For a one-step reaction, the peak potential follows the following equation[1]:

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

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_O is the diffusion coefficient, ν is the scan rate, and k^o is the kinetic rate constant. Equation S1 can be simplified to:

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

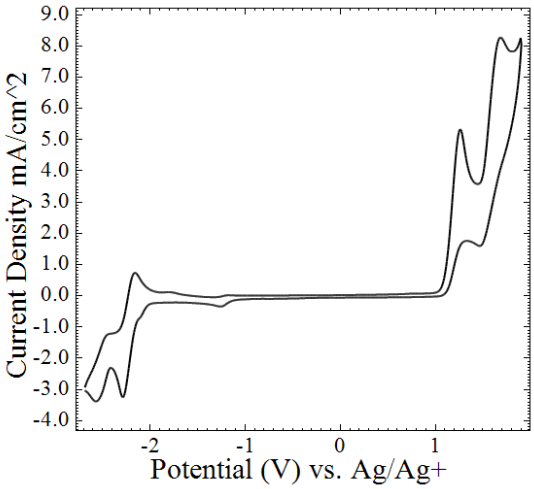
Where C is a constant. Plots of E_P-E_O versus ln(ν) were used to determine α.

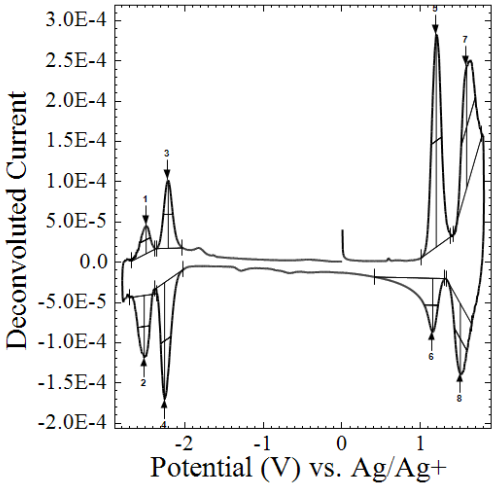
For quasireversible reactions, the Nicholson method was used to determine the kinetic rate constants, which utilizes a dimensionless parameter defined as [2]:

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

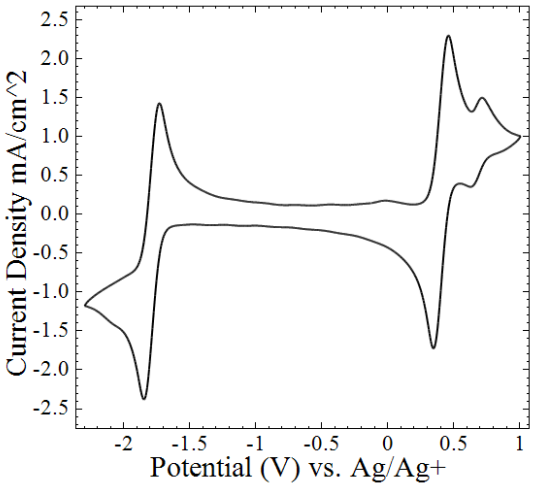
Assuming the diffusion coefficients of the oxidized and reduced species are equal. This was found to be the case for complex **5**, and was already found to be true for complex **2**.[3]

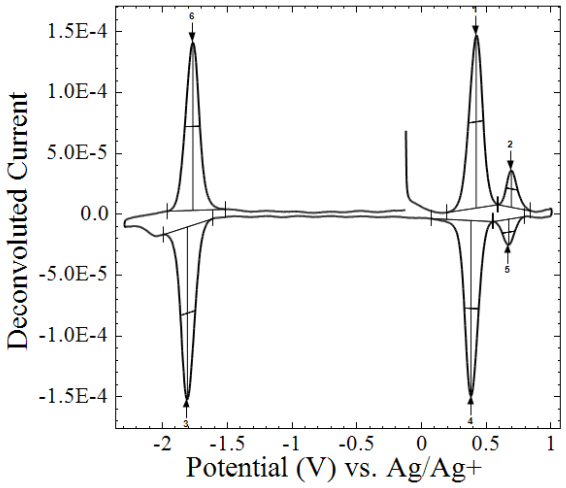
$Cr(acac)_3$

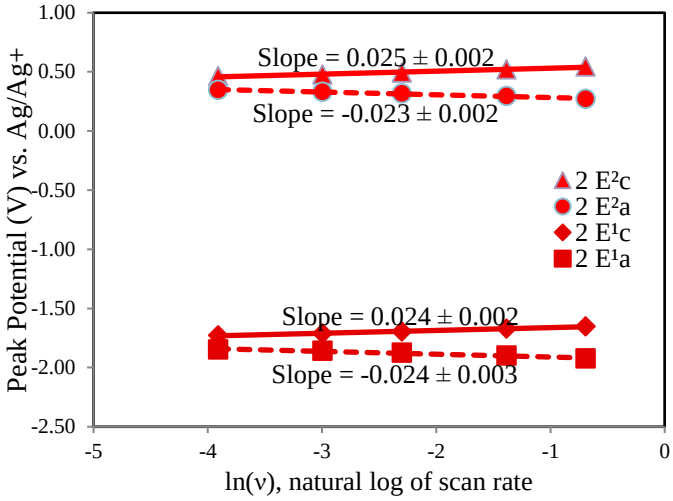

Current Density mA/cm^2
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-2
-1
0
1
Potential (V) vs. Ag/Ag+


Deconvoluted Current
3.0E-4
2.5E-4
2.0E-4
1.5E-4
1.0E-4
5.0E-5
0.0
-5.0E-5
-1.0E-4
-1.5E-4
-2.0E-4
1
2
3
4
5
6
7
8
-2
-1
0
1
Potential (V) vs. Ag/Ag+

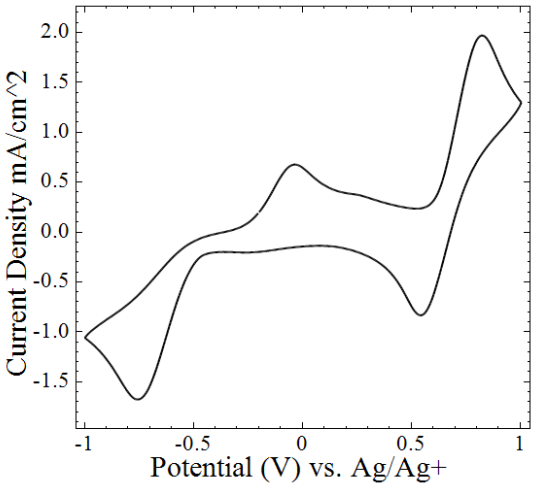
$V(acac)_3$

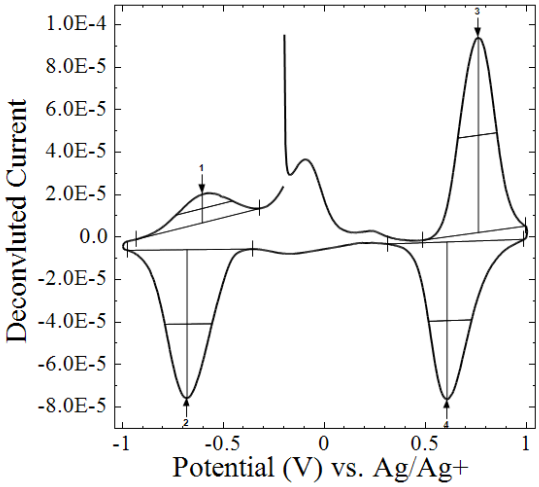

Current Density mA/cm^2
Potential (V) vs. Ag/Ag+


Deconvoluted Current
Potential (V) vs. Ag/Ag+

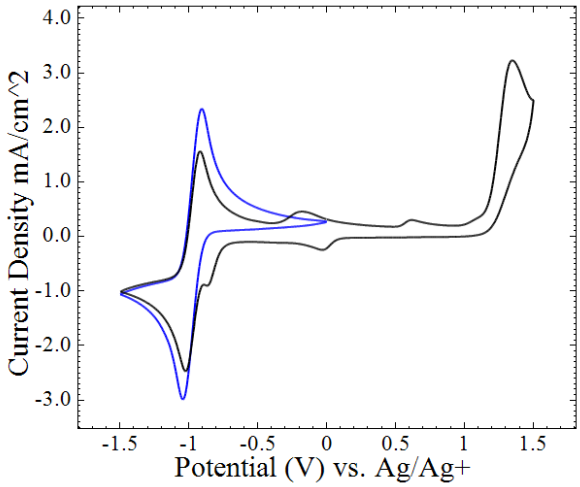

Slope = 0.025 ± 0.002
Slope = -0.023 ± 0.002
2 E²c
2 E²a
2 E¹c
2 E¹a
Slope = 0.024 ± 0.002
Slope = -0.024 ± 0.003
Peak Potential (V) vs. Ag/Ag+
ln(v), natural log of scan rate

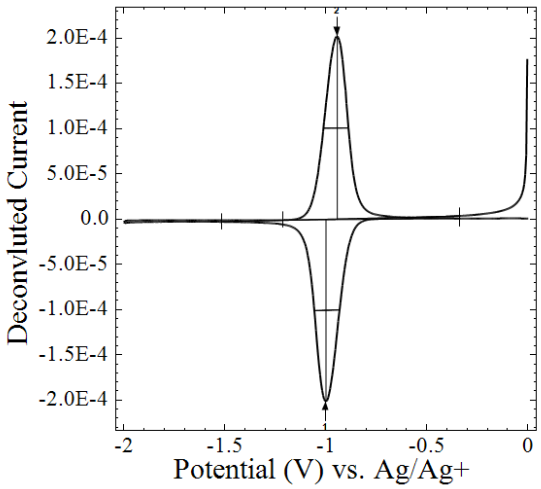
$Mn(acac)_3$

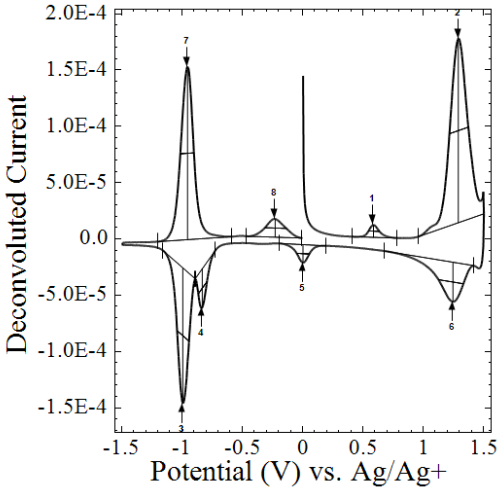

Current Density mA/cm^2
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-1
-0.5
0
0.5
1
Potential (V) vs. Ag/Ag+

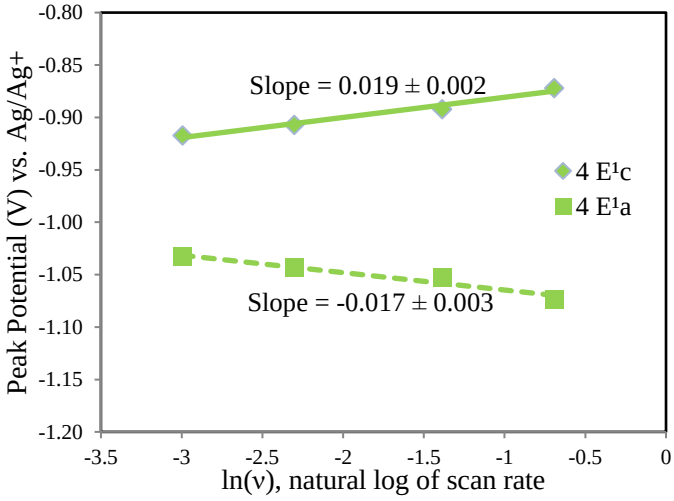

Deconvluted Current
1.0E-4
8.0E-5
6.0E-5
4.0E-5
2.0E-5
0.0
-2.0E-5
-4.0E-5
-6.0E-5
-8.0E-5
1
2
3
4
-1
-0.5
0
0.5
1
Potential (V) vs. Ag/Ag+

$Fe(acac)_3$

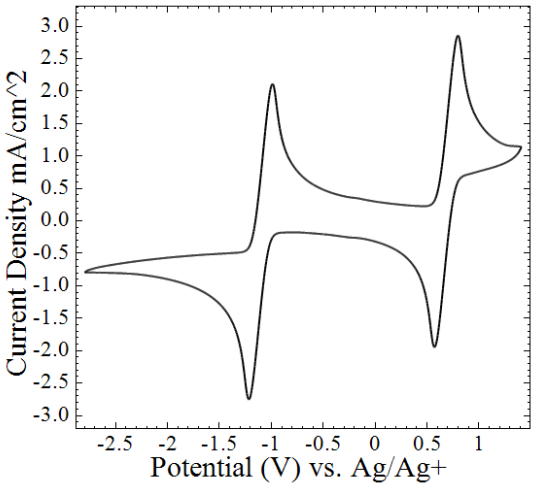

Current Density mA/cm^2
Potential (V) vs. Ag/Ag+

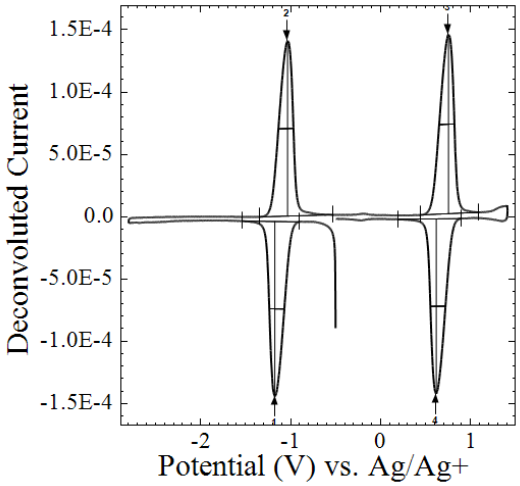

Deconvluted Current
Potential (V) vs. Ag/Ag+

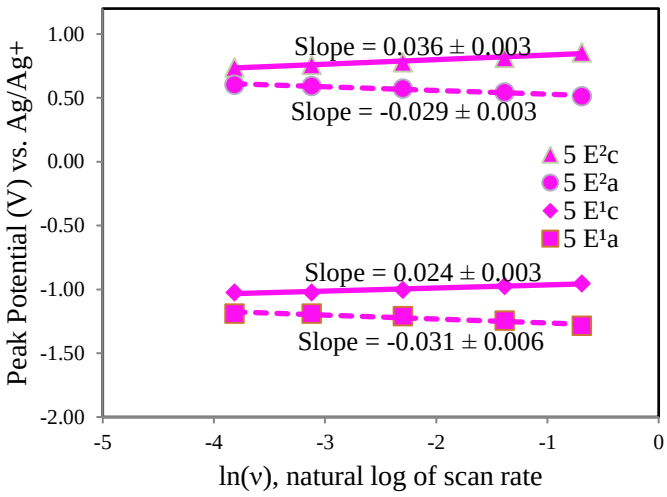

Deconvoluted Current
Potential (V) vs. Ag/Ag+


Slope = 0.019 ± 0.002
Slope = -0.017 ± 0.003
4 E¹c
4 E¹a
Peak Potential (V) vs. Ag/Ag+
ln(v), natural log of scan rate

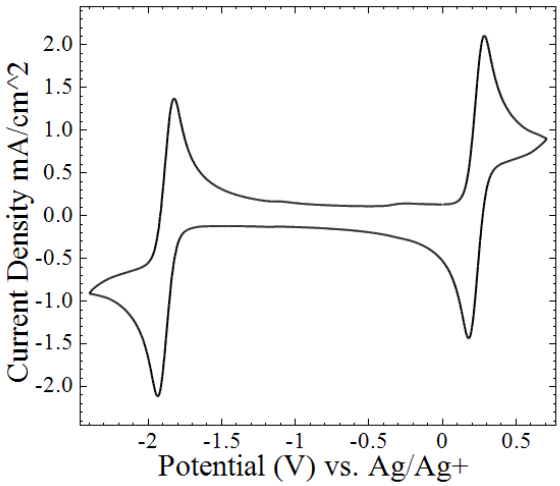
$Ru(acac)_3$

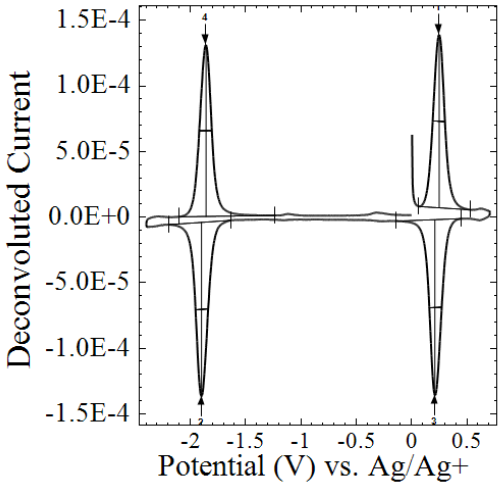

Current Density mA/cm^2
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-2.5 -2 -1.5 -1 -0.5 0 0.5 1
Potential (V) vs. Ag/Ag+

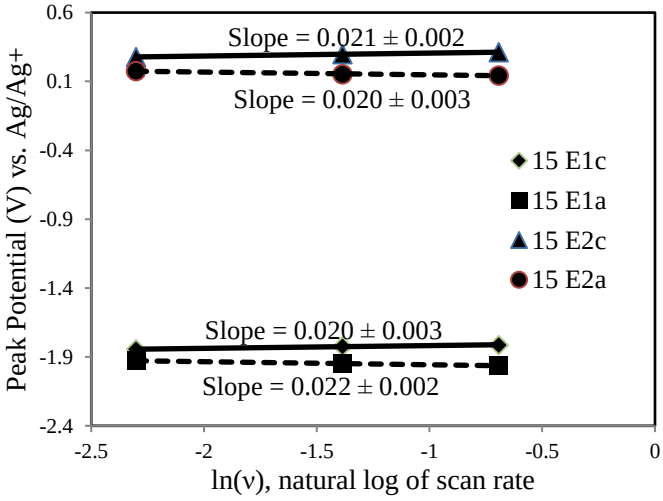

Deconvoluted Current
1.5E-4
1.0E-4
5.0E-5
0.0
-5.0E-5
-1.0E-4
-1.5E-4
-2 -1 0 1
Potential (V) vs. Ag/Ag+


Peak Potential (V) vs. Ag/Ag+
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
-5 -4 -3 -2 -1 0
ln(ν), natural log of scan rate
Slope = 0.036 ± 0.003
Slope = -0.029 ± 0.003
Slope = 0.024 ± 0.003
Slope = -0.031 ± 0.006
5 E²c
5 E²a
5 E¹c
5 E¹a

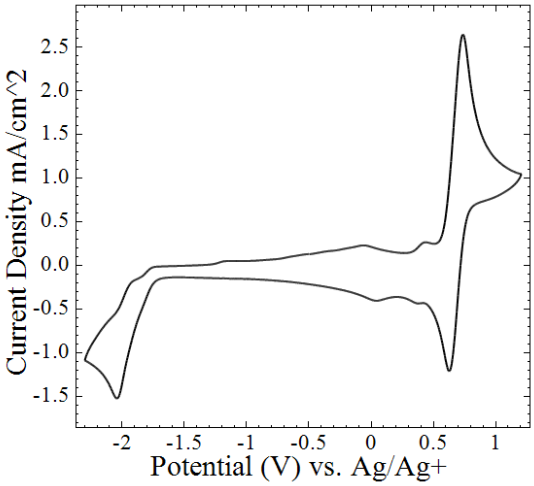
Complex **15**

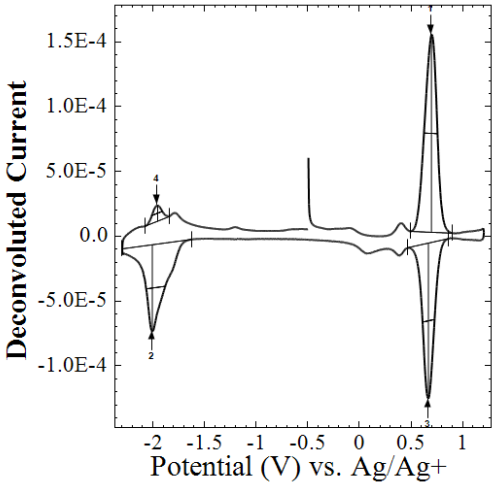


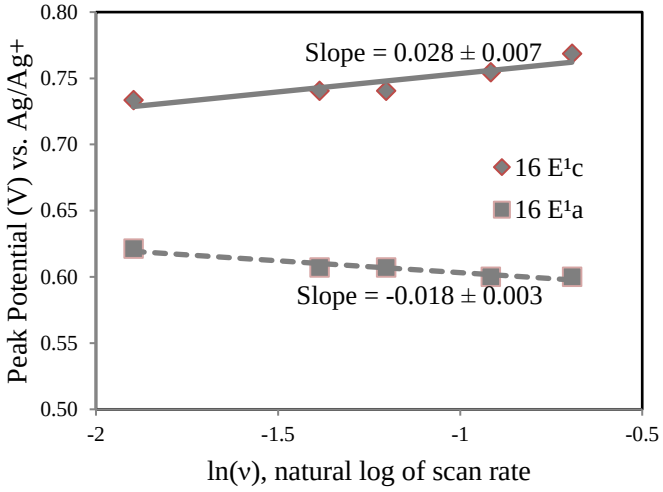




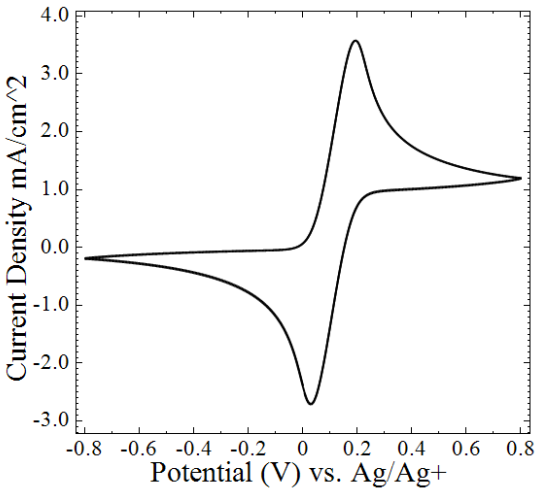
$VO(acac)_2$

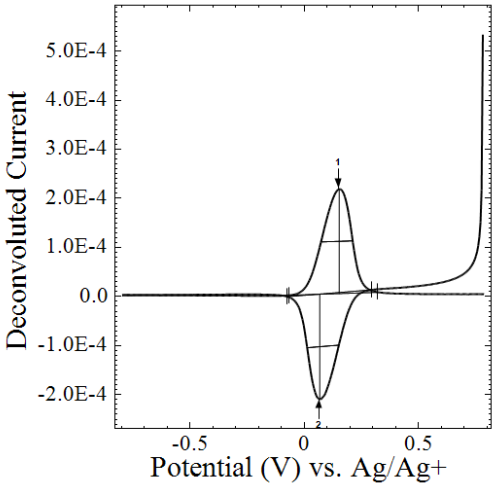

Current Density mA/cm^2
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2
-1.5
-1
-0.5
0
0.5
1
Potential (V) vs. Ag/Ag+

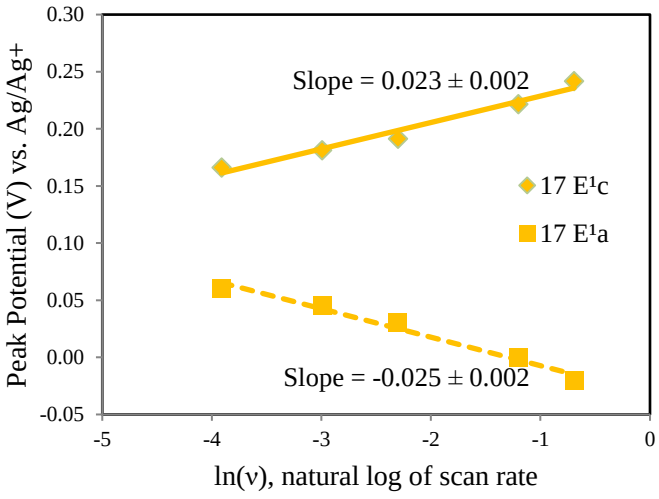

Deconvoluted Current
1.5E-4
1.0E-4
5.0E-5
0.0
-5.0E-5
-1.0E-4
4
2
3
-2
-1.5
-1
-0.5
0
0.5
1
Potential (V) vs. Ag/Ag+


Peak Potential (V) vs. Ag/Ag+
0.80
0.75
0.70
0.65
0.60
0.55
0.50
Slope = 0.028 ± 0.007
16 E¹c
16 E¹a
Slope = -0.018 ± 0.003
-2
-1.5
-1
-0.5
ln(ν), natural log of scan rate

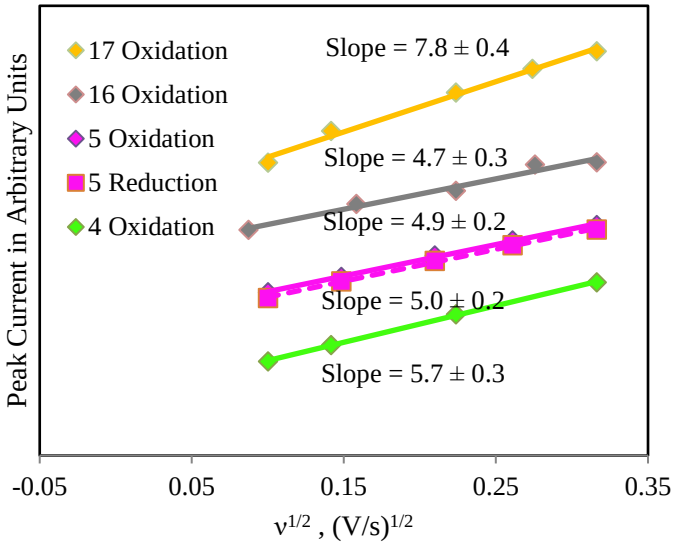
FCN


Current Density mA/cm^2
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-0.8 -0.6 -0.4 -0.2 0 0.2 0.4 0.6 0.8
Potential (V) vs. Ag/Ag+


Deconvoluted Current
5.0E-4
4.0E-4
3.0E-4
2.0E-4
1.0E-4
0.0
-1.0E-4
-2.0E-4
-0.5 0 0.5
Potential (V) vs. Ag/Ag+


Peak Potential (V) vs. Ag/Ag+
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-5 -4 -3 -2 -1 0
ln(ν), natural log of scan rate
Slope = 0.023 ± 0.002
Slope = -0.025 ± 0.002
17 E¹c
17 E¹a

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]

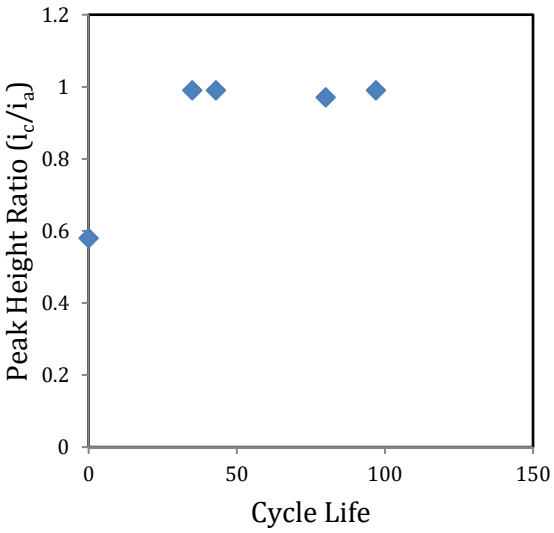
Bulk Electrolysis Parameters and Results

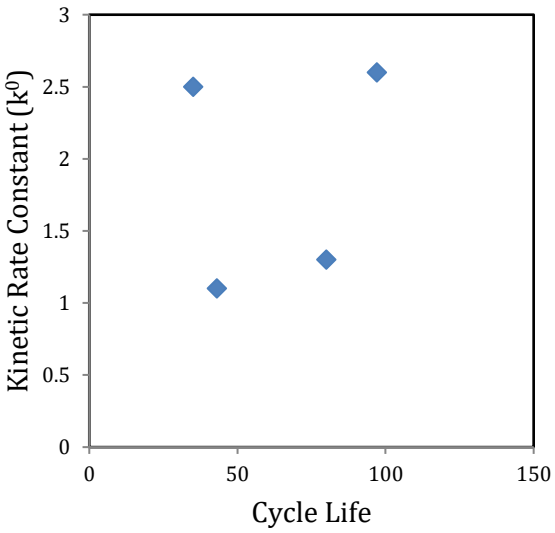
Table S2: Bulk electrolysis cycling parameters and quantified cycle lives. Solutions characterized using bulk electrolysis consisted of 0.01M active species with 0.5M $TBABF_4$ in acetonitrile.

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)

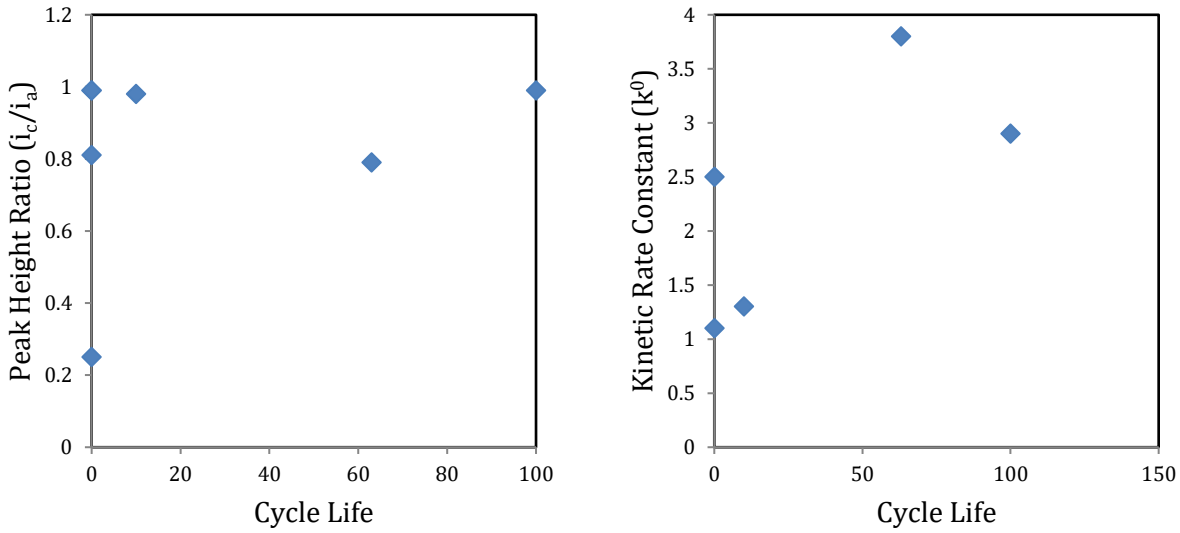


Table S3: DFT calculated parameters for each redox reaction selected for bulk electrolysis characterization.

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. Suttil, 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. Wyvratt and L. T. Thompson, *J. Mater. Chem. A*, 2016, **Submitted**.