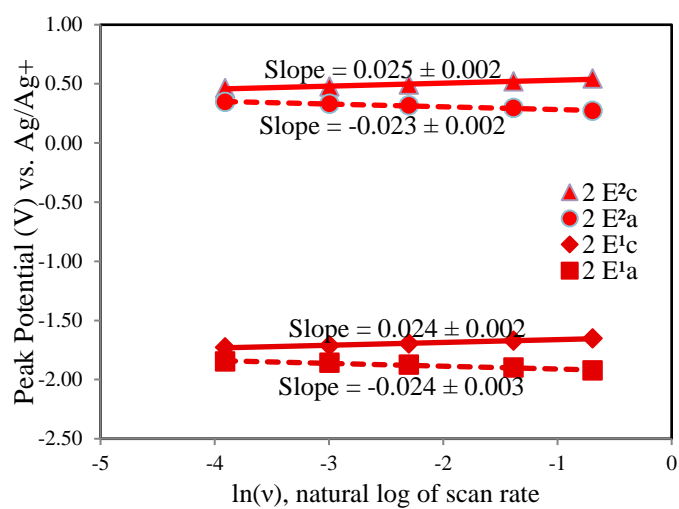
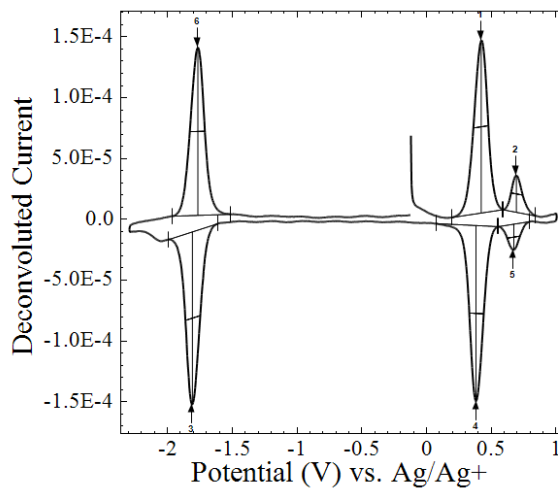
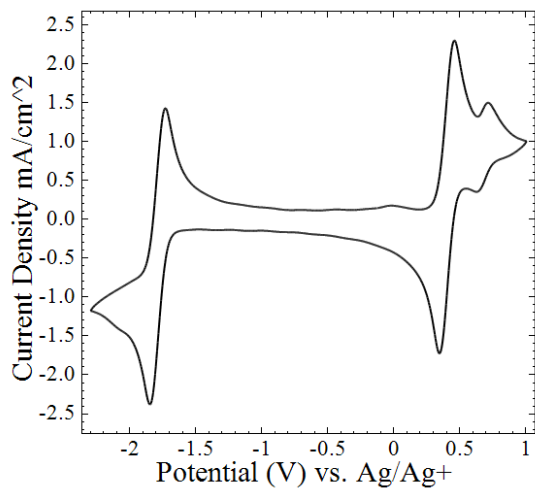
$$\psi = \frac{k^0 RT}{(\pi D_0 F v)^{\frac{1}{2}}} \quad (\text{S3})$$

Assuming the diffusion coefficients of the oxidized and reduced species are equal. This was found to be the case for complex **5**, and was already found to be true for complex **2**.³

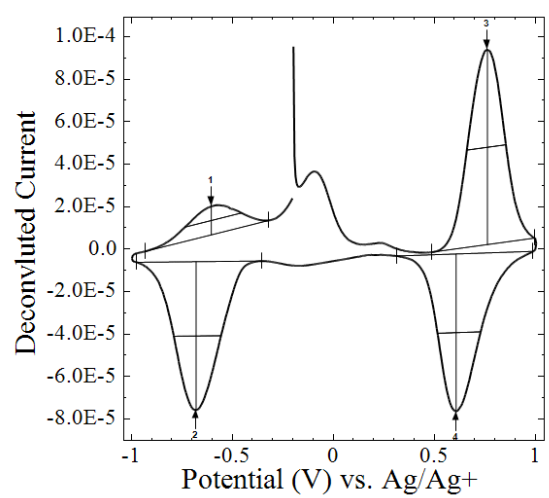
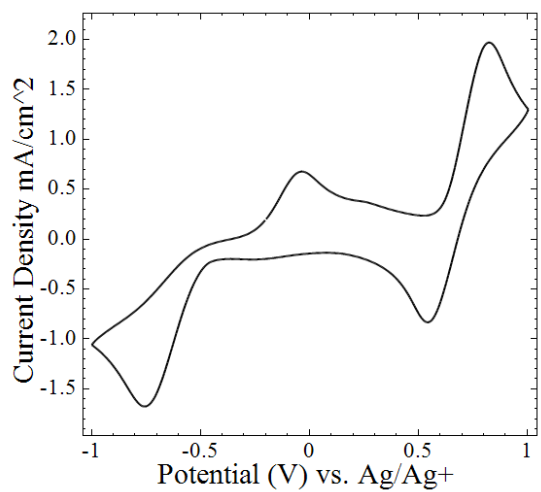
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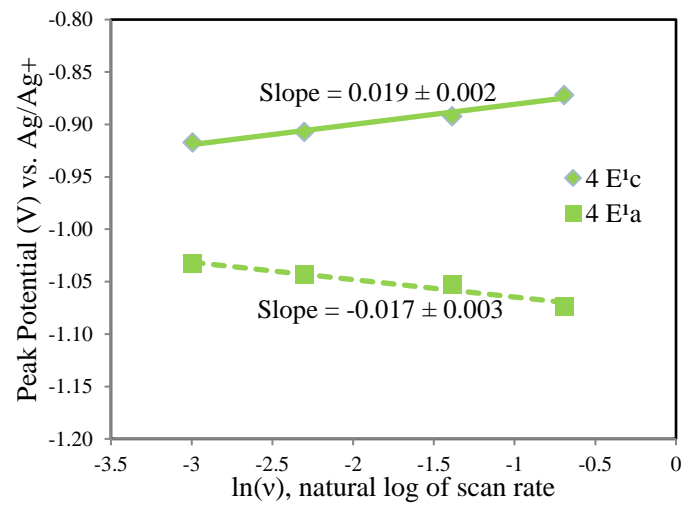
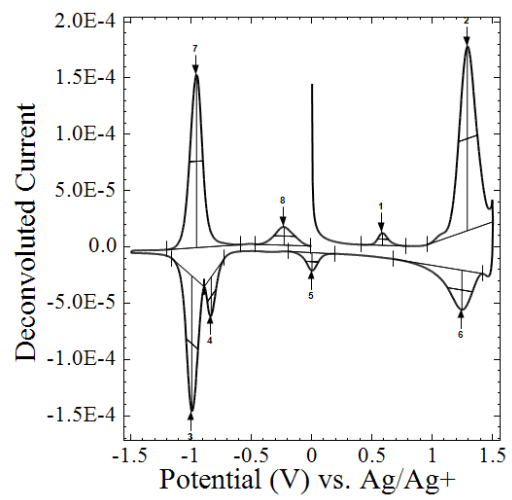
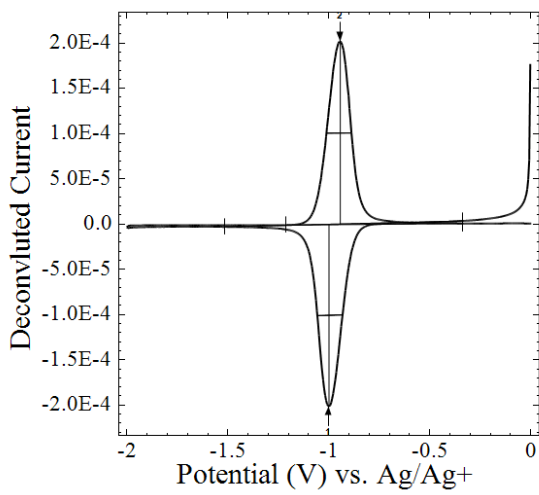
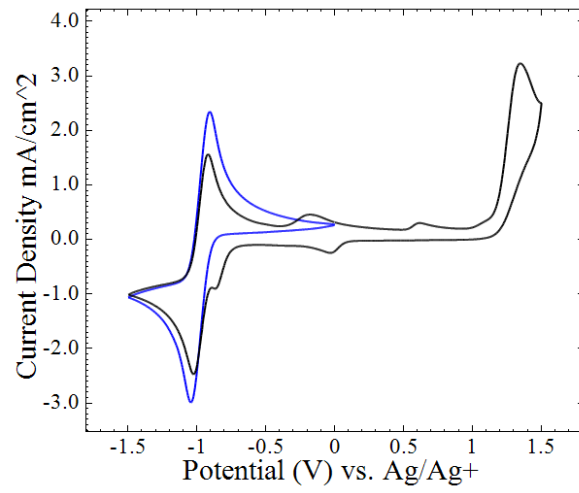
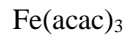


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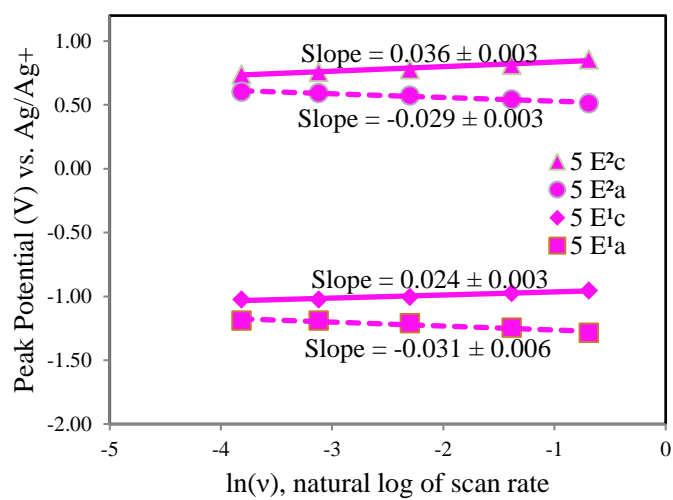
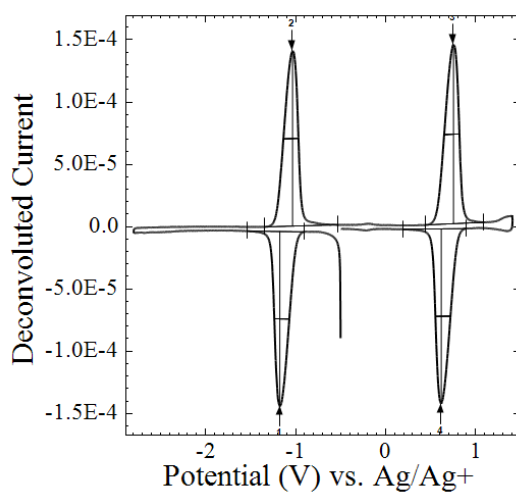
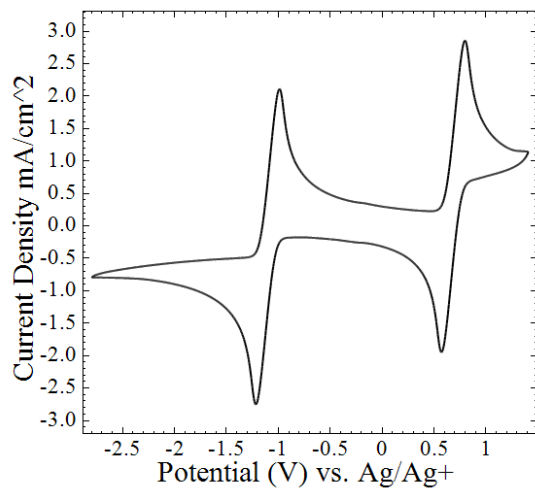


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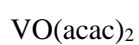
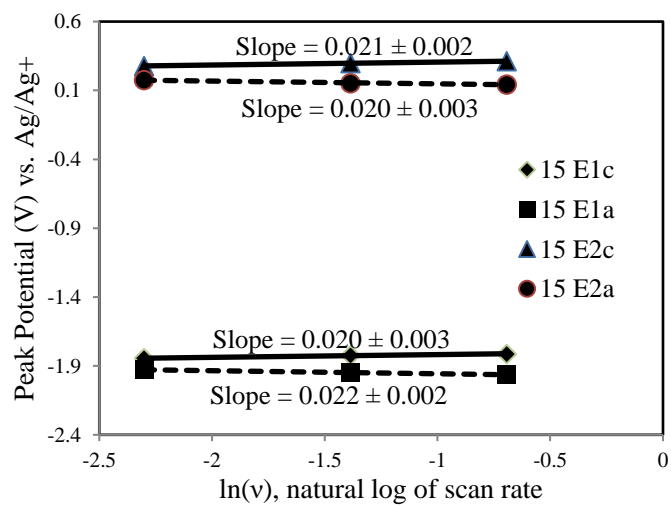
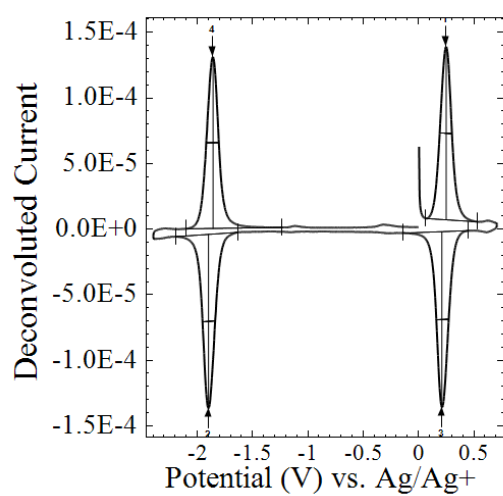
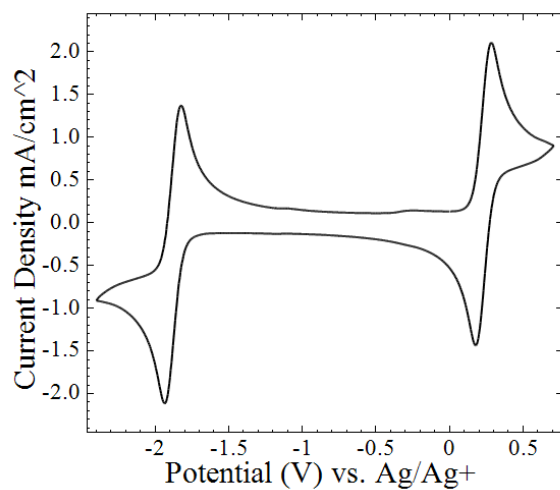


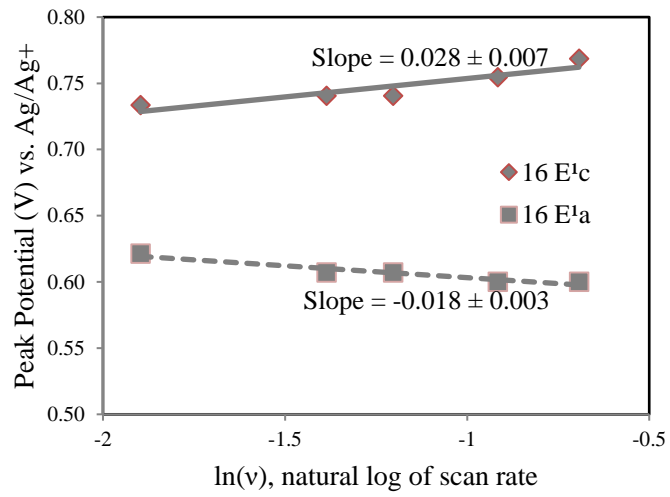
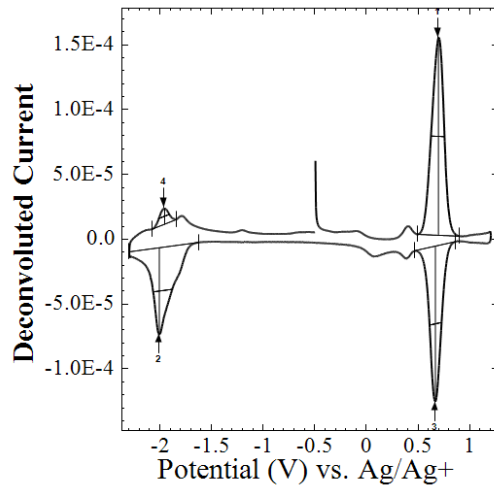
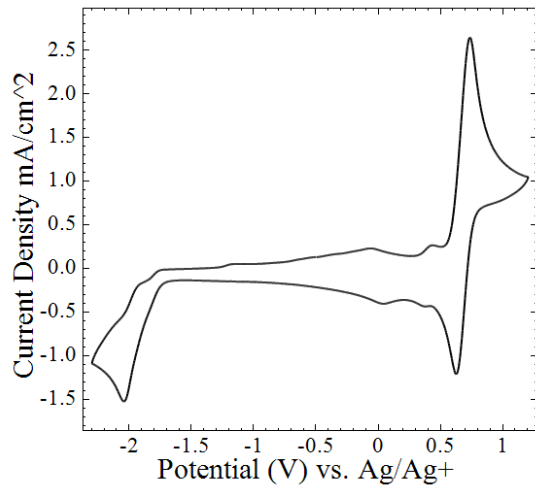


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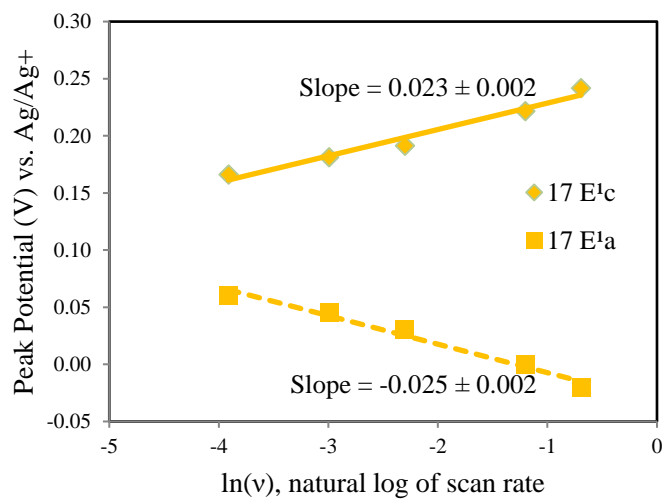
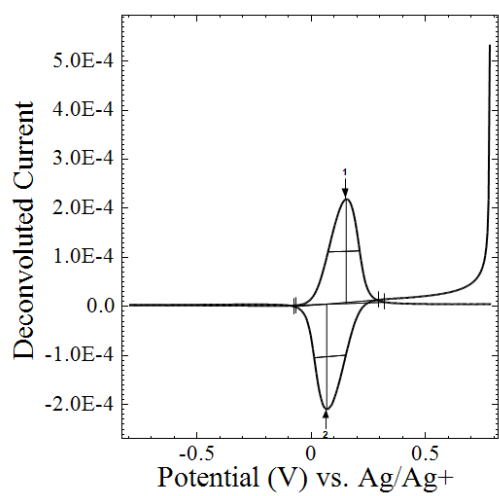
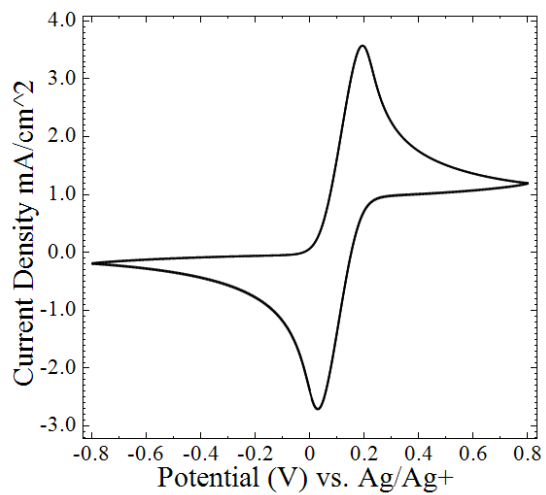


Complex 15

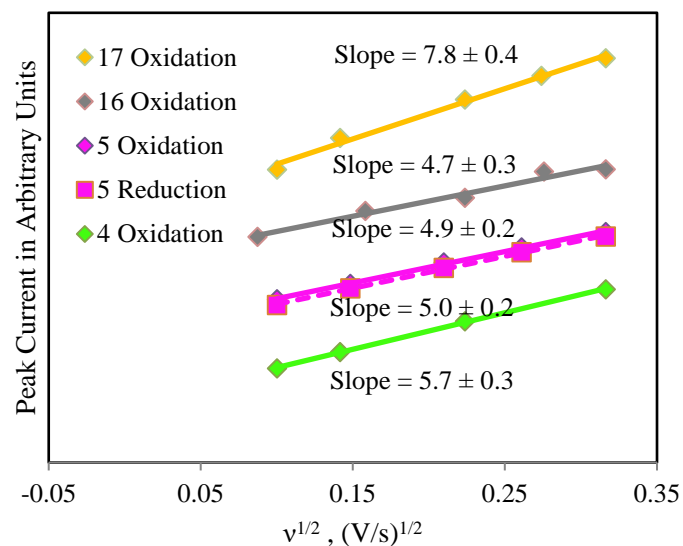




FCN



Randles-Sevcik Plots



Solubility Results

Table S1: Experimentally determined solubilities in acetonitrile.

Complex	Solubility [M]
1	0.404 ± 0.002^a
2	0.653 ± 0.003^a
3	0.60 ± 0.02
4	0.88 ± 0.04
5	0.40 ± 0.02
6	0.00212 ± 0.00002^a
7	0.0547 ± 0.0003^a
8	0.43 ± 0.02^a
9	1.92 ± 0.04^a
10	0.86 ± 0.05^a
11	1.25 ± 0.01^a
12	1.13 ± 0.01^a
13	1.80 ± 0.04^a
14	$>1.8^a$
15	1.32 ± 0.04^a
16	0.048 ± 0.002
17	0.10 ± 0.01

^a Values obtained from previous study.⁴

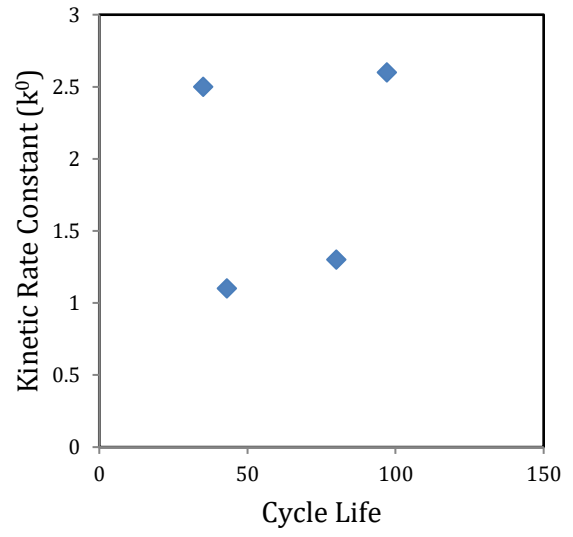
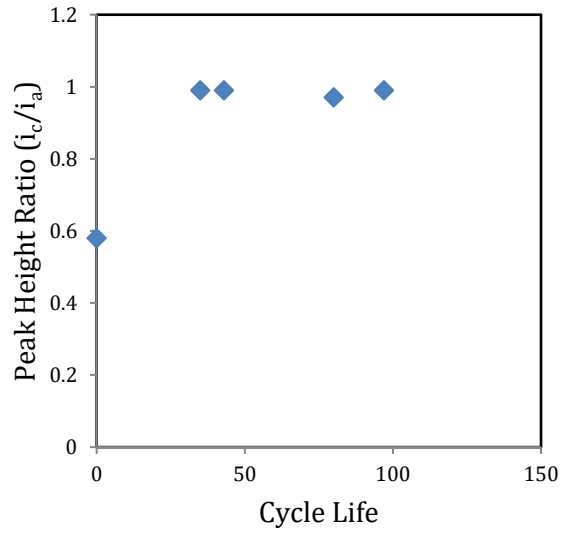
Bulk Electrolysis Parameters and Results

Table S2: Bulk electrolysis cycling parameters and quantified cycle lives. Solutions characterized using bulk electrolysis consisted of 0.01M active species with 0.5M TBABF₄ in acetonitrile.

Complex (Redox Couple)	Charging Potential [V vs. Ag/Ag ⁺]	Discharging Potential [V vs. Ag/Ag ⁺]	First Charge [e ⁻ /molecule]	Average Coulombic Efficiency	Cycle Life [Cycles to 80% Capacity]
1 (E ²)	-2.3	-1.7	1.00	4.6%	0
1 (E ³)	1.4	0.2	1.01	0.0%	0
2 (E ¹) ^a	-2.1	-1.4	0.97	98.0%	35
2 (E ²) ^a	0.5	0.0	1.00	71.2%	20
3 (E ²)	1.2	0.2	1.02	1.0%	0
4 (E ¹)	-1.4	-0.5	1.01	98.7%	97
5 (E ¹)	-1.5	-0.7	0.95	98.3%	43
5 (E ²)	0.8	0.3	0.90	4.9%	0
15 (E ¹)	-2.2	-1.6	0.95	97.0%	35
15 (E ²)	0.3	-0.1	0.90	48.8%	0
16 (E ²)	1.0	-0.5	1.00	95.3%	63
17 (E ¹)	0.4	-0.5	0.92	99.3%	100

^a Values obtained from previous study.⁴

Cycle Life Correlation Plots (Reduction Couple)



Cycle Life Correlation Plots (Oxidation Couple)

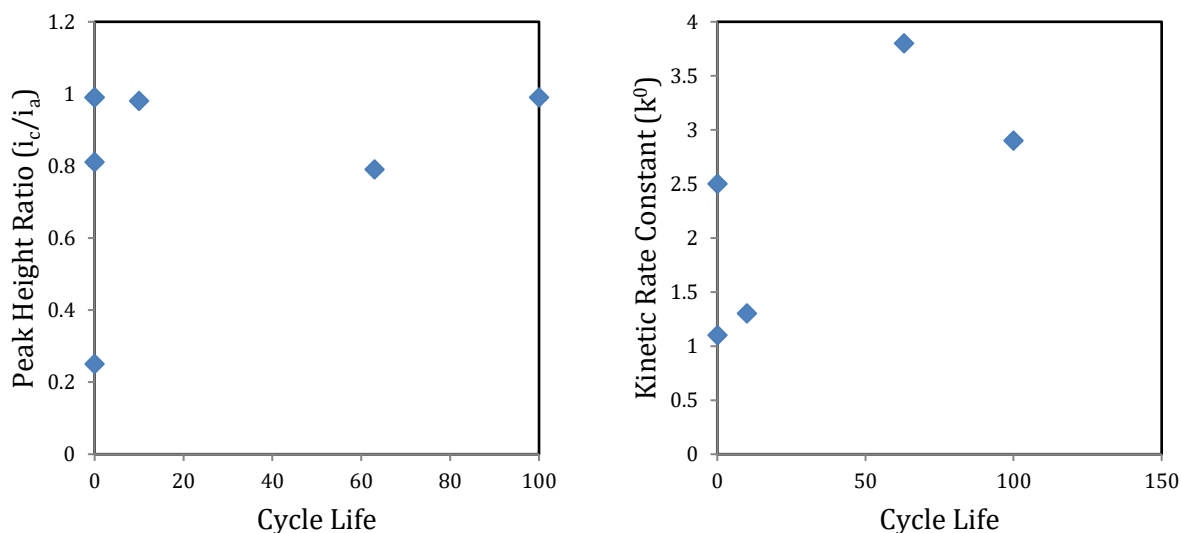


Table S3: DFT calculated parameters for each redox reaction selected for bulk electrolysis characterization.

Complex (Redox Couple)	Average M-O Bond Length Change [Å]	Charge Stored on Metal [%]	LUMO/HOMO Density on Metal [%]
1 (E ²)	0.008	17	23
1 (E ³)	-0.033	21	21
2 (E ¹)	0.081	0	66
2 (E ²)	-0.079	19	57
3 (E ²)	-0.120	-14	34
4 (E ¹)	0.104	-42	75
5 (E ¹)	0.044	27	67
5 (E ²)	-0.041	15	53
15 (E ¹)	0.071	38	63
15 (E ²)	-0.073	2	55
16 (E ²)	-0.100	-2	77
17 (E ¹)		85	78

- 1 A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, Inc, New York, NY, 2nd edn., 2001.
- 2 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706–723.
- 3 J. A. Suttill, J. F. Kucharyson, I. L. Escalante-Garcia, P. J. Cabrera, B. R. James, P. R. F. Savinell, M. S. Sanford and L. Thompson, *J. Mater. Chem. A*, 2015, **3**, 7929–7938.
- 4 J. F. Kucharyson, J. R. Gaudet, B. M. Wyvrat and L. T. Thompson, *J. Mater. Chem. A*, 2016, **Submitted**.