

APPENDIX A

Electrochemical active surface area

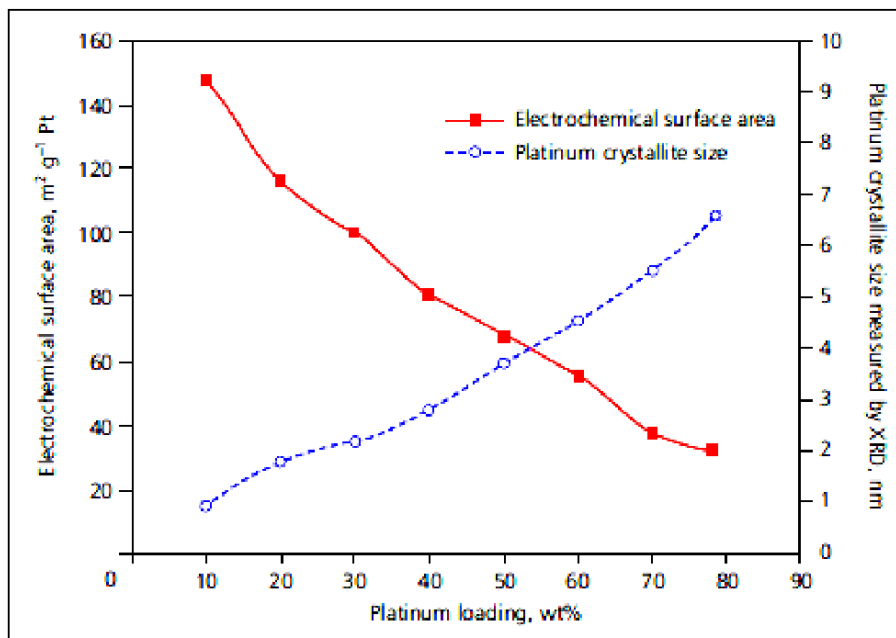


Figure A.1 Plot showing the increase in platinum crystalline size (as measured by X-ray diffraction and the corresponding decrease in electrochemically active surface area (ECA) per unit mass of platinum with increased platinum loading in a conventionally prepared fuel cell catalyst ^[134].

Calculation for initial theoretical Pt content in electrocatalyst

Mole of Pt = mole of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$

$$= (\text{mass of } \text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}) / (\text{molecular weight of}$$

$$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O})$$

$$= 0.8\text{g}/518$$

$$= 1.544 \times 10^{-3}$$

Mass of Pt = (molecular weight of Pt) x (mole of Pt)

$$= 195 \times (1.544 \times 10^{-3})$$

$$= 0.3012$$

$$\text{Wt. \% loading of Pt} = \{(\text{mass of Pt}) / (\text{mass of Pt} + (\text{mass of C}))$$

$$= [0.3012 / (0.3012 + 0.7)]$$

$$= 30.1\%$$

APPENDIX B

XRD patterns of Ta₂O₅

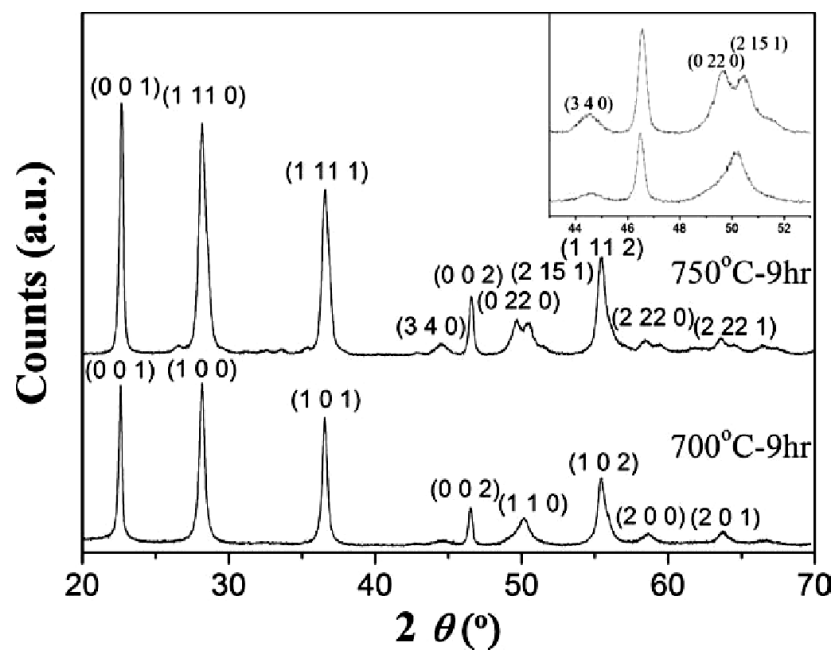


Figure B.1 XRD patterns of Ta₂O₅ annealed at 700°C and 750°C for 3h ^[145]

APPENDIX C

Influence of H_2SO_4 concentration and temperature on catalytic activity

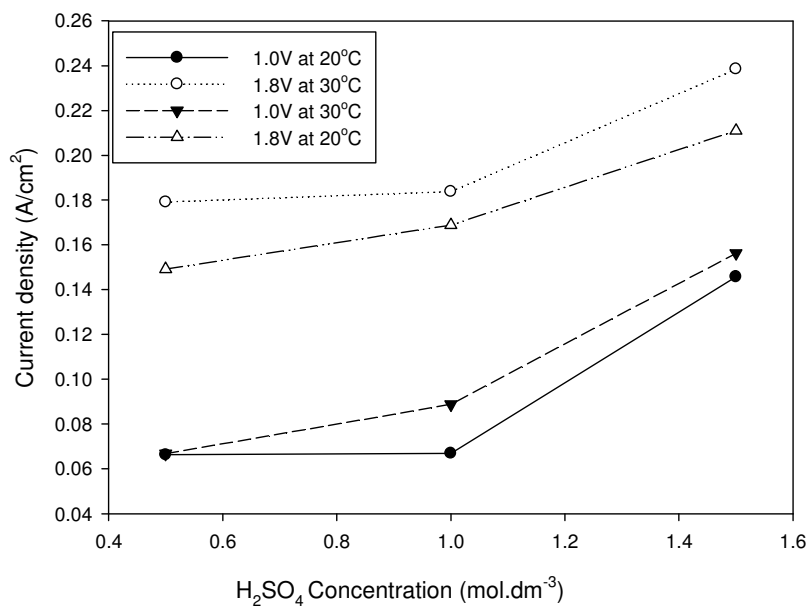


Figure C.1 The influence of H_2SO_4 concentration and temperature on Pt/C at 0rpm

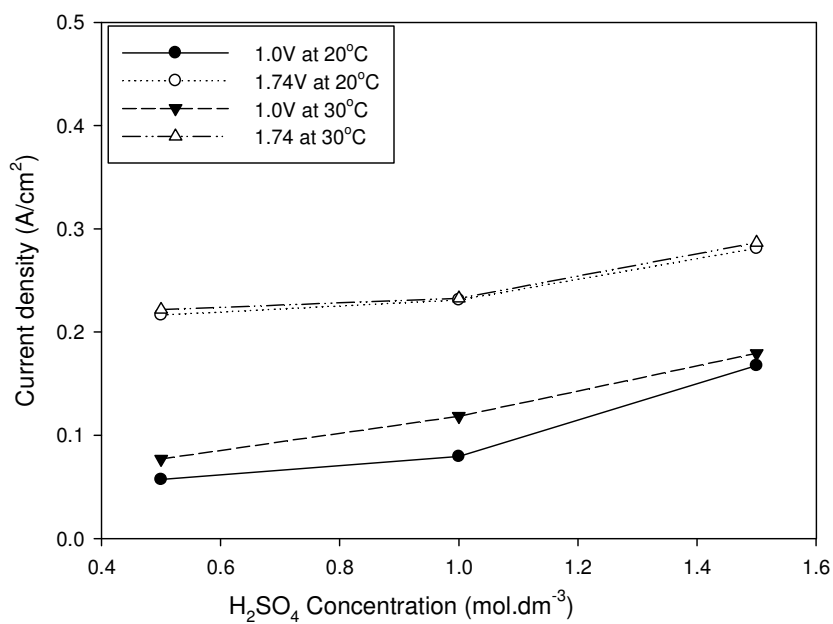


Figure C.2 The influence of H_2SO_4 concentration and temperature on Pt/C at 100rpm

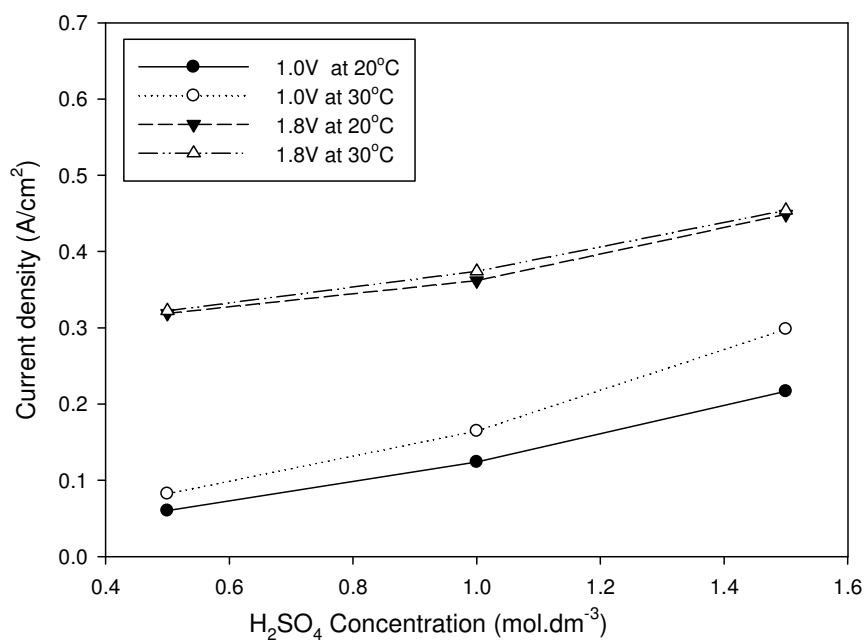


Figure C.3 The influence of H₂SO₄ concentration and temperature on Pt/C at 400rpm

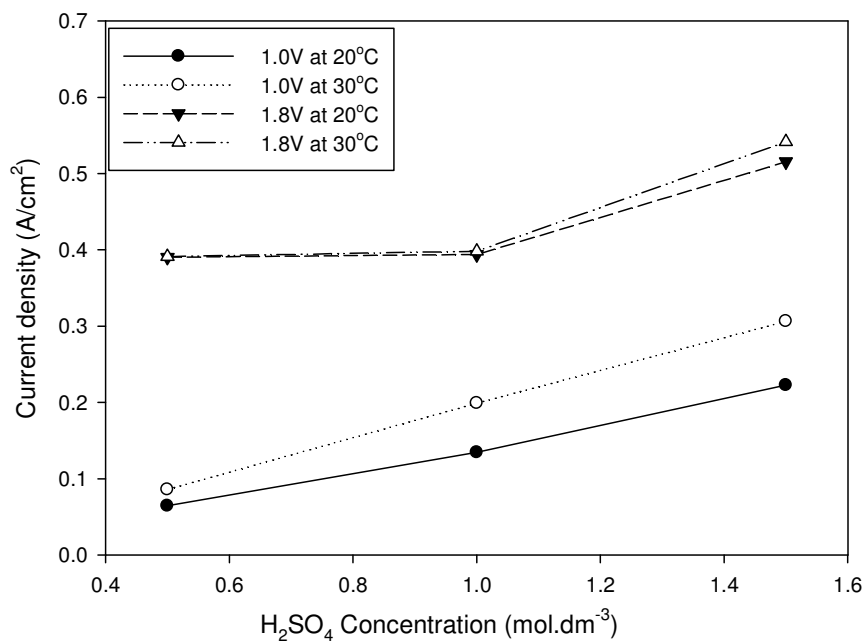


Figure C.4 The influence of H₂SO₄ concentration and temperature on Pt/C at 900rpm

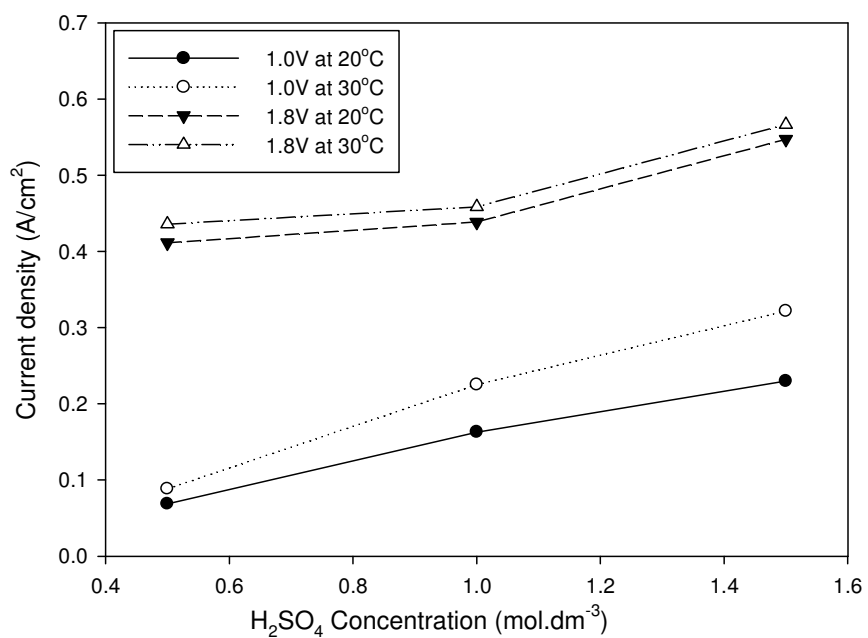


Figure C.5 The influence of H₂SO₄ concentration and temperature on Pt/C at 1600rpm

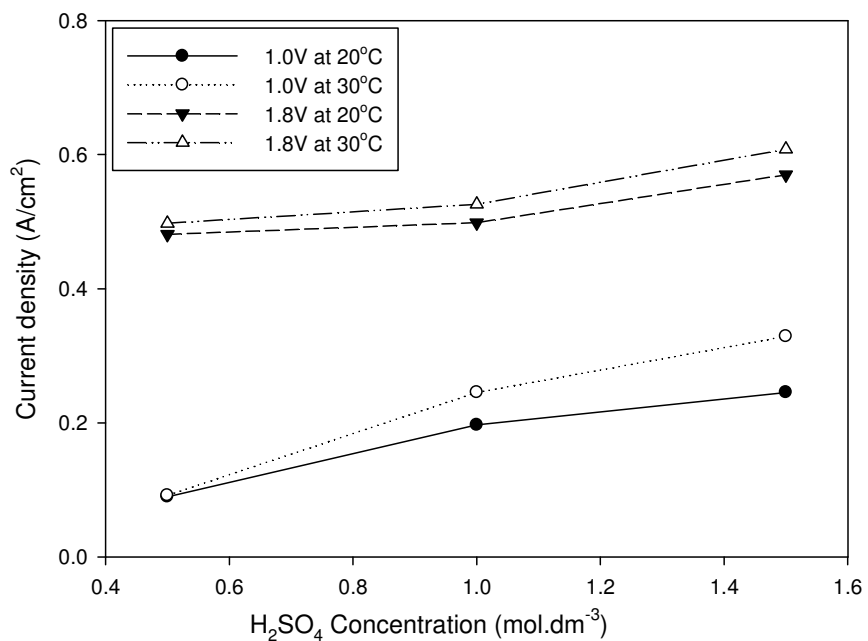


Figure C.6 The influence of H₂SO₄ concentration and temperature on Pt/C at 2500rpm

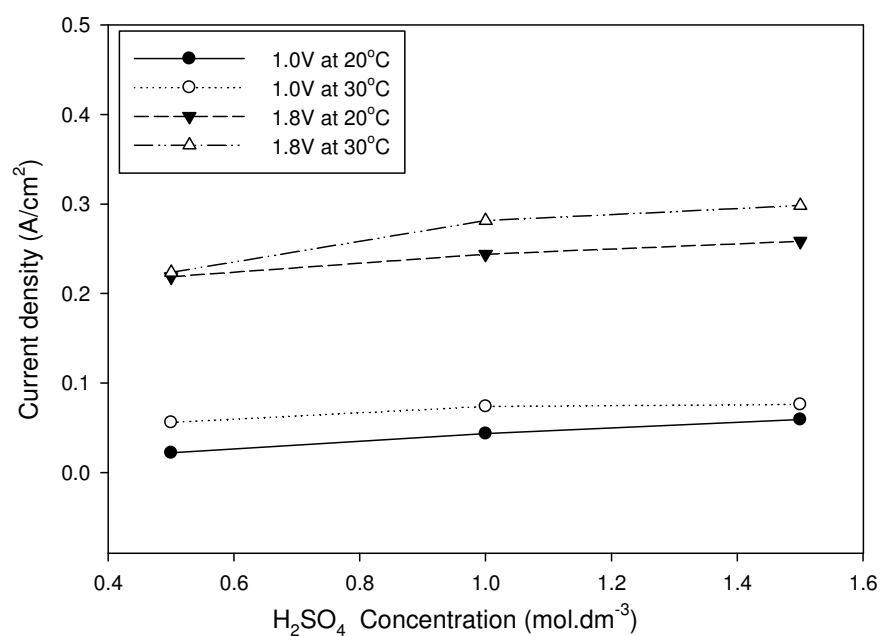


Figure C.7 The influence of H₂SO₄ concentration and temperature on Pt/Nb₂O₅-C at 0rpm

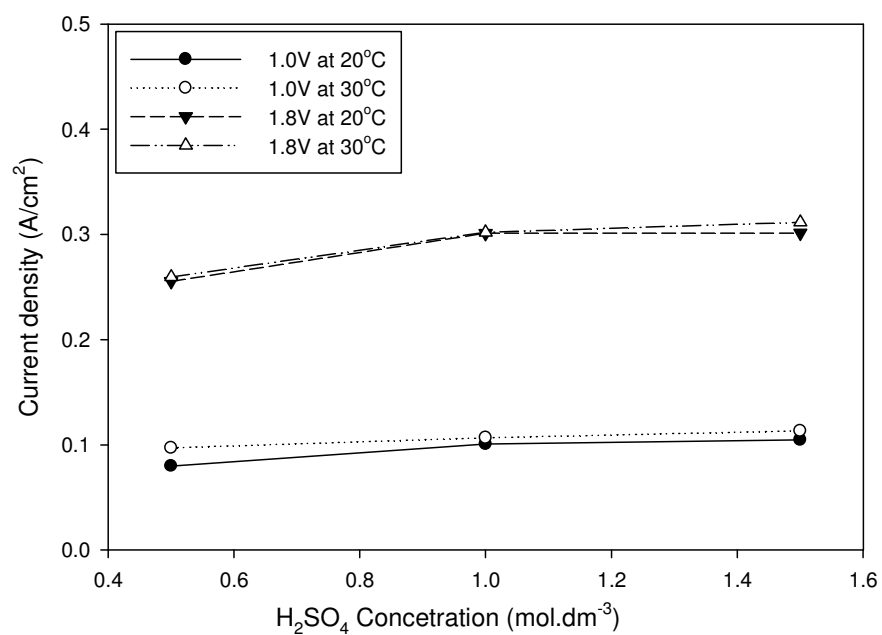


Figure C.8 The influence of H₂SO₄ concentration and temperature on Pt/Nb₂O₅-C at 100rpm

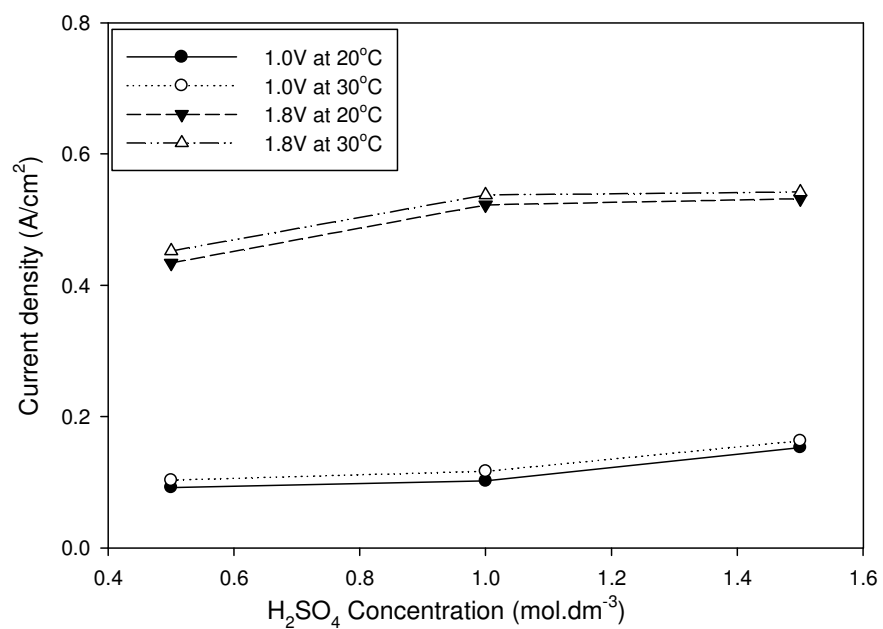


Figure C.9 The influence of H₂SO₄ concentration and temperature on Pt/Nb₂O₅-C at 400rpm

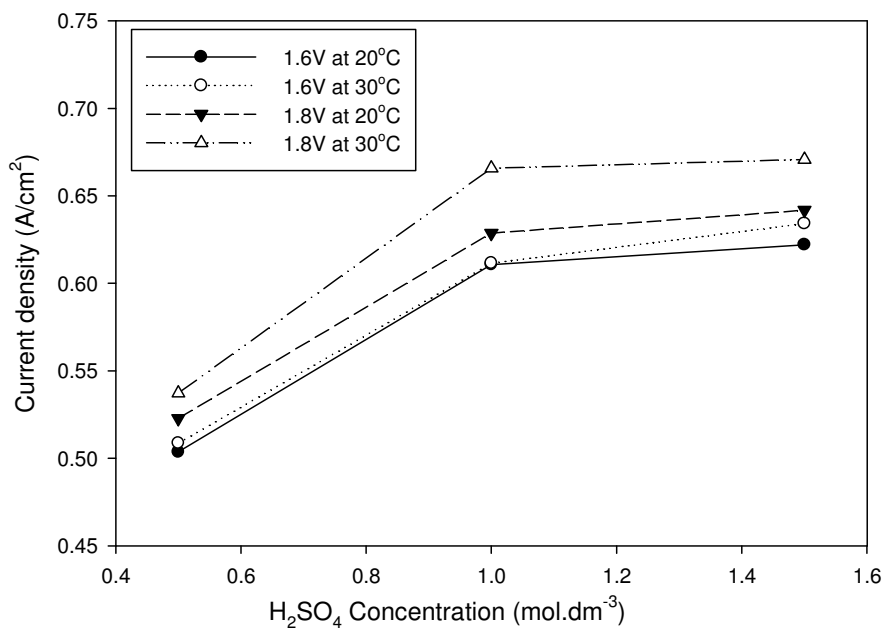


Figure C.10 The influence of H₂SO₄ concentration and temperature on Pt/Nb₂O₅-C at 900rpm

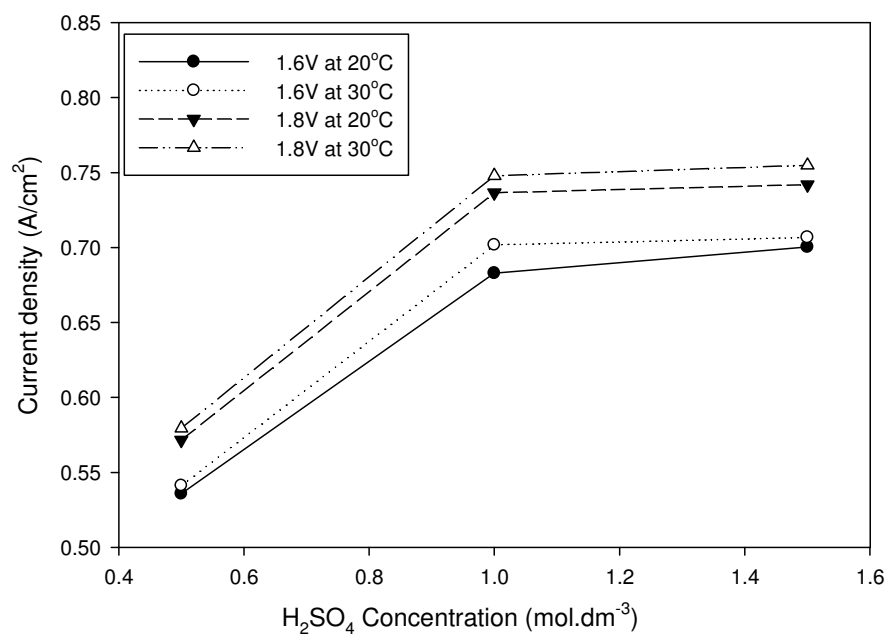


Figure C.11 The influence of H₂SO₄ concentration and temperature on Pt/Nb₂O₅-C at 1600rpm

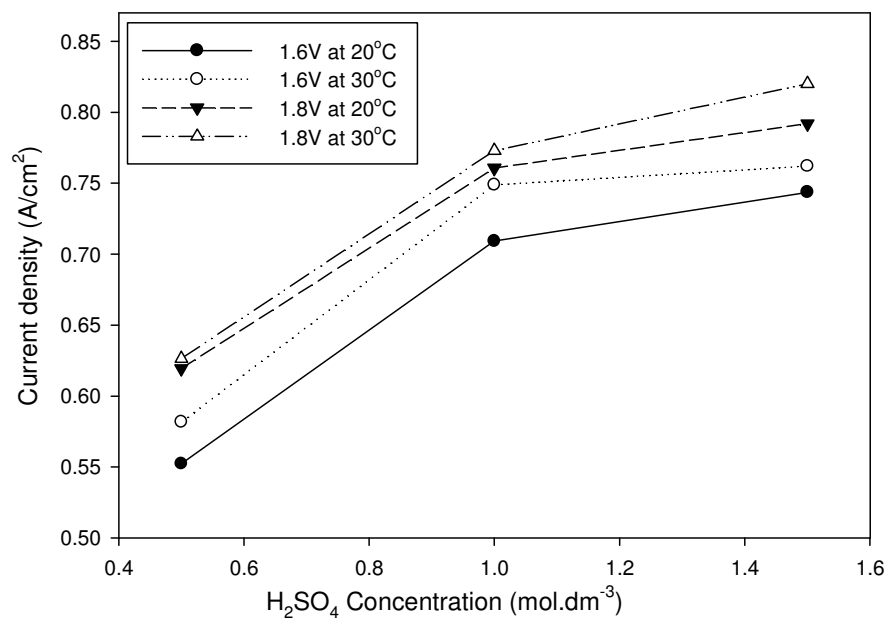


Figure C.12 The influence of H₂SO₄ concentration and temperature on Pt/Nb₂O₅-C at 2500rpm

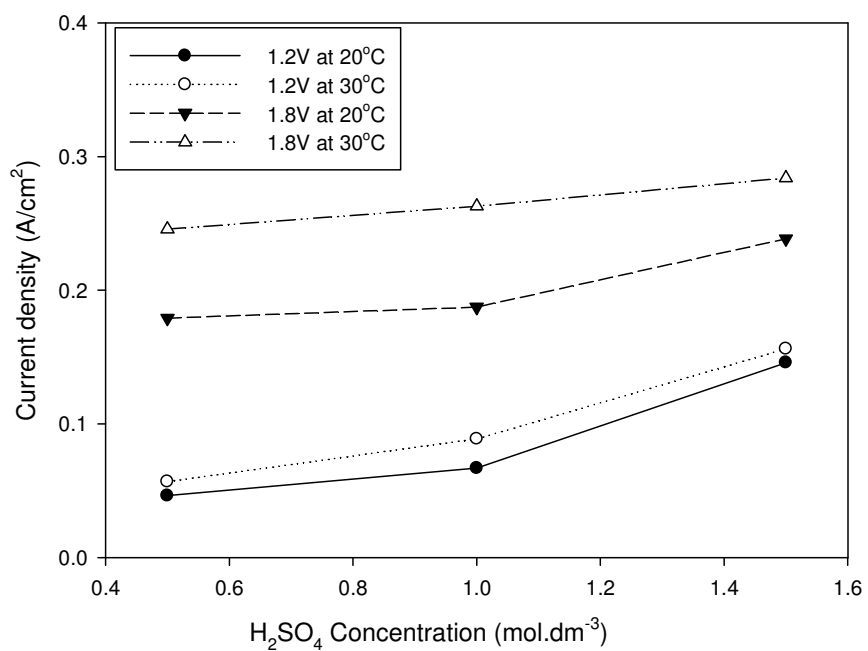


Figure C.13 The influence of H₂SO₄ concentration and temperature on Pt/Ta₂O₅-C at 0rpm

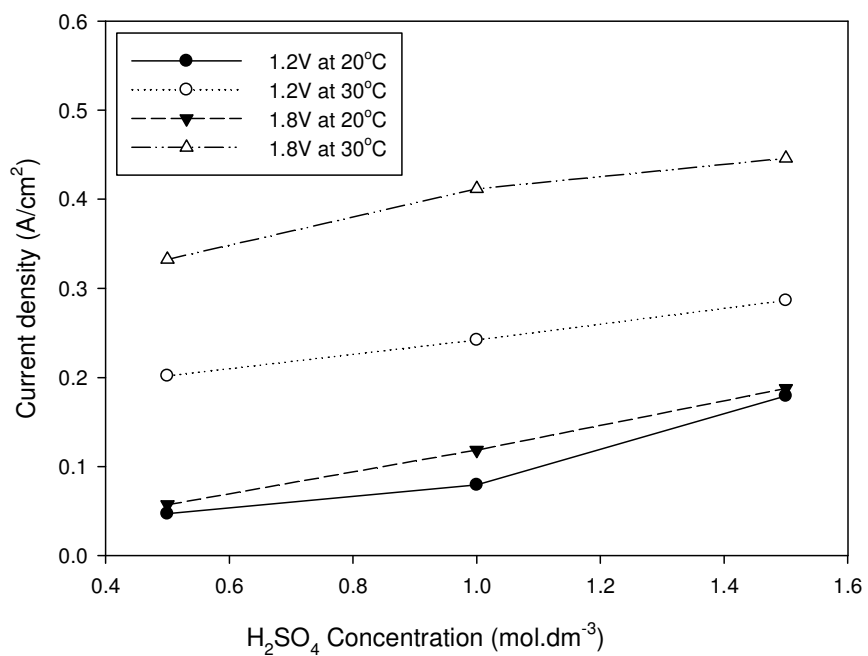


Figure C.14 The influence of H₂SO₄ concentration and temperature on Pt/ Ta₂O₅-C at 100rpm

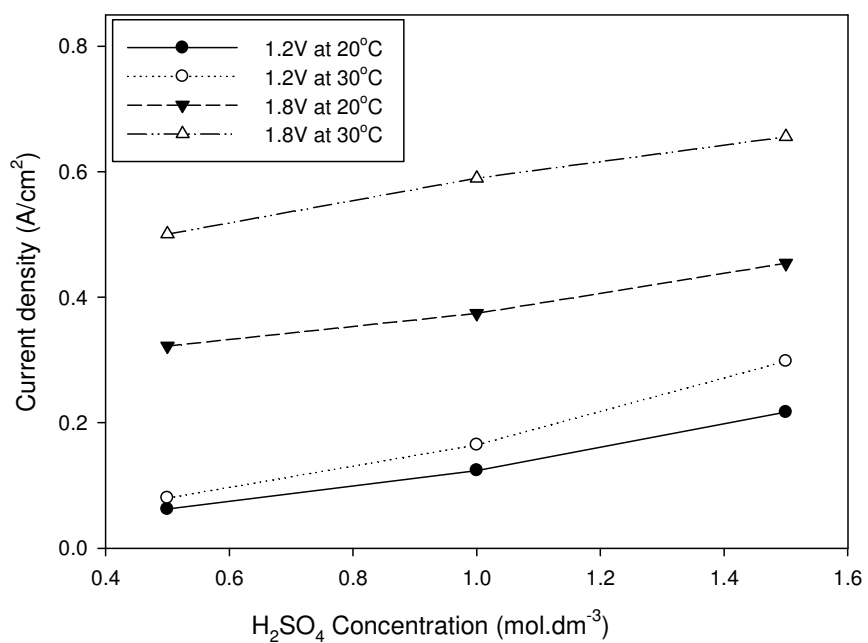


Figure C.15 The influence of H₂SO₄ concentration and temperature on Pt/ Ta₂O₅-C at 400rpm

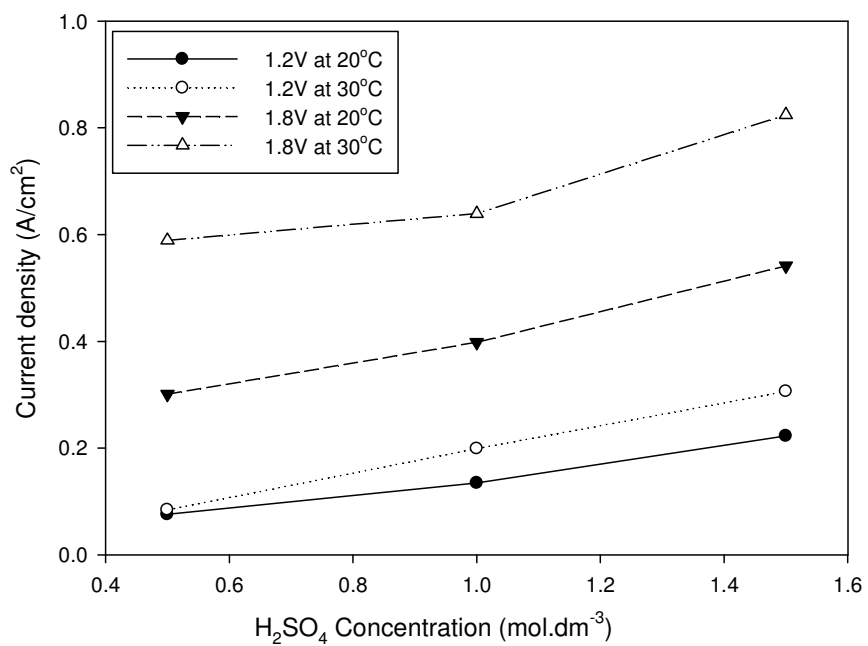


Figure C.16 The influence of H₂SO₄ concentration and temperature on Pt/ Ta₂O₅-C at 900rpm

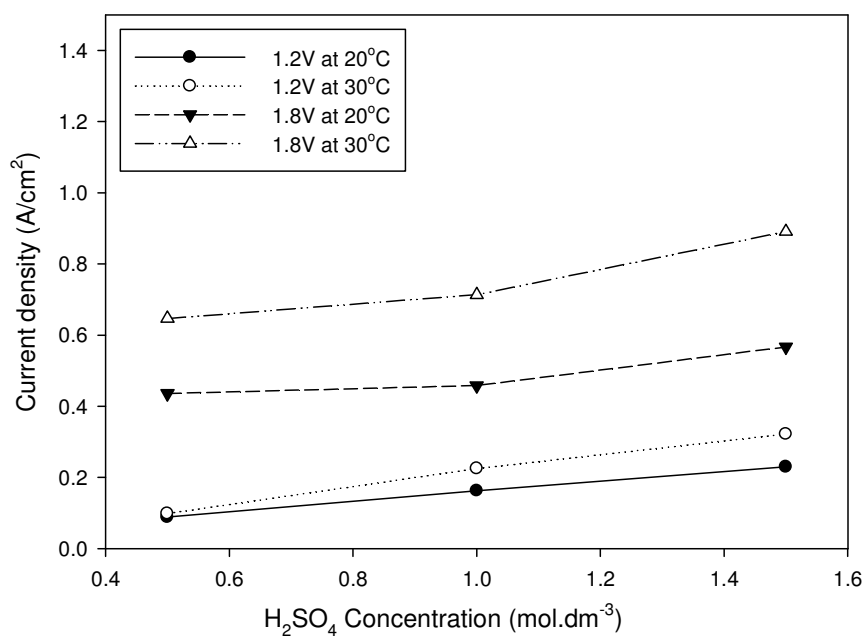


Figure C.17 The influence of H₂SO₄ concentration and temperature on Pt/Ta₂O₅-C at 1600rpm

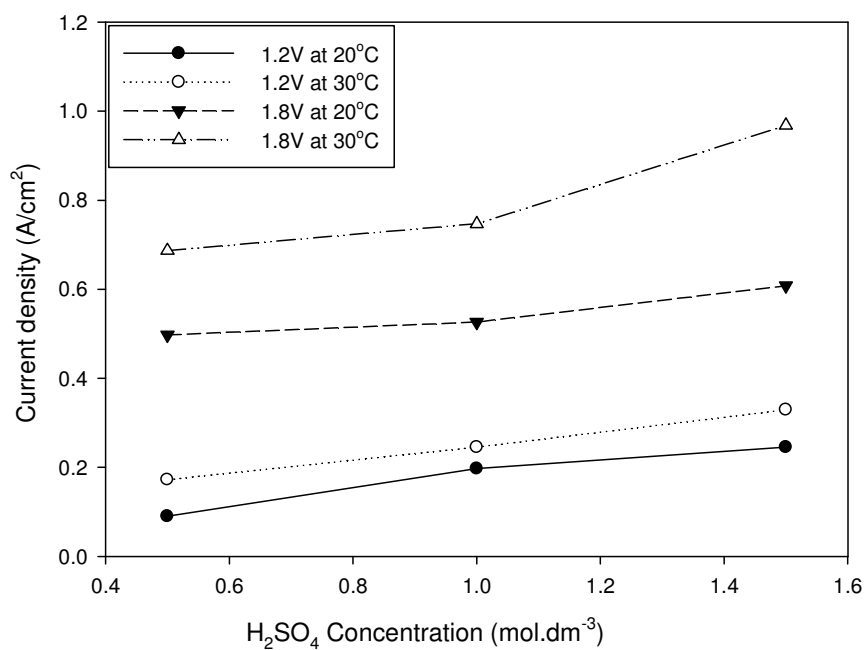


Figure C.18 The influence of H₂SO₄ concentration and temperature on Pt/ Ta₂O₅-C at 2500rpm

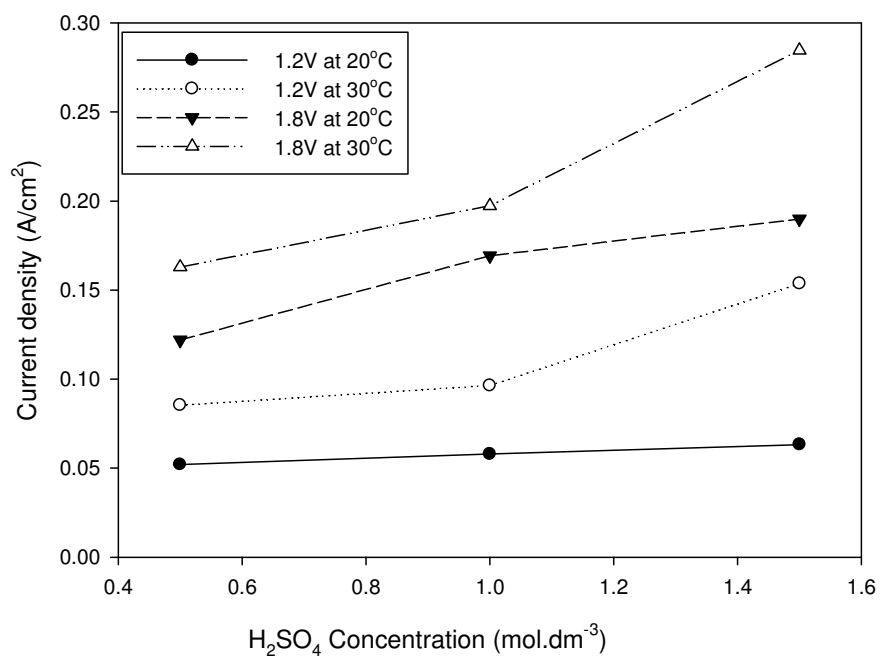


Figure C.19 The influence of H₂SO₄ concentration and temperature on Pt/ZrO₂-C at 0rpm

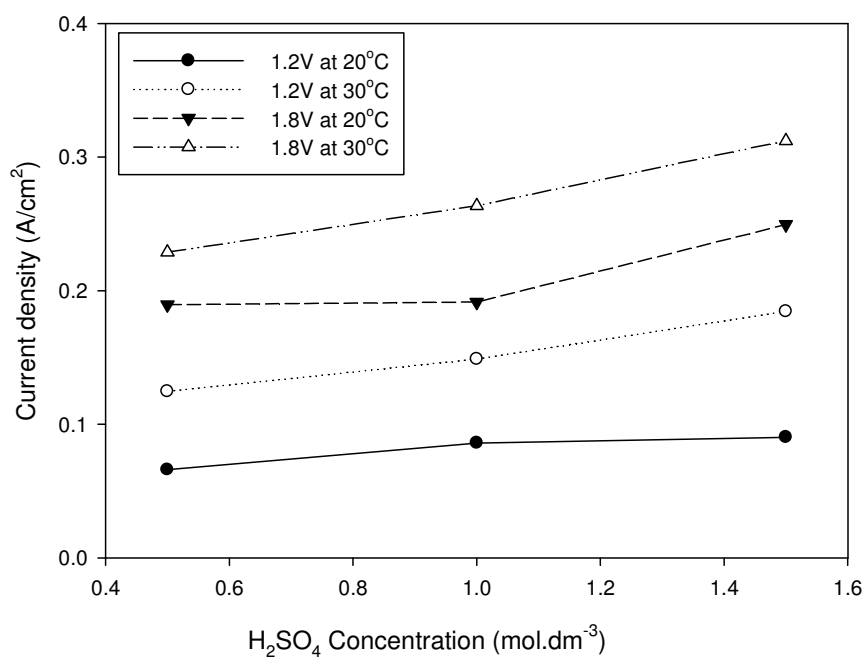


Figure C.20 The influence of H₂SO₄ concentration and temperature on Pt/ZrO₂-C at 100rpm

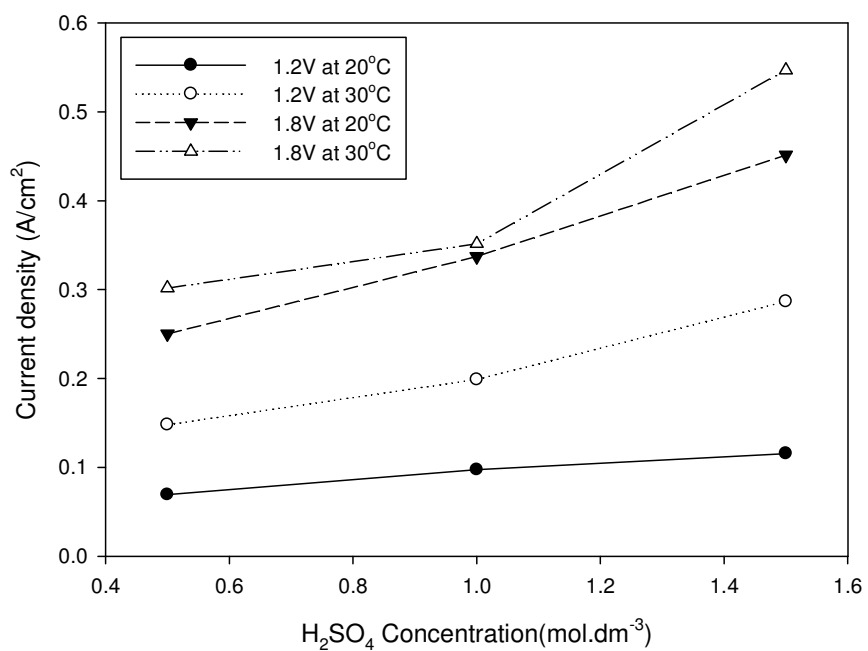


Figure C.21 The influence of H₂SO₄ concentration and temperature on Pt/ZrO₂-C at 400rpm

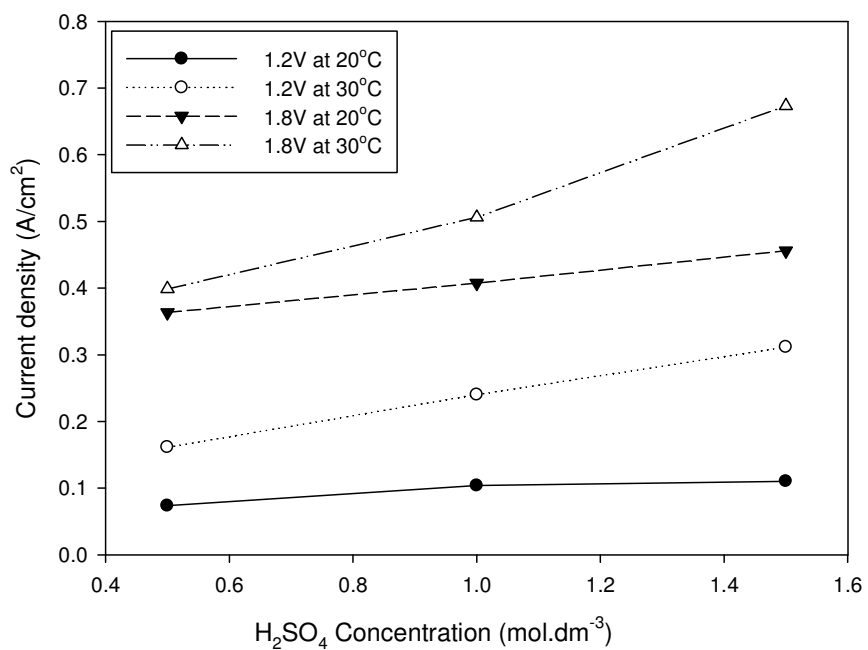


Figure C.22 The influence of H₂SO₄ concentration and temperature on Pt/ZrO₂-C at 900rpm

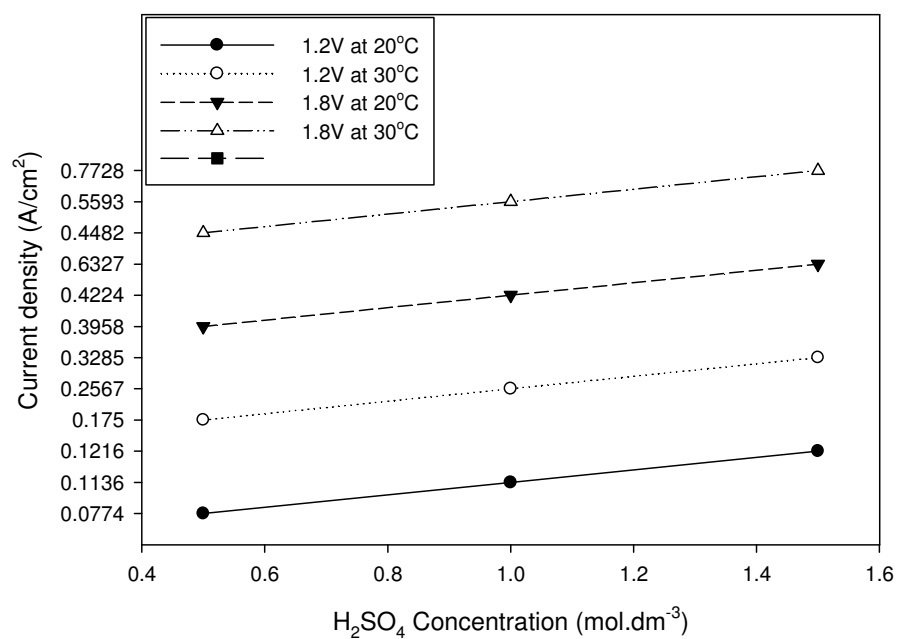


Figure C.23 The influence of H₂SO₄ concentration and temperature on Pt/ZrO₂-C at 1600rpm

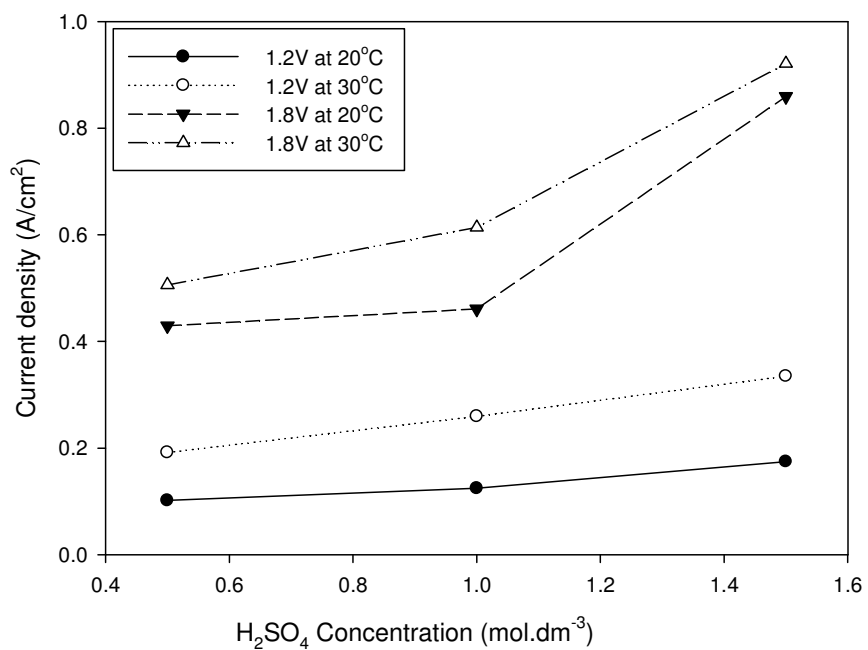


Figure C.24 The influence of H₂SO₄ concentration and temperature on Pt/ZrO₂-C at 2500rpm

APPENDIX D

Levich and Koutecky–Levich plots

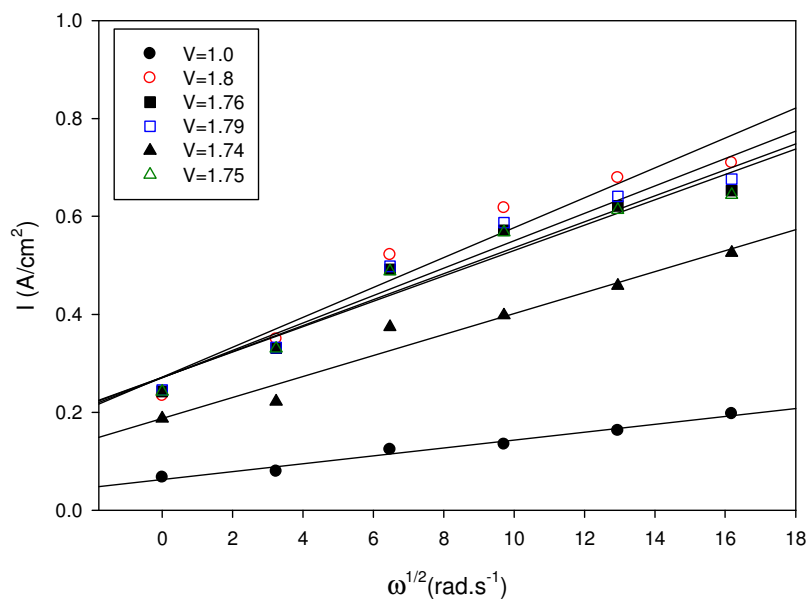


Figure D.1 Levich plot of Pt/C in 1.0M H₂SO₄ at 20°C

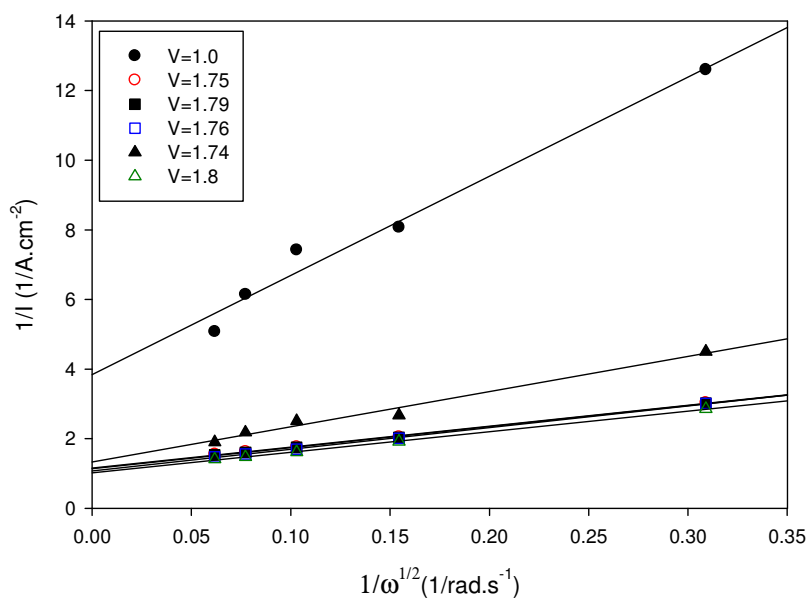


Figure D.2 Koutecky-Levich plot of Pt/C in 1.0M H₂SO₄ at 20°C

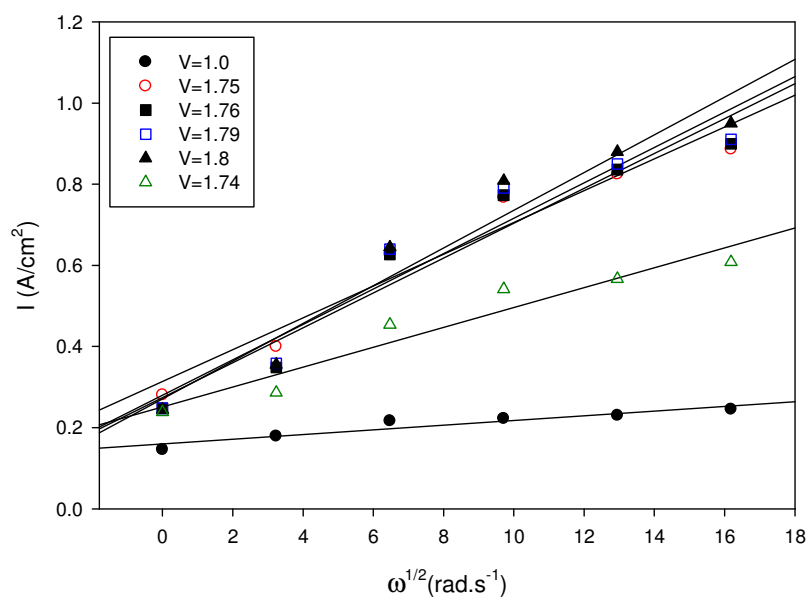


Figure D.3 Levich plot of Pt/C in 1.5M H₂SO₄ at 20°C

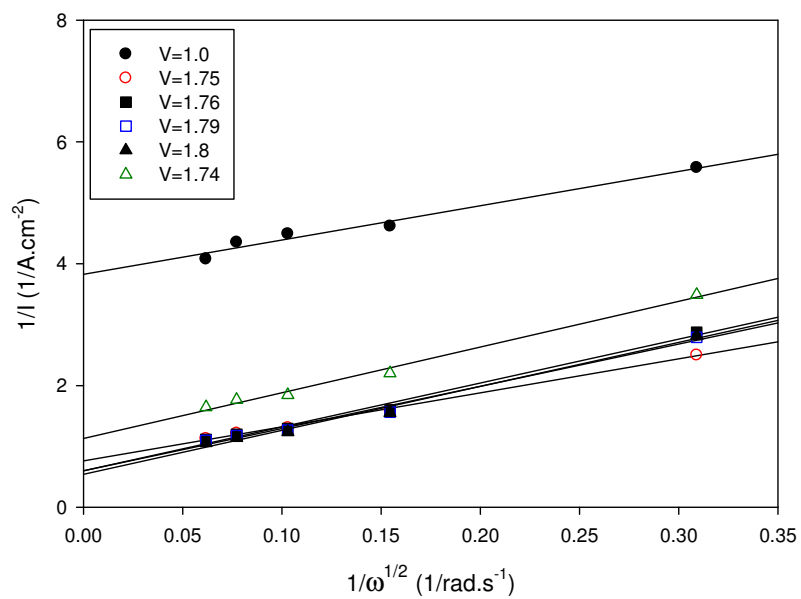


Figure D.4 Koutecky-Levich plot of Pt/C in 1.5M H₂SO₄ at 20°C

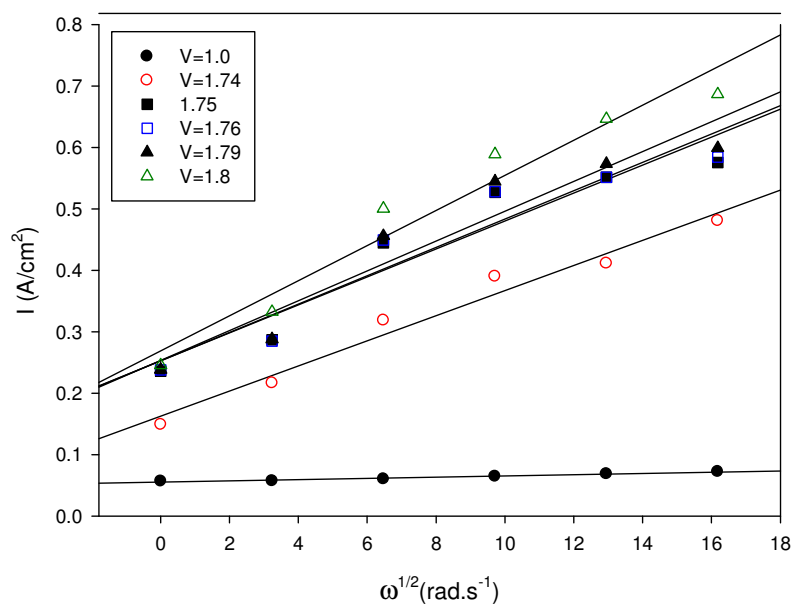


Figure D.5 Levich plot of Pt/C in 0.5M H₂SO₄ at 30°C

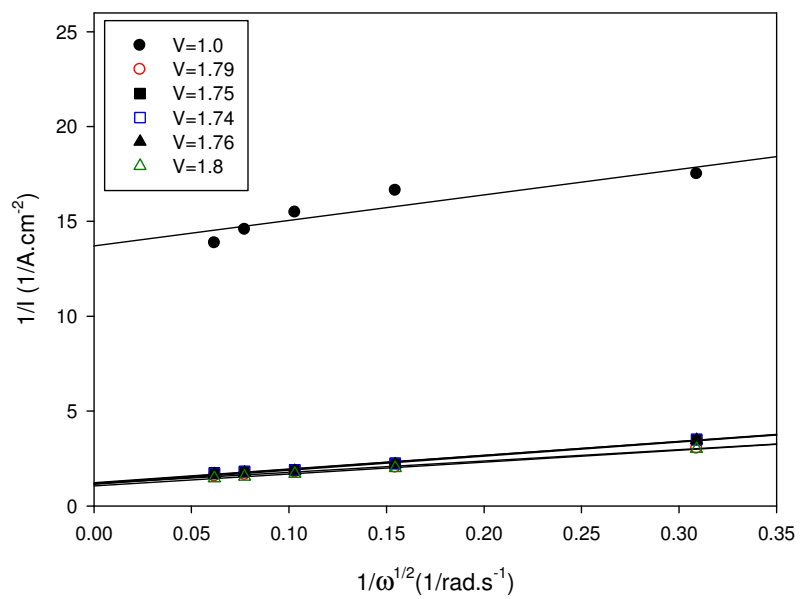


Figure D.6 Koutecky-Levich plot of Pt/C in 0.5M H₂SO₄ at 30°C

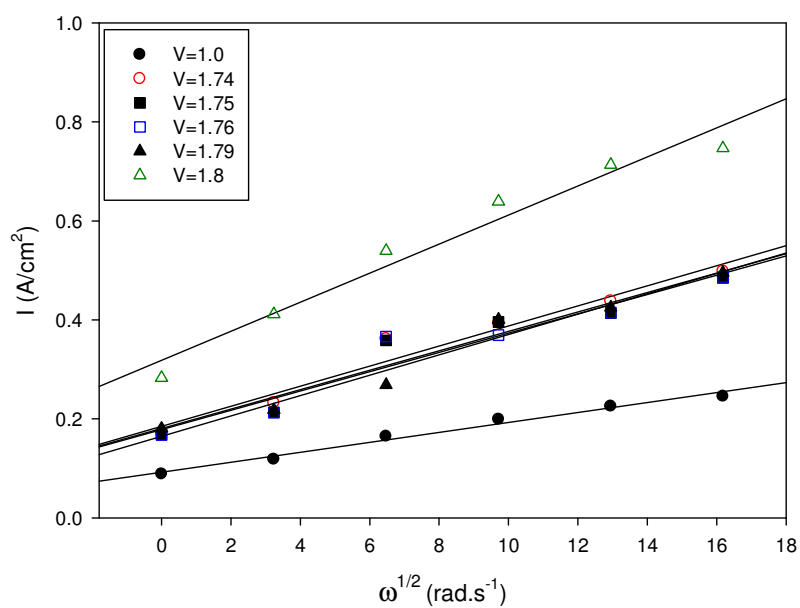


Figure D.7 Levich plot of Pt/C in 1.0M H₂SO₄ at 30°C

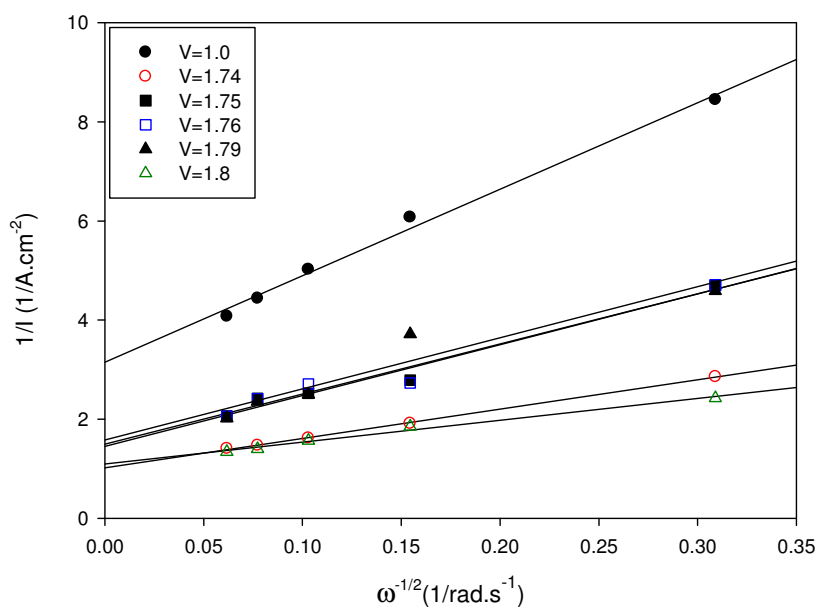


Figure D.8 Koutecky-Levich plot of Pt/C in 1.0M H₂SO₄ at 30°C

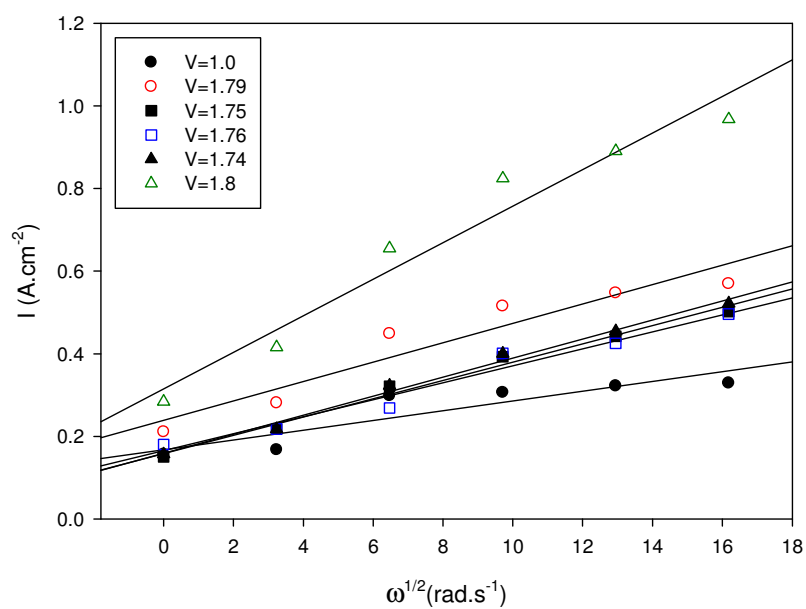


Figure D.9 Levich plot of Pt/C in 1.5M H₂SO₄ at 30°C

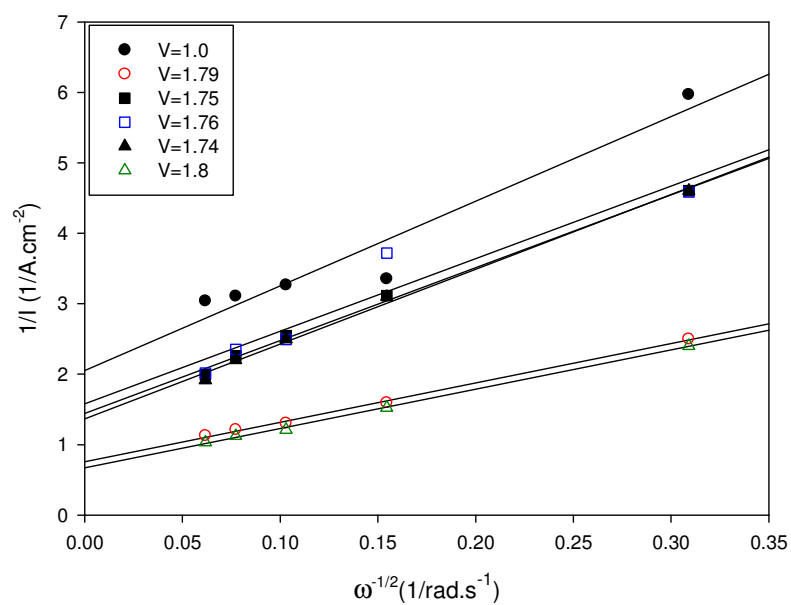


Figure D.10 Koutecky-Levich plot of Pt/C in 1.5M H₂SO₄ at 30°C

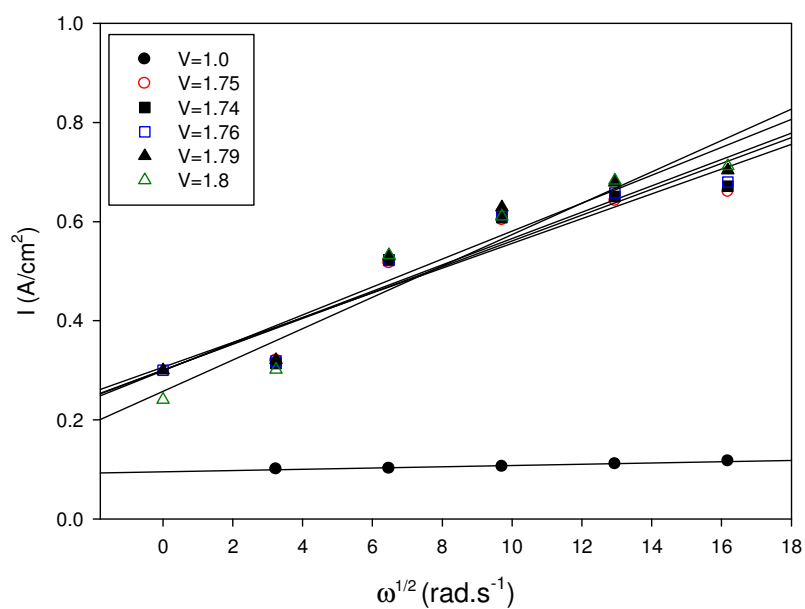


Figure D.11 Levich plot of Pt/Nb₂O₅-C in 1.0M H₂SO₄ at 20°C

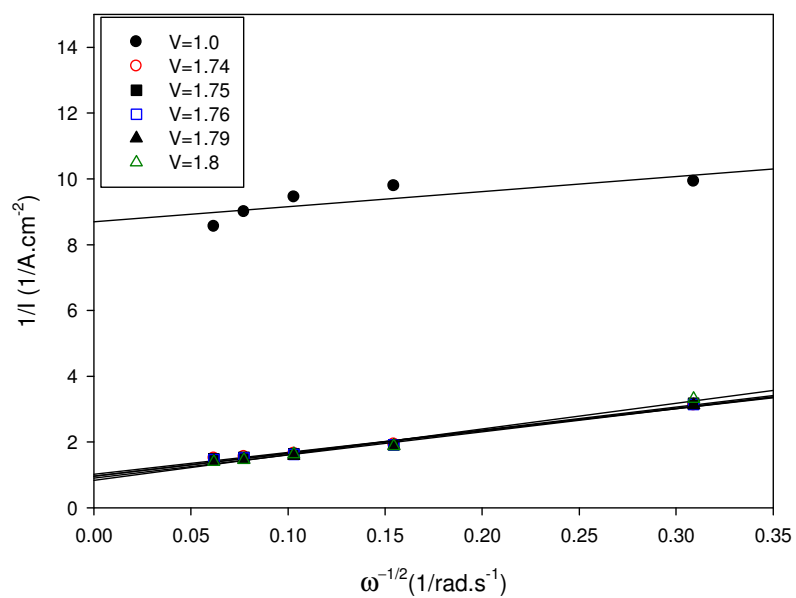


Figure D.12 Koutecky-Levich plot of Pt/Nb₂O₅-C in 1.0M H₂SO₄ at 20°C

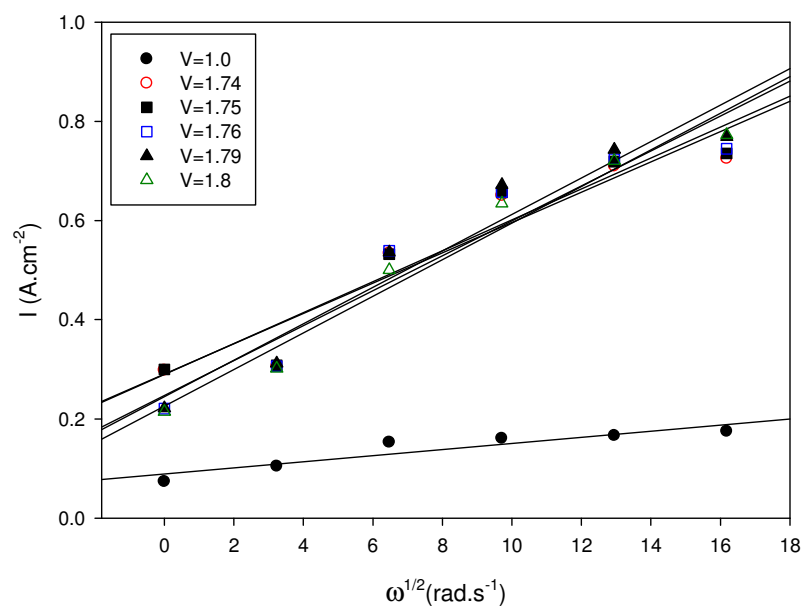


Figure D.13 Levich plot of Pt/Nb₂O₅-C in 1.5M H₂SO₄ at 20°C

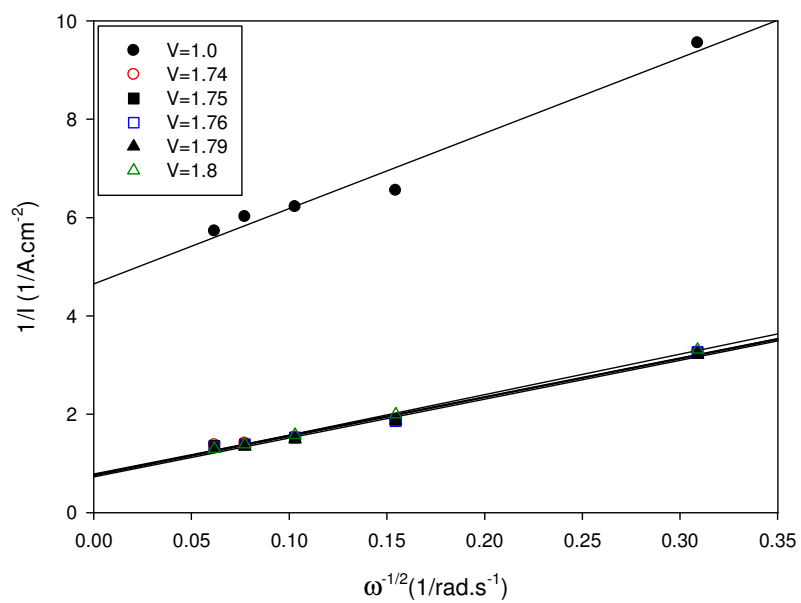


Figure D.14 Koutecky-Levich plot of Pt/Nb₂O₅-C in 1.5M H₂SO₄ at 20°C

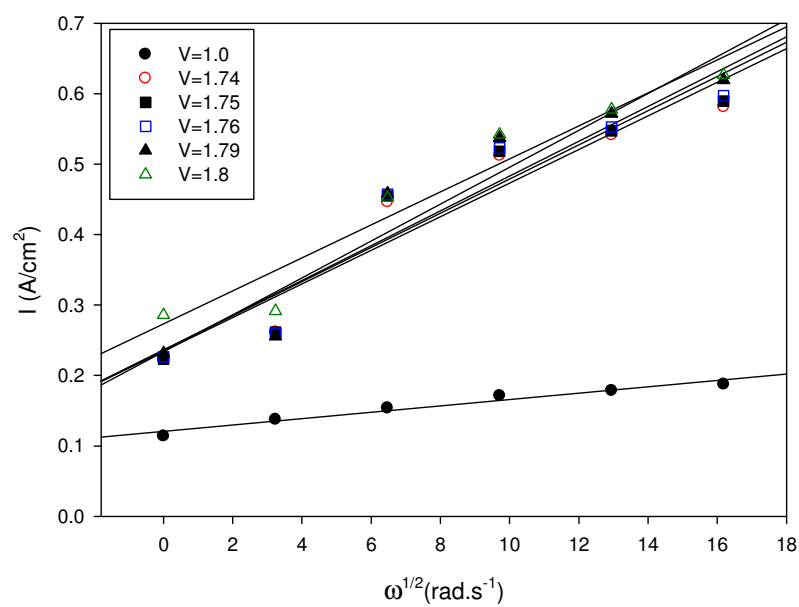


Figure D.15 Levich plot of Pt/Nb₂O₅-C in 0.5M H₂SO₄ at 30°C

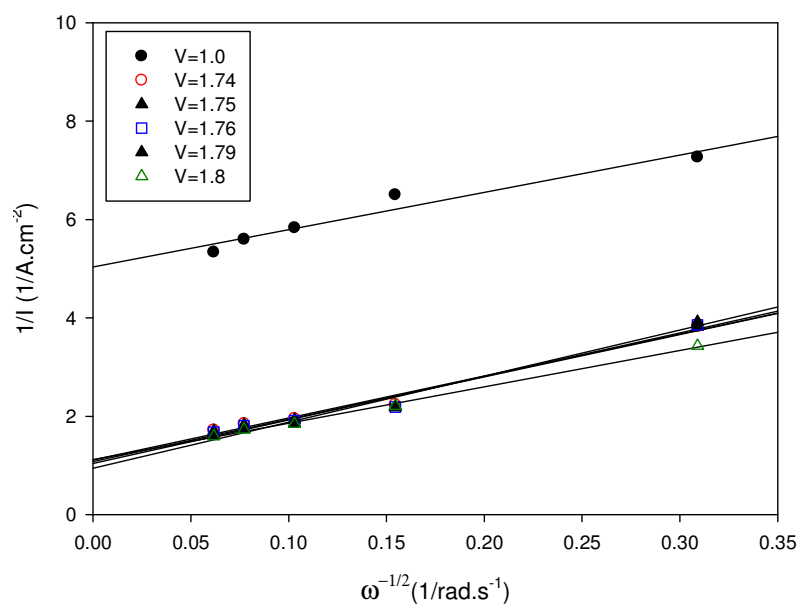


Figure D.16 Koutecky-Levich plot of Pt/Nb₂O₅-C in 0.5M H₂SO₄ at 30°C

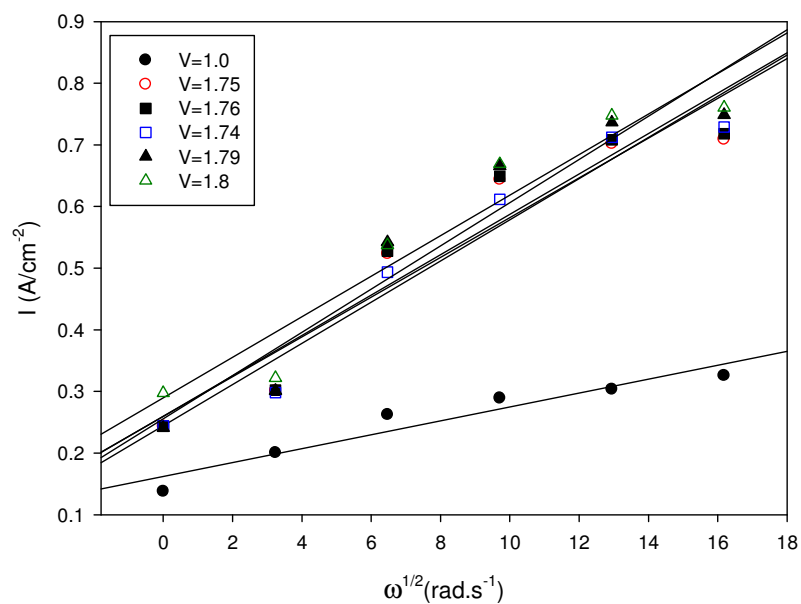


Figure D.17 Levich plot of Pt/Nb₂O₅-C in 1.0M H₂SO₄ at 30°C

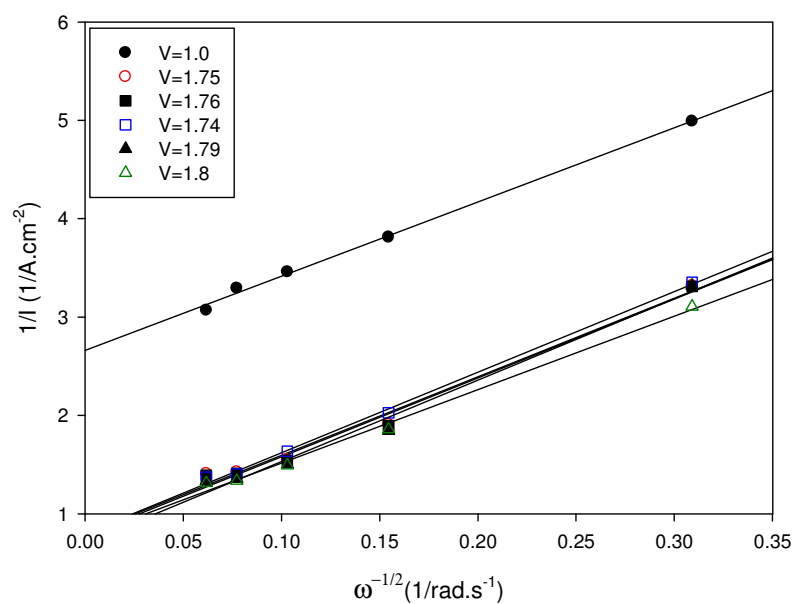


Figure D.18 Koutecky-Levich plot of Pt/Nb₂O₅-C in 1.0M H₂SO₄ at 30°C

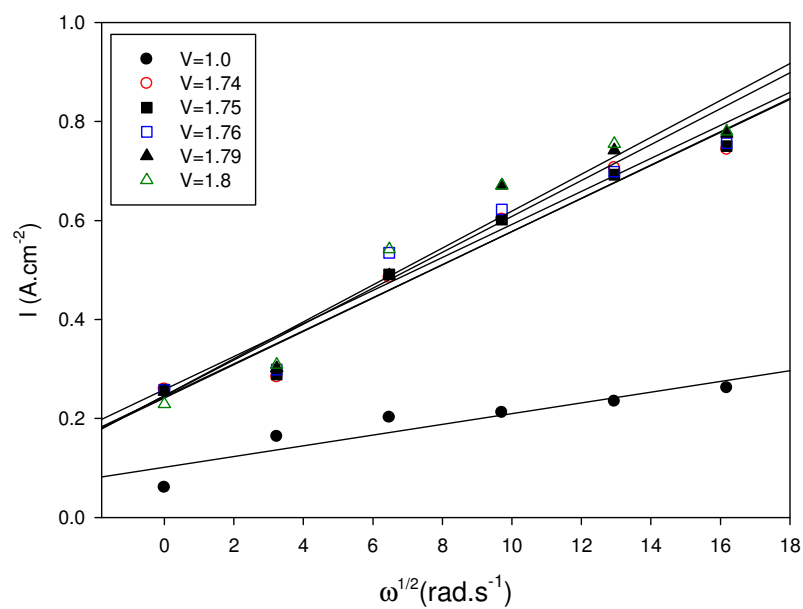


Figure D.19 Levich plot of Pt/Nb₂O₅-C in 1.5M H₂SO₄ at 30°C

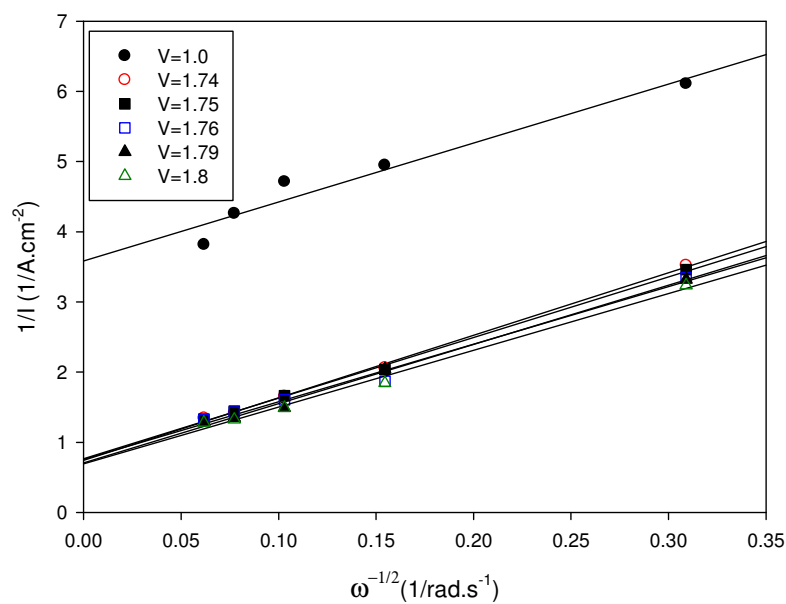


Figure D.20 Koutecky-Levich plot of Pt/Nb₂O₅-C in 1.5M H₂SO₄ at 30°C

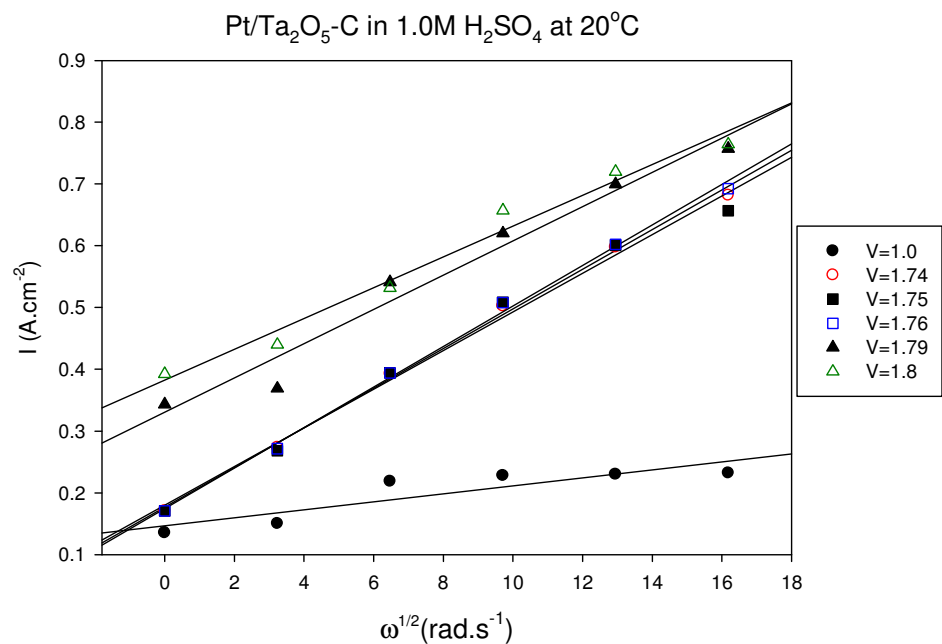


Figure D.21 Levich plot of Pt/Ta₂O₅-C in 1.0M H₂SO₄ at 20°C

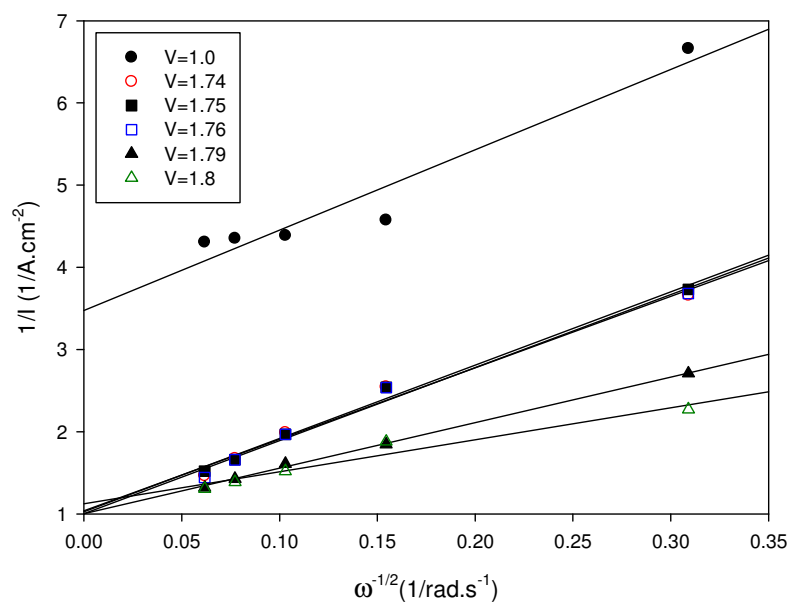


Figure D.22 Koutecky-Levich plot of Pt/Ta₂O₅-C in 1.0M H₂SO₄ at 20°C

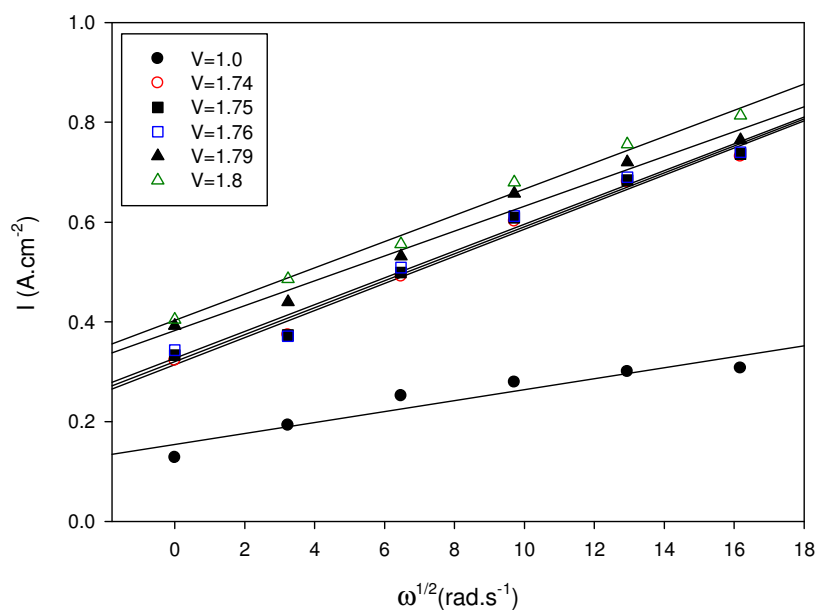


Figure D.23 Levich plot of Pt/Ta₂O₅-C in 1.5M H₂SO₄ at 20°C

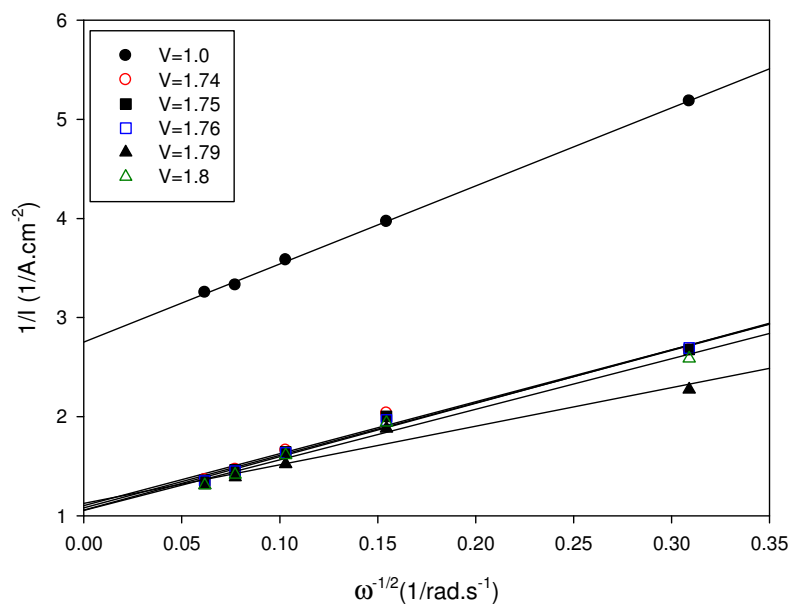


Figure D.24 Koutecky-Levich plot of Pt/Ta₂O₅-C in 1.5M H₂SO₄ at 20°C

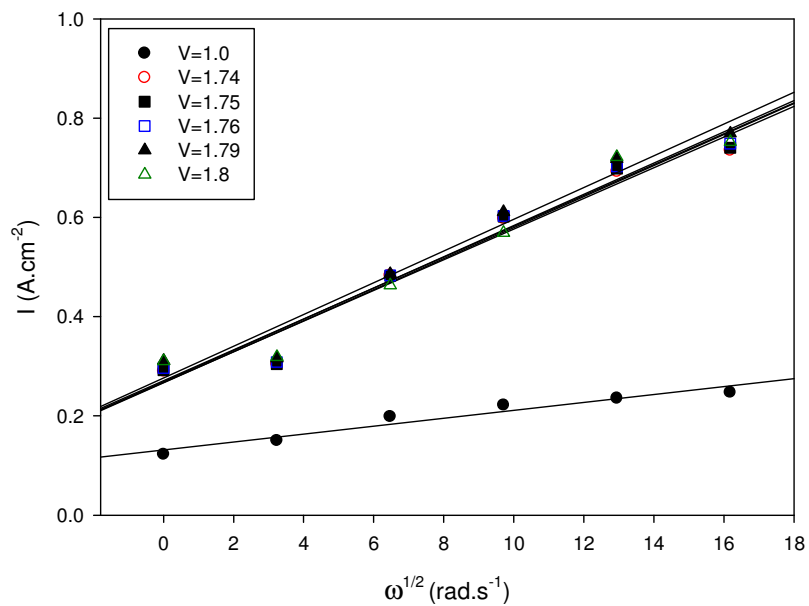


Figure D.25 Levich plot of Pt/Ta₂O₅-C in 0.5M H₂SO₄ at 30°C

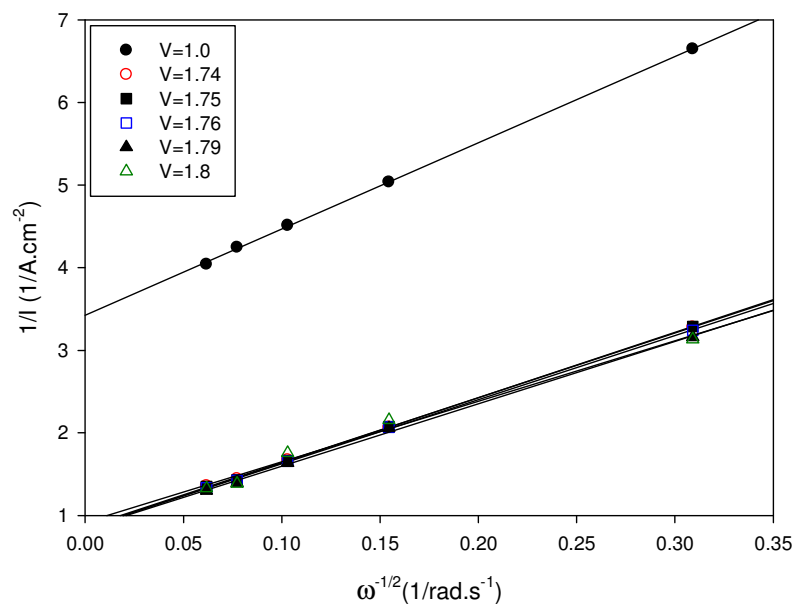


Figure D.26 Koutecky-Levich plot of Pt/Ta₂O₅-C in 0.5M H₂SO₄ at 30°C

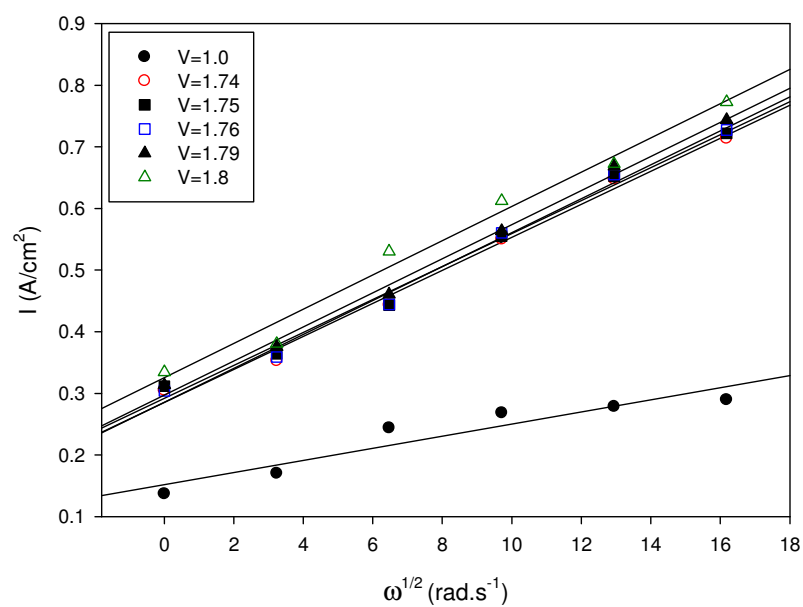


Figure D.27 Levich plot of Pt/Ta₂O₅-C in 1.0M H₂SO₄ at 30°C

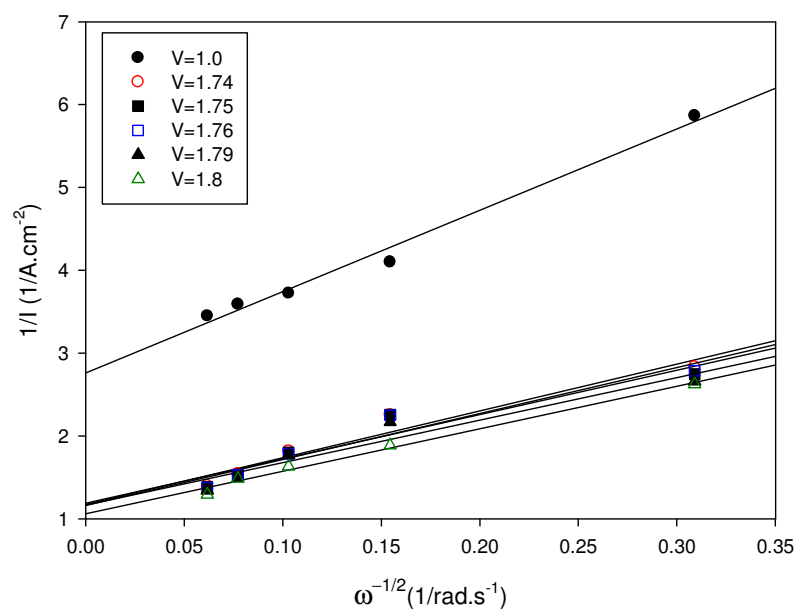


Figure D.28 Koutecky-Levich plot of Pt/Ta₂O₅-C in 1.0M H₂SO₄ at 30°C

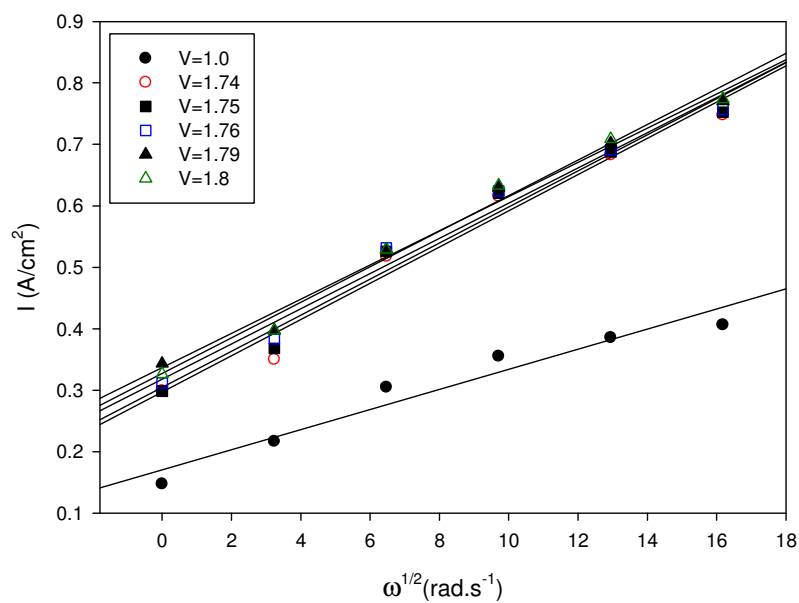


Figure D.29 Levich plot of Pt/Ta₂O₅-C in 1.5M H₂SO₄ at 30°C

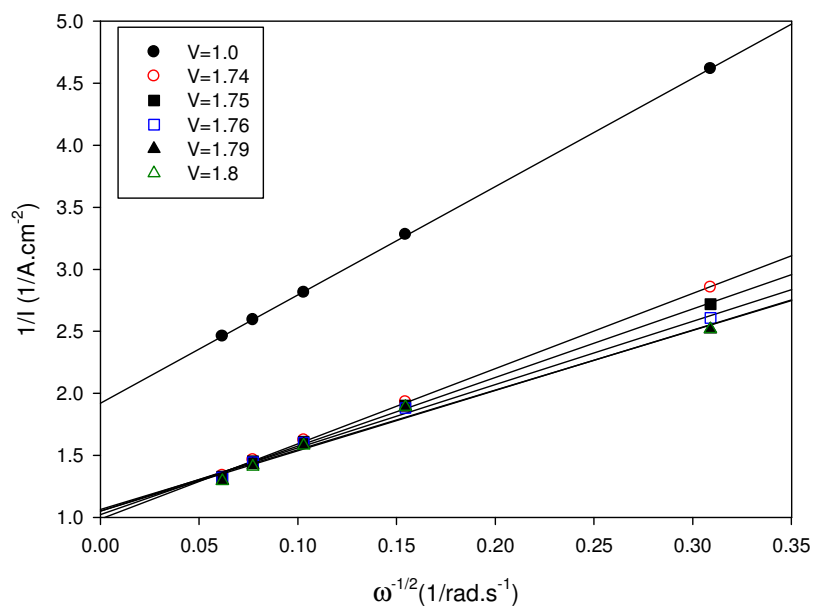


Figure D.30 Koutecky-Levich plot of Pt/Ta₂O₅-C in 1.5M H₂SO₄ at 30°C

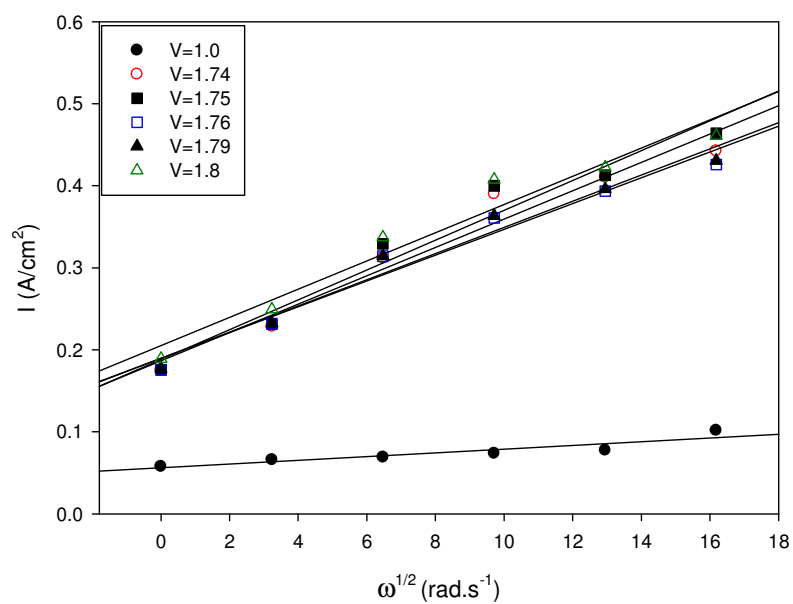


Figure D.31 Levich plot of Pt/ZrO₂-C in 1.0M H₂SO₄ at 20°C

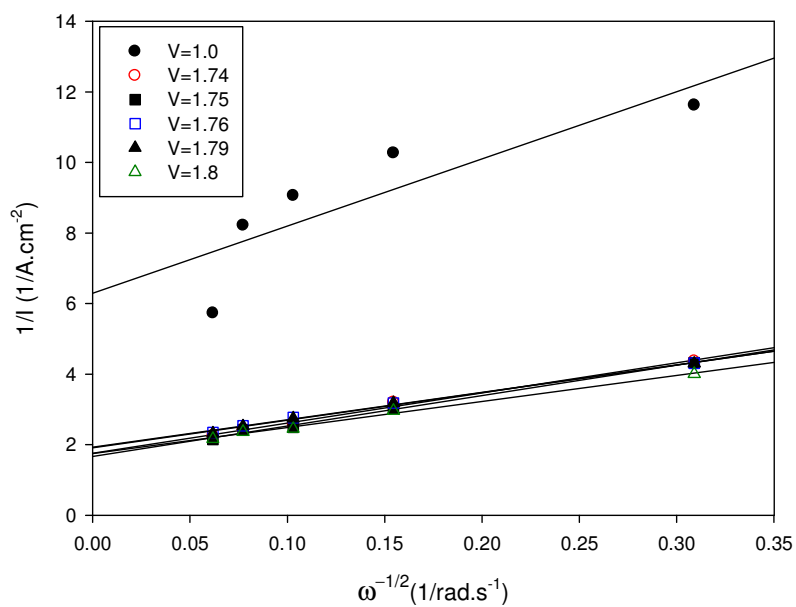


Figure D.32 Koutecky-Levich plot of Pt/ZrO₂-C in 1.0M H₂SO₄ at 20°C

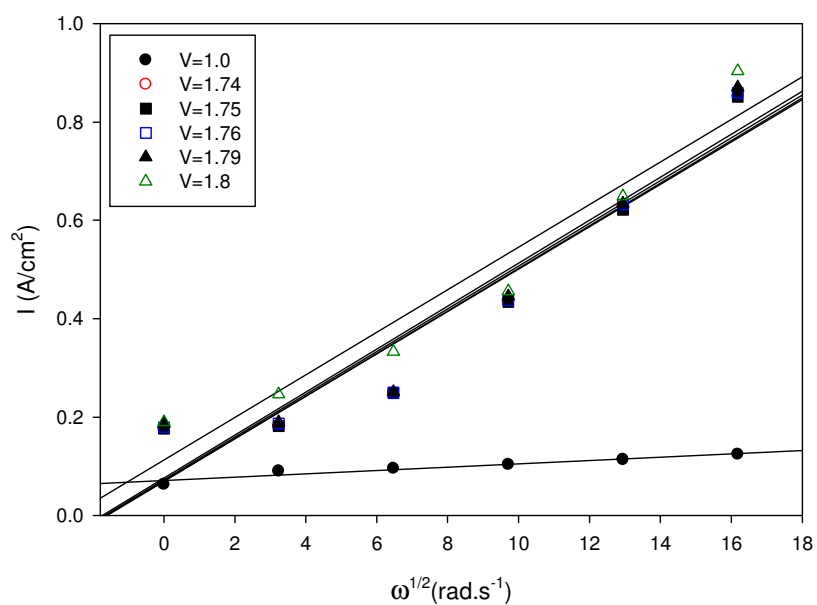


Figure D.33 Levich plot of Pt/ZrO₂-C in 1.5M H₂SO₄ at 20°C

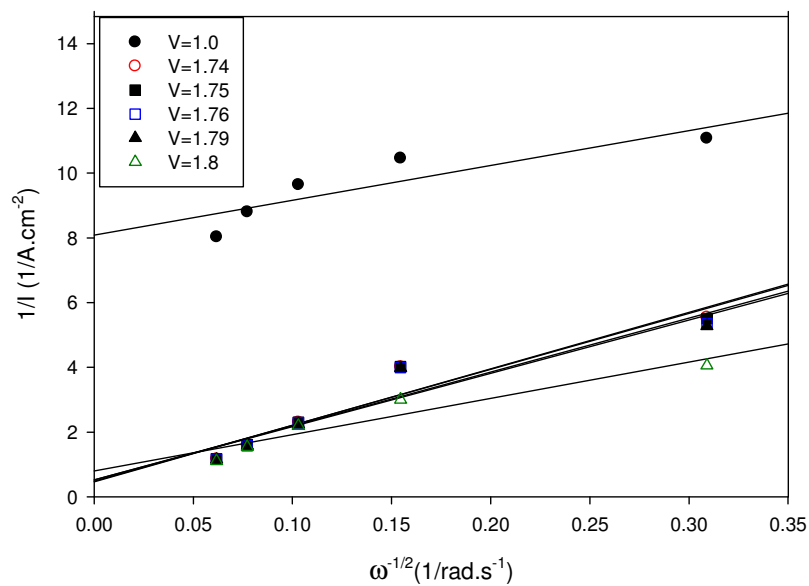


Figure D.34 Koutecky-Levich plot of Pt/ZrO₂-C in 1.5M H₂SO₄ at 20°C

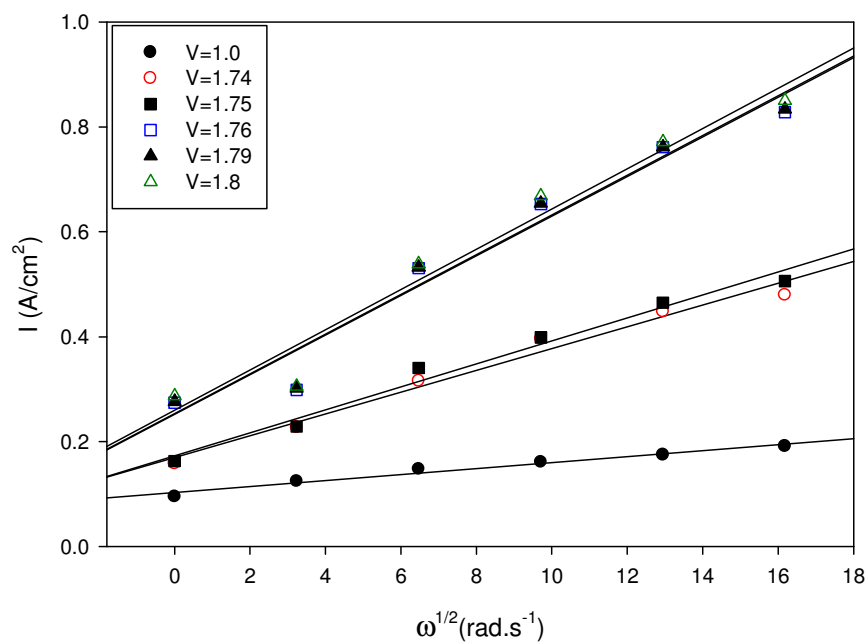


Figure D.35 Levich plot of Pt/ZrO₂-C in 0.5M H₂SO₄ at 30°C

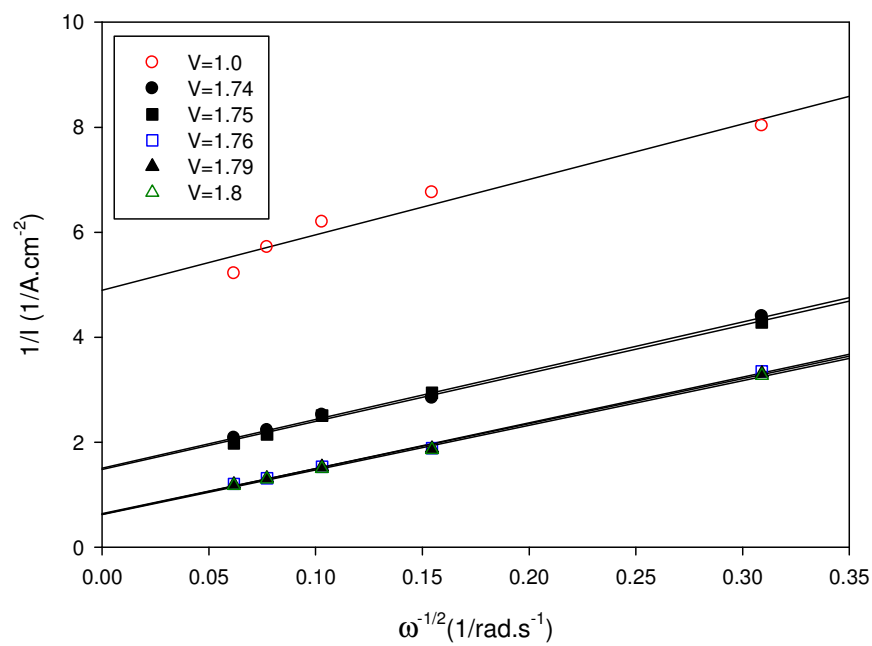


Figure D.36 Koutecky-Levich plot of Pt/ZrO₂-C in 0.5M H₂SO₄ at 30°C

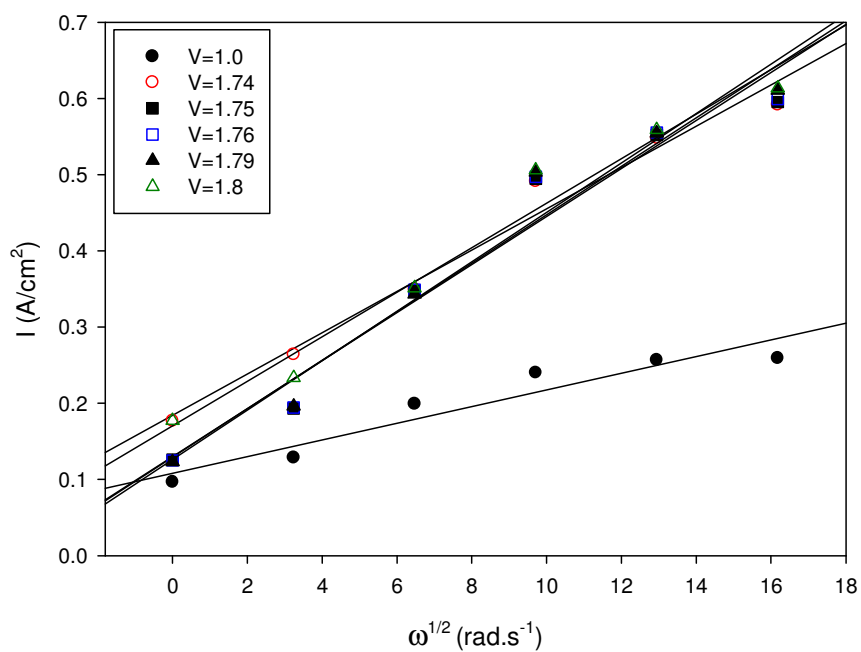


Figure D.37 Levich plot of Pt/ZrO₂-C in 1.0M H₂SO₄ at 30°C

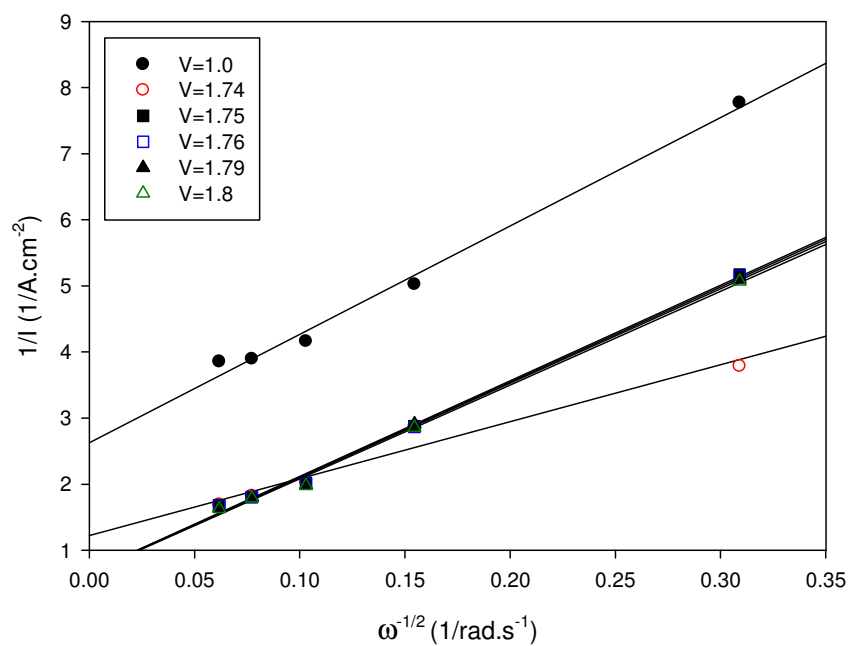


Figure D.38 Koutecky-Levich plot of Pt/ZrO₂-C in 1.0M H₂SO₄ at 30°C

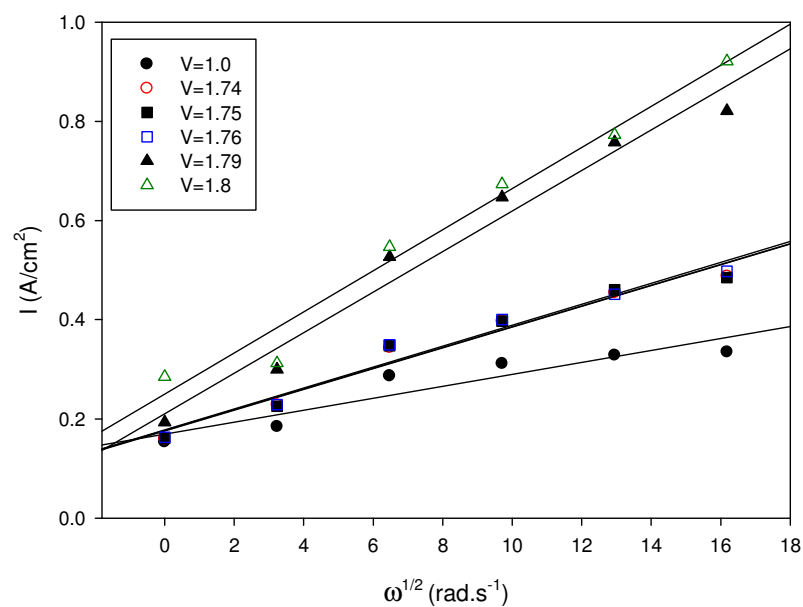


Figure D.39 Koutecky-Levich plot of Pt/ZrO₂-C in 1.5M H₂SO₄ at 30°C

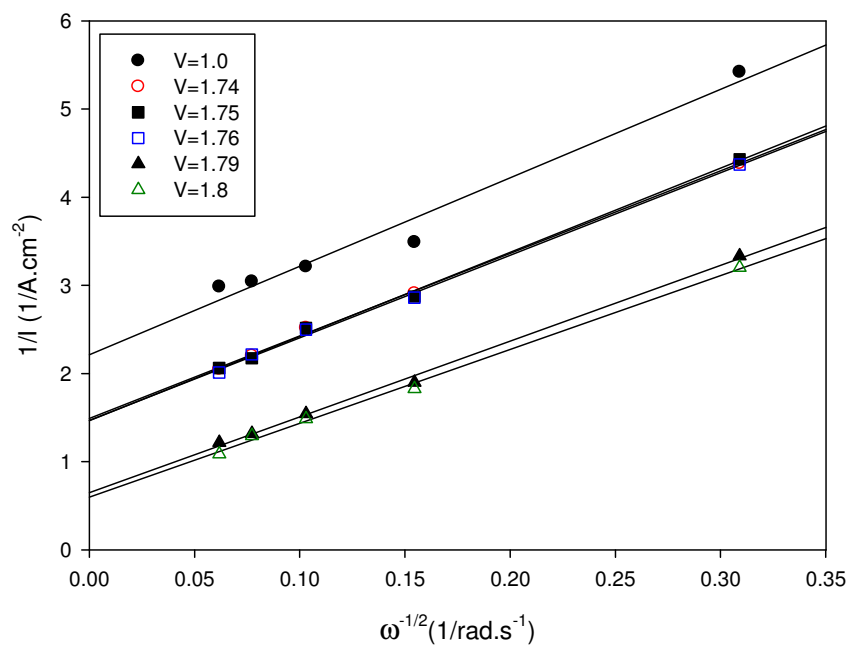


Figure D.40 Koutecky-Levich plot of Pt/ZrO₂-C in 1.5M H₂SO₄ at 30°C

Calculation of number of electrons transferred and heterogeneous rate constant

$$I_{\text{lim,c}} = 0.620nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C_o^b$$

$$n = \frac{0.620FAD^{2/3}\nu^{-1/6}C_o^b}{\text{Slope}}$$

$$F = A.s.mol^{-1}$$

$$A = 0.1964cm^{-2}$$

$$D = 2.1 \times 10^{-5} cm^2/s$$

$$\nu = 1.078 \times 10^{-4} cm^2/s$$

$$C = 0.15mol.cm^{-3}$$

Slope from the Levich plot regression line

$$\text{e.g. Slope} = 0.02637$$

Substitute all the values to calculate and determine the number of electrons transferred

$$n = 0.00430271$$

$$I_c = nFAk_hC_o^b$$

$$k_h = \frac{1}{nFAC_o^by}$$

y is the y intercept from the Koutecky – Levich plot regression line

$$\text{e.g. } y = 1.7$$

Substitute all the values to calculate and determine the heterogeneous rate constant

$$k_h = 0.048096709$$

Table E.1 Electrons transferred and heterogeneous rate constant over Pt/C at different temperatures and acid concentrations

Temperature (°C)	H ₂ SO ₄ Conc (mol.dm ⁻³)	Potential (V)	Number of electrons	k _h
20	0.5	1.74	0.00430271	0.048096709
	0.5	1.75	0.00432718	0.046859906
	0.5	1.77	0.0043386	0.046335945
	0.5	1.78	0.00432392	0.044952098
	0.5	1.8	0.0044055	0.043165713
	1	1.74	0.00445065	0.05395659
	1	1.75	0.00446714	0.053212649
	1	1.77	0.00453307	0.052086709
	1	1.78	0.00454956	0.049569233
	1	1.8	0.00461549	0.049819162
	1.5	1.74	0.00431469	0.056232668
	1.5	1.75	0.00433135	0.054880921
	1.5	1.77	0.004348	0.052540624
	1.5	1.78	0.00436466	0.051669061
	1.5	1.8	0.00441464	0.049807025
	0.5	1.74	0.00432392	0.048143963
	0.5	1.75	0.00437287	0.047325008
	0.5	1.77	0.00438918	0.046465759
	0.5	1.78	0.0044055	0.044612608
	0.5	1.8	0.00442182	0.041874682
30	1	1.74	0.00461549	0.051502242
	1	1.75	0.00445065	0.053773064
	1	1.77	0.00445065	0.051328834
	1	1.78	0.00461549	0.049176334
	1	1.8	0.00445065	0.052697603
	1.5	1.74	0.00466453	0.056285124
	1.5	1.75	0.00474782	0.05110267
	1.5	1.77	0.00478114	0.051818665
	1.5	1.78	0.0047978	0.052376435
	1.5	1.8	0.00483112	0.049203585

Table E.2 Electrons transferred and heterogeneous rate constant over Pt/Ta₂O₅-C at different temperatures and acid concentrations

Temperature (°C)	H ₂ SO ₄ Conc (mol.dm ⁻³)	Potential (V)	Number of electrons	k _h
20	0.5	1.74	0.004895	0.047913941
	0.5	1.75	0.00522133	0.045526338
	0.5	1.77	0.00522133	0.045836041
	0.5	1.78	0.00522133	0.045836041
	0.5	1.8	0.0053845	0.046669423
	1	1.74	0.00511001	0.06749693
	1	1.75	0.00511001	0.064342868
	1	1.77	0.00527485	0.063519432
	1	1.78	0.00527485	0.063519432
	1	1.8	0.00543969	0.059334248
	1.5	1.74	0.00483112	0.090912991
	1.5	1.75	0.00566407	0.05751138
	1.5	1.77	0.00616384	0.063137343
	1.5	1.78	0.00649702	0.064455631
	1.5	1.8	0.00658031	0.059338228
30	0.5	1.74	0.00515607	0.062598054
	0.5	1.75	0.00522133	0.06297101
	0.5	1.77	0.00571083	0.058670132
	0.5	1.78	0.005874	0.059299432
	0.5	1.8	0.005874	0.061885128
	1	1.74	0.0053845	0.044146752
	1	1.75	0.0053845	0.04444707
	1	1.77	0.00554767	0.043139803
	1	1.78	0.00554767	0.044038549
	1	1.8	0.00571083	0.043690524
	1.5	1.74	0.00560453	0.061541318
	1.5	1.75	0.00659356	0.049865722
	1.5	1.77	0.00576937	0.059202577
	1.5	1.78	0.00576937	0.059782995
	1.5	1.8	0.0059342	0.058697825

Table E.3 Electrons transferred and heterogeneous rate constant over Pt/Nb₂O₅-C at different temperatures and acid concentrations

Temperature (°C)	H ₂ SO ₄ Conc (mol.dm ⁻³)	Potential (V)	Number of electrons	k _h
20	0.5	1.74	0.00456867	0.052742842
	0.5	1.75	0.00465025	0.046989809
	0.5	1.77	0.00468288	0.048468638
	0.5	1.78	0.00465025	0.050435728
	0.5	1.8	0.00473183	0.044520491
	1	1.74	0.00456604	0.046414965
	1	1.75	0.00473253	0.048587132
	1	1.77	0.00453307	0.052086709
	1	1.78	0.00454956	0.052248651
	1	1.8	0.00461549	0.052029569
	1.5	1.74	0.00474782	0.047499277
	1.5	1.75	0.00481446	0.045670801
	1.5	1.77	0.00481446	0.047450183
	1.5	1.78	0.00499771	0.048884673
	1.5	1.8	0.0051643	0.049009465
	0.5	1.74	0.00473183	0.047056468
	0.5	1.75	0.00481342	0.047460431
	0.5	1.77	0.00484605	0.049051947
30	0.5	1.78	0.00481342	0.051471171
	0.5	1.8	0.004895	0.052080371
	1	1.74	0.00473088	0.053117295
	1	1.75	0.00476385	0.050237811
	1	1.77	0.00476385	0.050237811
	1	1.78	0.00478033	0.049726303
	1	1.8	0.00478033	0.049063285
	1.5	1.74	0.00483112	0.049203585
	1.5	1.75	0.00491441	0.052637534
	1.5	1.77	0.00494773	0.051525347
	1.5	1.78	0.00496439	0.048873359
	1.5	1.8	0.00483112	0.054344258

Table E.4 Electrons transferred and heterogeneous rate constant over Pt/ZrO₂-C at different temperatures and acid concentrations

Temperature (°C)	H ₂ SO ₄ Conc (mol.dm ⁻³)	Potential (V)	Number of electrons	k _h
20	0.5	1.74	0.0017139	0.10314938
	0.5	1.75	0.00163819	0.113028275
	0.5	1.77	0.00180136	0.104996232
	0.5	1.78	0.00180136	0.109775387
	0.5	1.8	0.00196453	0.10065783
	1	1.74	0.00181323	0.10961751
	1	1.75	0.00181323	0.110235326
	1	1.77	0.00197807	0.101049049
	1	1.78	0.00197807	0.099968754
	1	1.8	0.00214291	0.088265216
	1.5	1.74	0.00191579	0.191991819
	1.5	1.75	0.00200575	0.138110358
	1.5	1.77	0.00216567	0.131006071
	1.5	1.78	0.00216567	0.110508522
	1.5	1.8	0.00233893	0.104454429
	0.5	1.74	0.00187642	0.106876595
30	0.5	1.75	0.00212117	0.093703927
	0.5	1.77	0.00212117	0.094232053
	0.5	1.78	0.00228433	0.087501192
	0.5	1.8	0.00277383	0.071289428
	1	1.74	0.00224181	0.106034028
	1	1.75	0.00225829	0.105976112
	1	1.77	0.00225829	0.105976112
	1	1.78	0.00224181	0.108979418
	1	1.8	0.00227478	0.109685112
	1.5	1.74	0.00216567	0.123590633
	1.5	1.75	0.00233226	0.115148193
	1.5	1.77	0.00233893	0.113093517
	1.5	1.78	0.00233893	0.114470607
	1.5	1.8	0.00227895	0.117447239

APPENDIX E

Linear polarisation scans at different rotation speeds

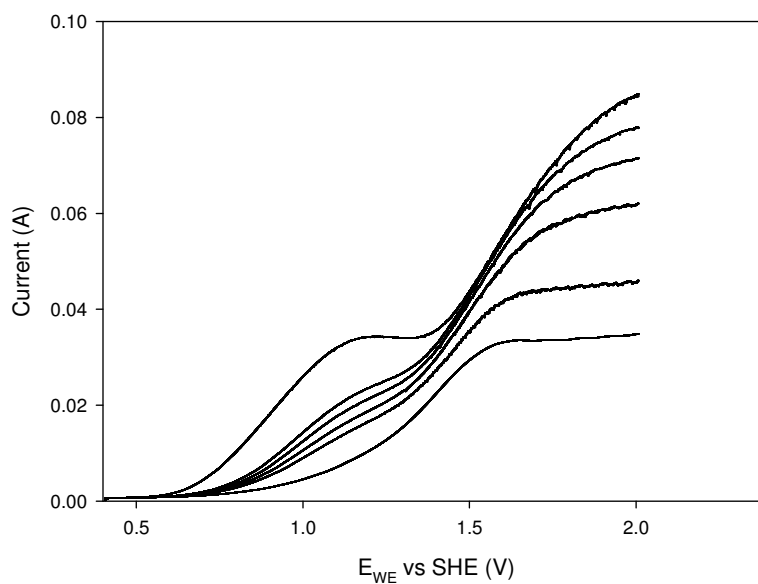


Figure F.1 LP scan of Pt/C at different rotation speeds in 0.5M H₂SO₄ at 20°C

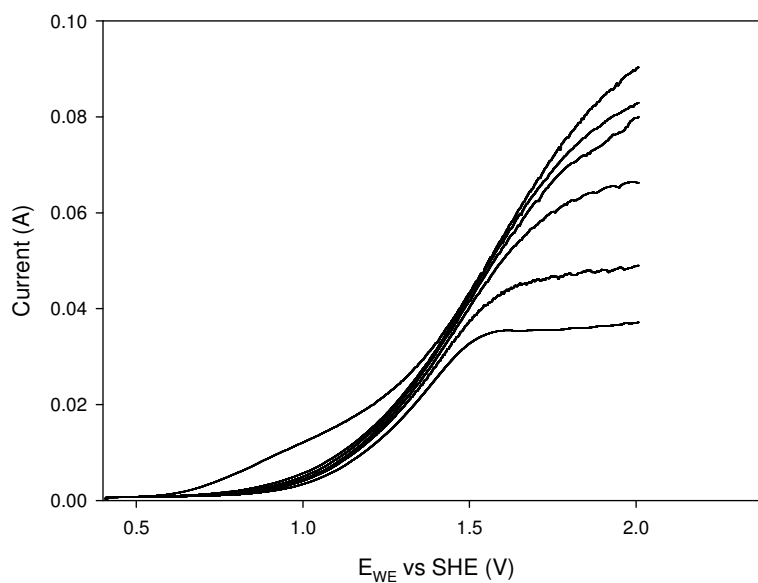


Figure F.2 LP scan of Pt/ZrO₂-C at different rotation speeds in 0.5M H₂SO₄ at 20°C

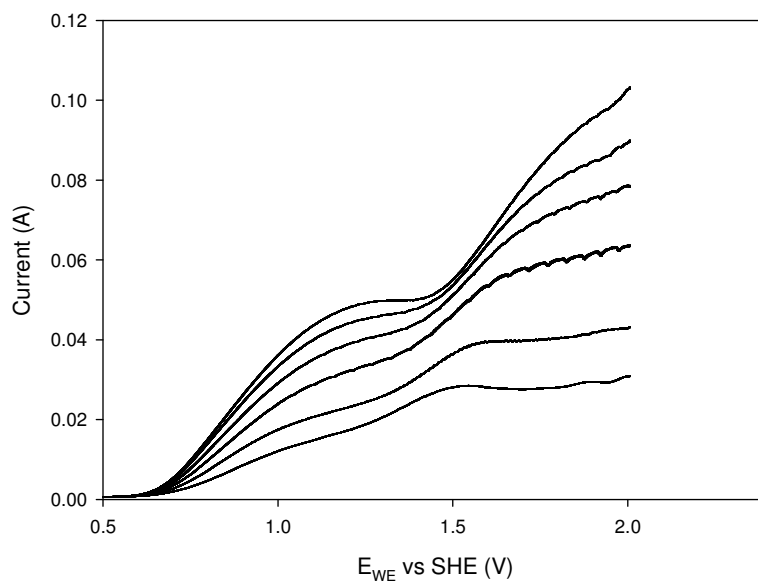


Figure F.3 LP scan of Pt/Ta₂O₅-C at different rotation speeds in 0.5M H₂SO₄ at 20°C

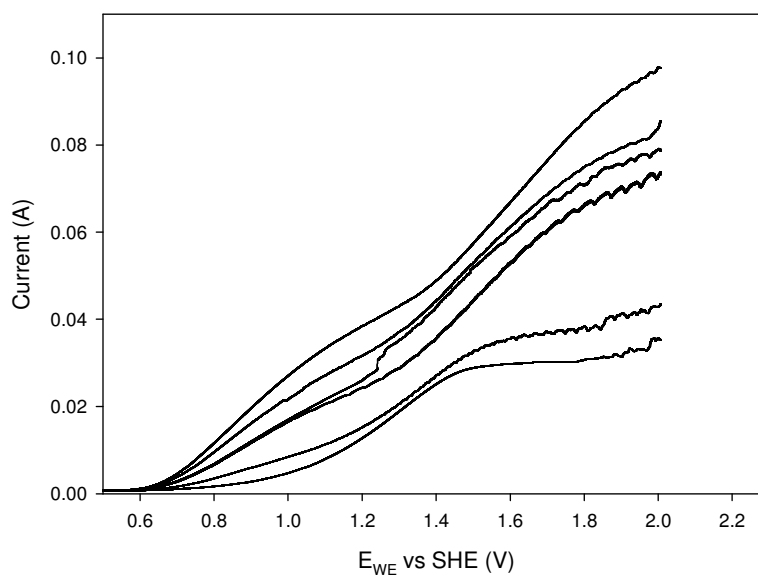


Figure F.4 LP scan of Pt/Nb₂O₅-C at different rotation speeds in 0.5M H₂SO₄ at 20°C

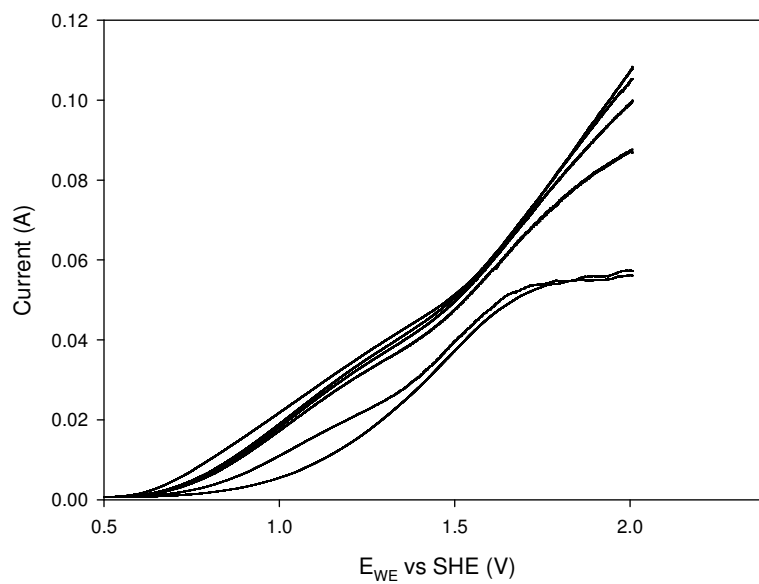


Figure F.5 LP scan of Pt/C at different rotation speeds in 0.5M H₂SO₄ at 30°C

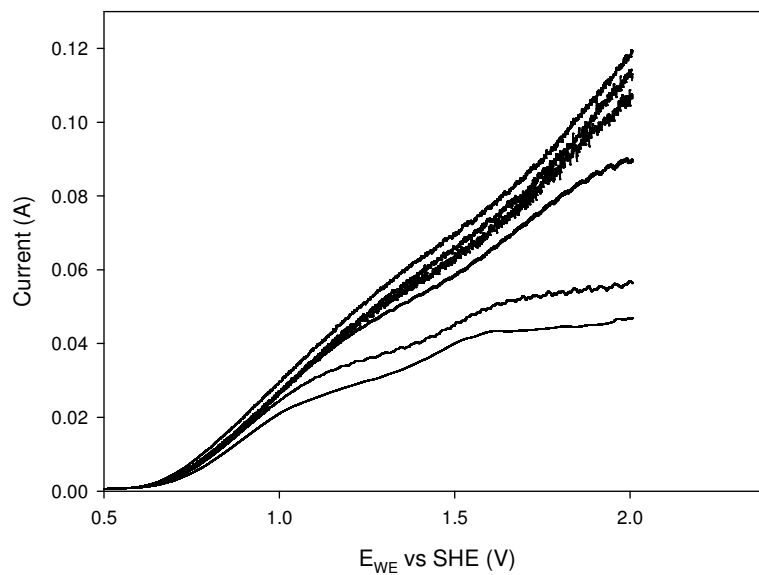


Figure F.6 LP scan of Pt/Nb₂O₅-C at different rotation speeds in 0.5M H₂SO₄ at 30°C

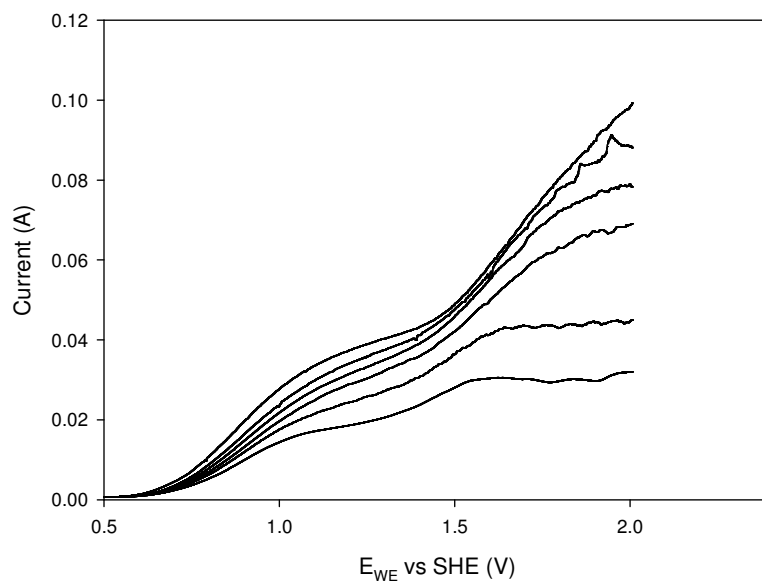


Figure F.7 LP scan of Pt/ZrO₂-C at different rotation speeds in 0.5M H₂SO₄ at 30°C

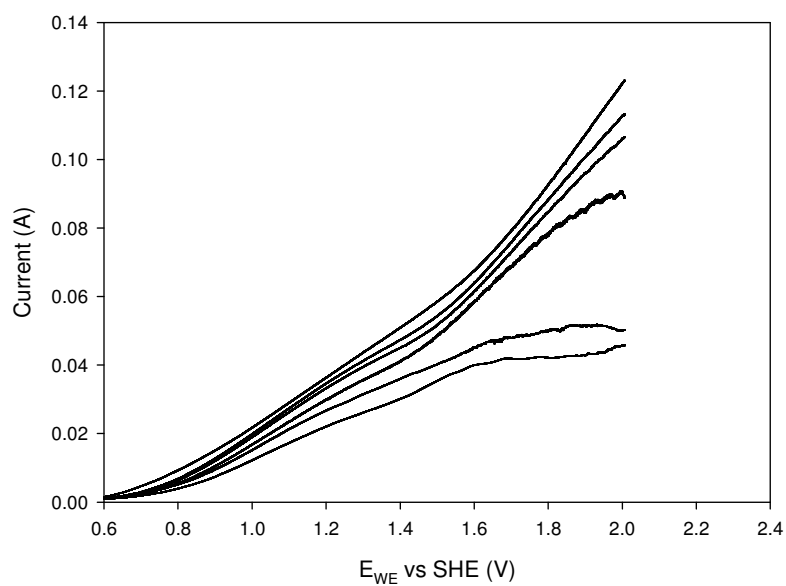


Figure F.8 LP scan of Pt/ Ta₂O₅-C at different rotation speeds in 0.5M H₂SO₄ at 30°C

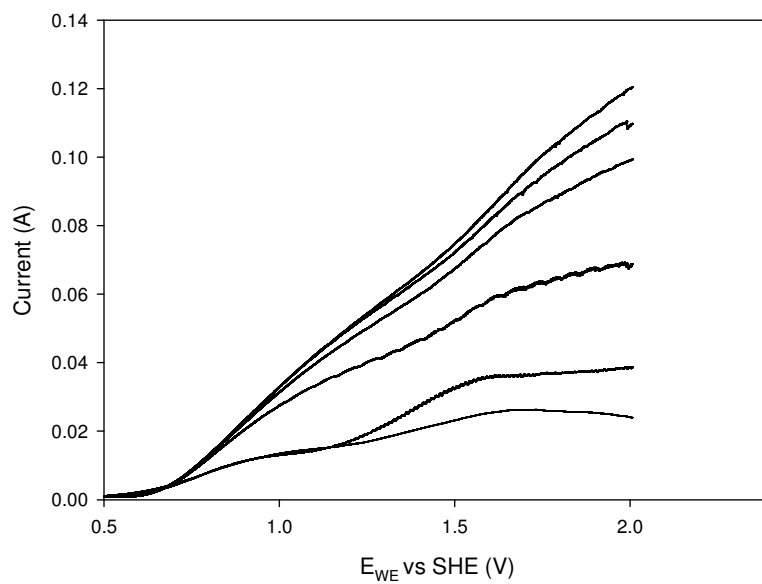


Figure F.9 LP scan of Pt/C at different rotation speeds in 1.0M H₂SO₄ at 20°C

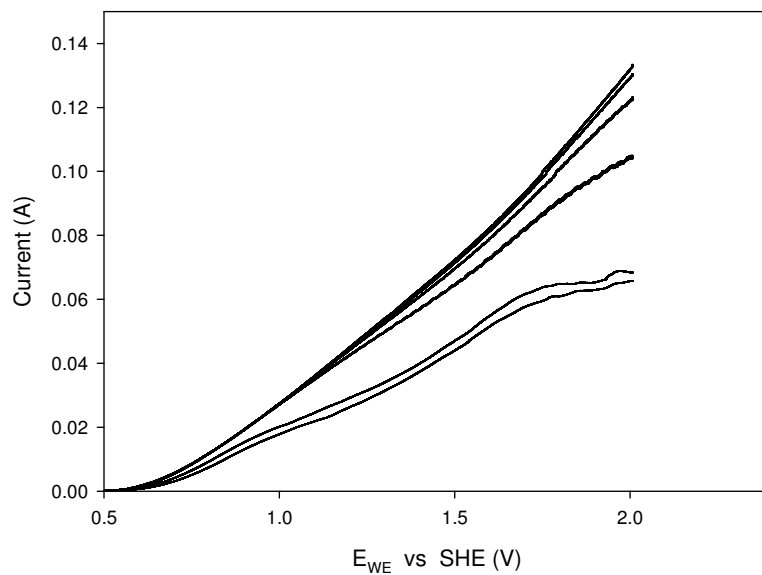


Figure F.10 LP scan of Pt/Nb₂O₅-C at different rotation speeds in 1.0M H₂SO₄ at 20°C

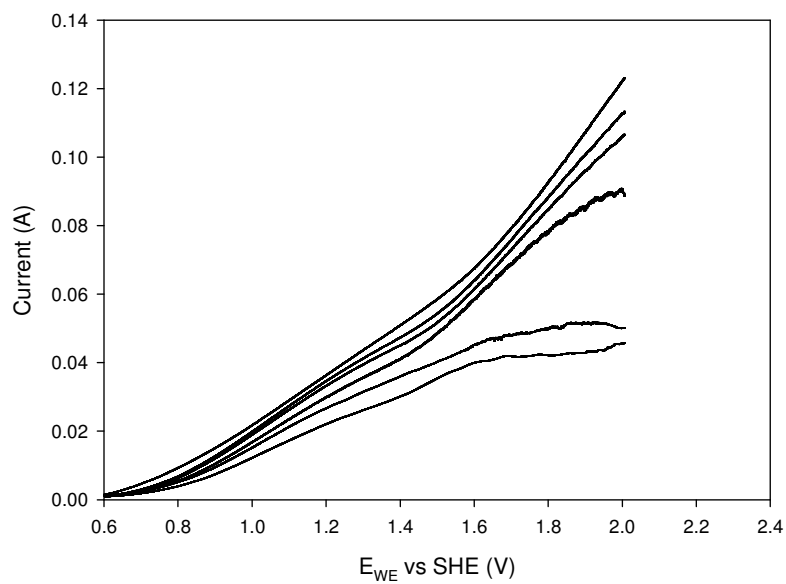


Figure F.11 LP scan of Pt/ZrO₂-C at different rotation speeds in 1.0M H₂SO₄ at 20°C

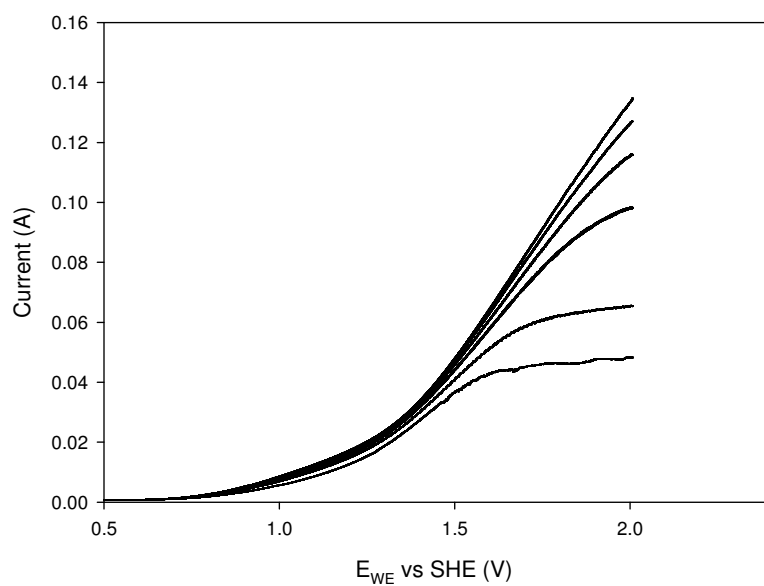


Figure F.12 LP scan of Pt/Ta₂O₅-C at different rotation speeds in 1.0M H₂SO₄ at 20°C

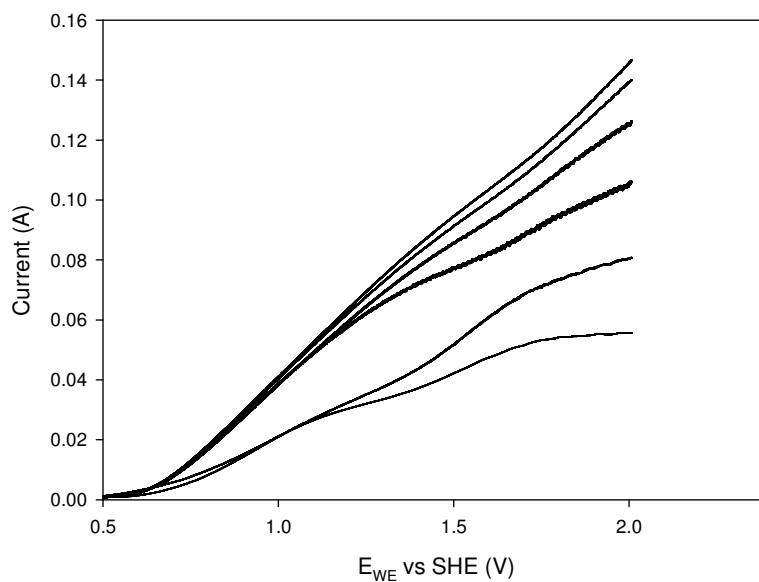


Figure F.13 LP scan of Pt/C at different rotation speeds in 1.0M H₂SO₄ at 30°C

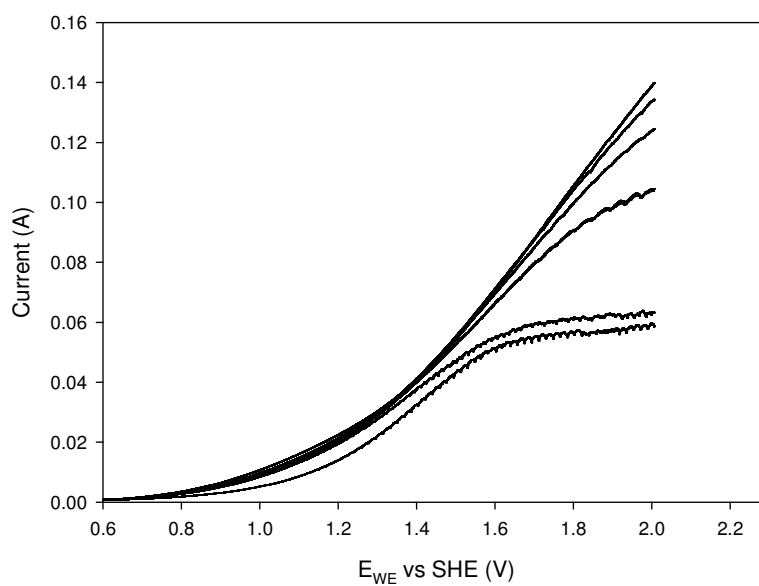


Figure F.14 LP scan of Pt/ZrO₂-C at different rotation speeds in 1.0M H₂SO₄ at 30°C

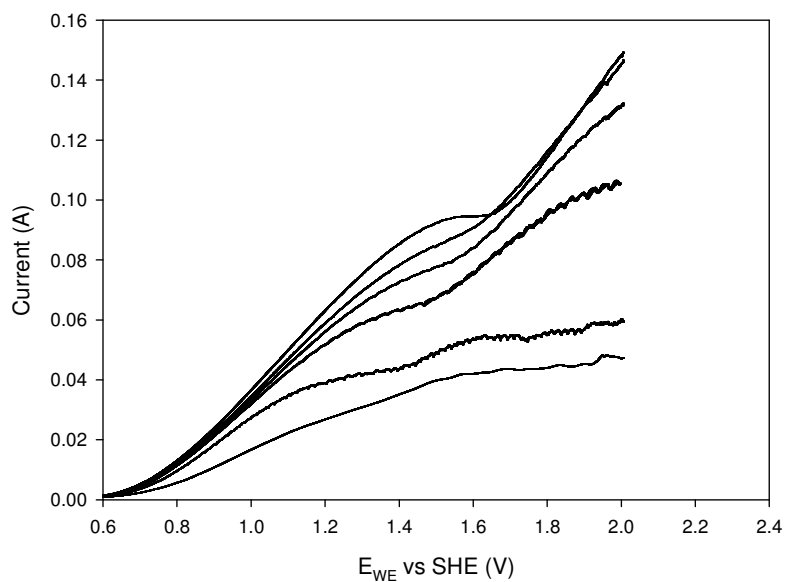


Figure F.15 LP scan of Pt/Ta₂O₅-C at different rotation speeds in 1.0M H₂SO₄ at 30°C

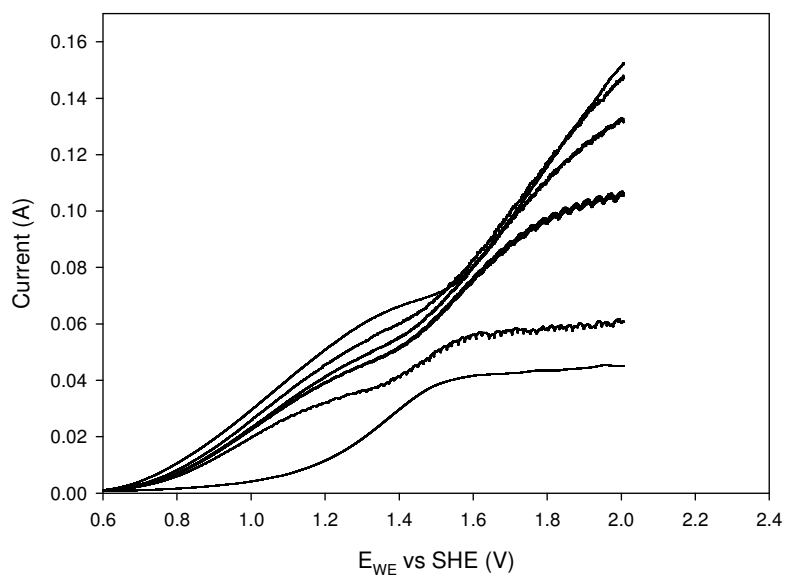


Figure F.16 LP scan of Pt/Nb₂O₅-C at different rotation speeds in 1.0M H₂SO₄ at 30°C

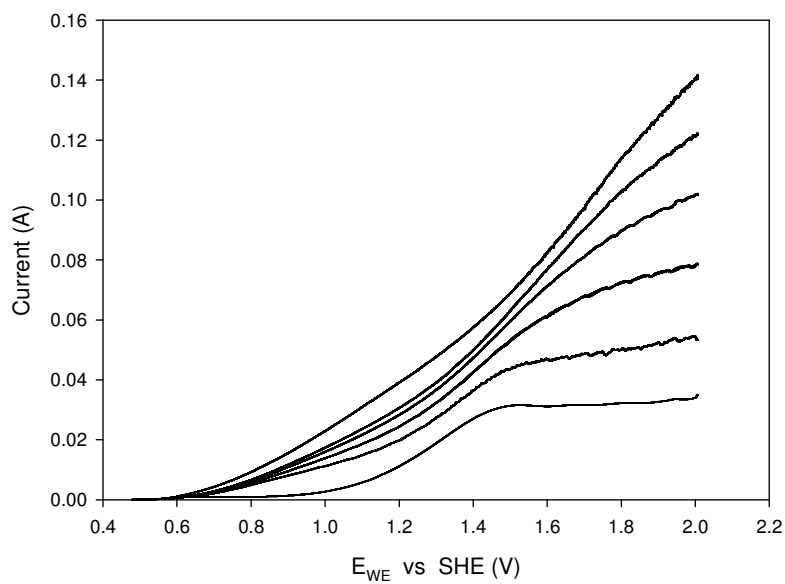


Figure F.17 LP scan of Pt/ZrO₂-C at different rotation speeds in 1.5M H₂SO₄ at 20°C

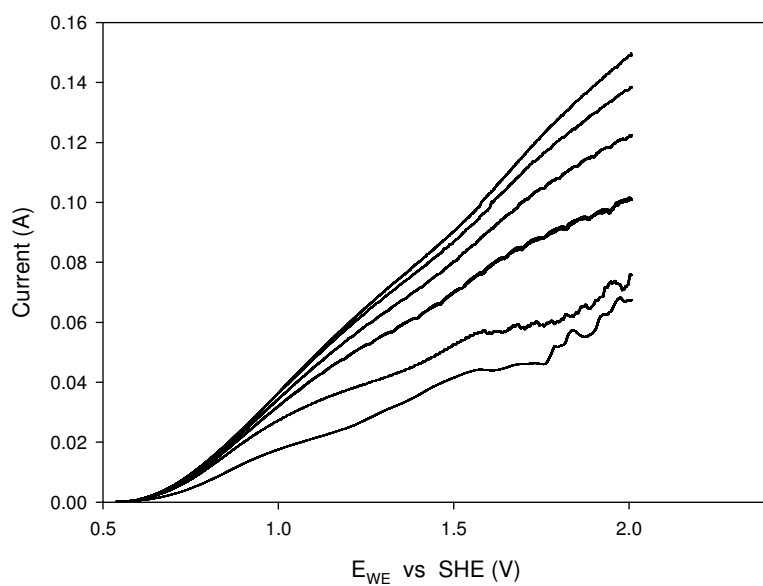


Figure F.18 LP scan of Pt/Ta₂O₅-C at different rotation speeds in 1.5M H₂SO₄ at 20°C

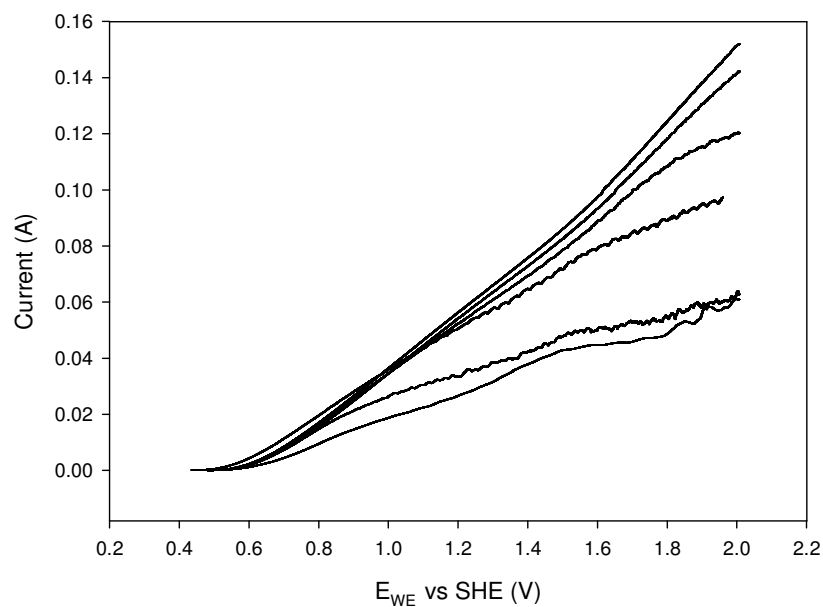


Figure F.19 LP scan of Pt/Nb₂O₅-C at different rotation speeds in 1.5M H₂SO₄ at 20°C

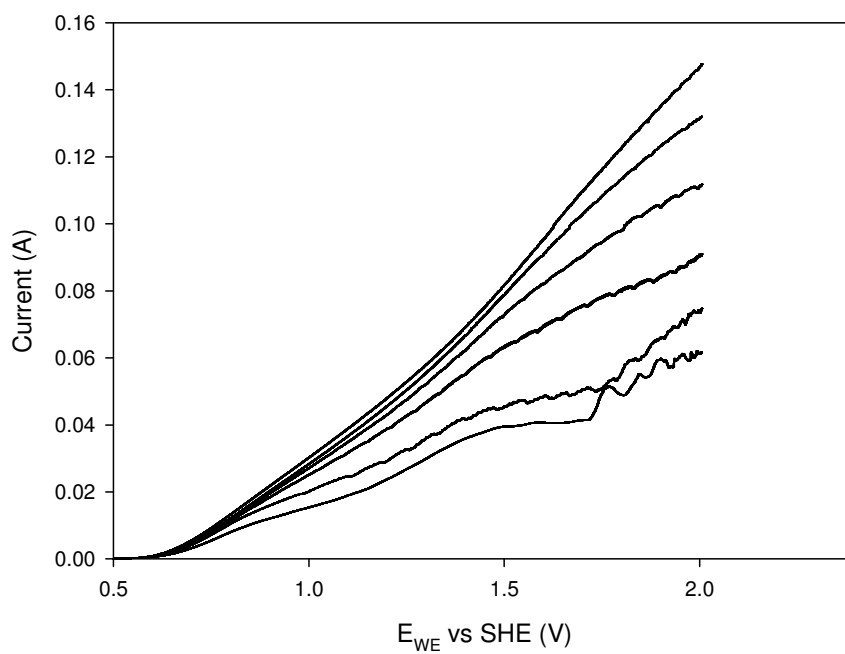


Figure F.20 LP scan of Pt/C at different rotation speeds in 1.5M H₂SO₄ at 20°C

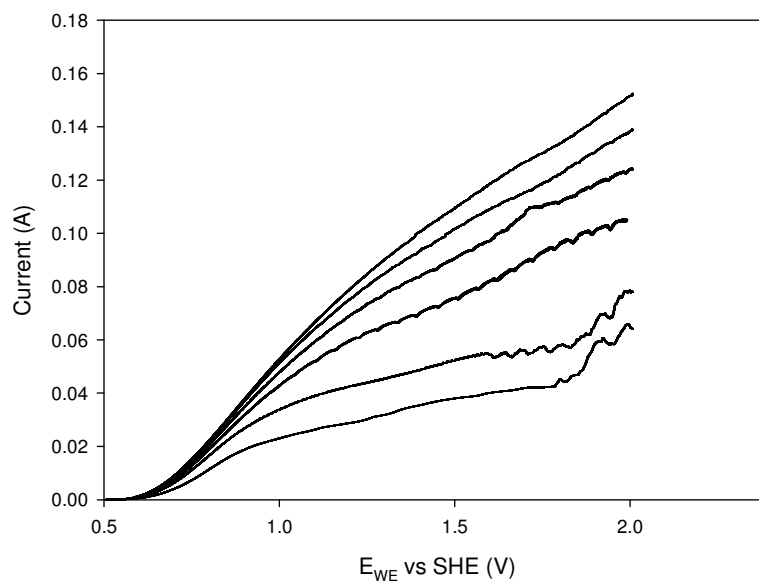


Figure F.21 LP scan of Pt/ZrO₂-C at different rotation speeds in 1.5M H₂SO₄ at 30°C

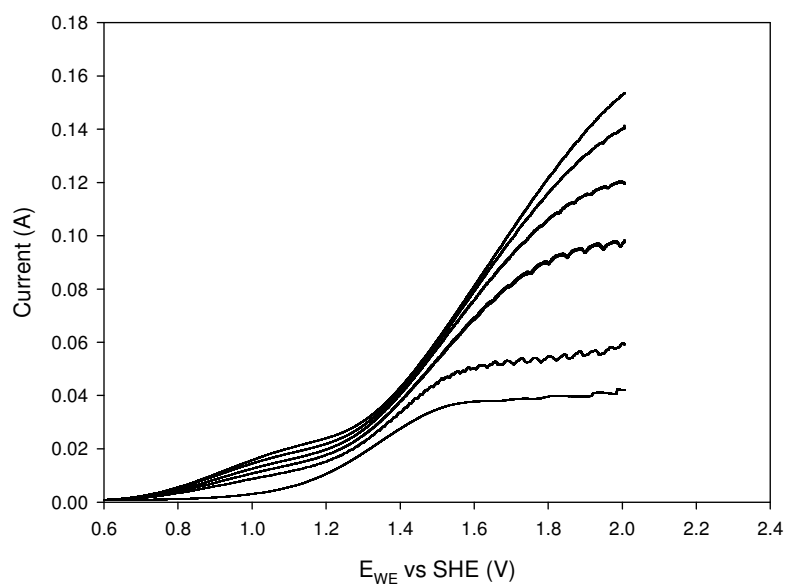


Figure F.22 LP scan of Pt/C at different rotation speeds in 1.5M H₂SO₄ at 30°C

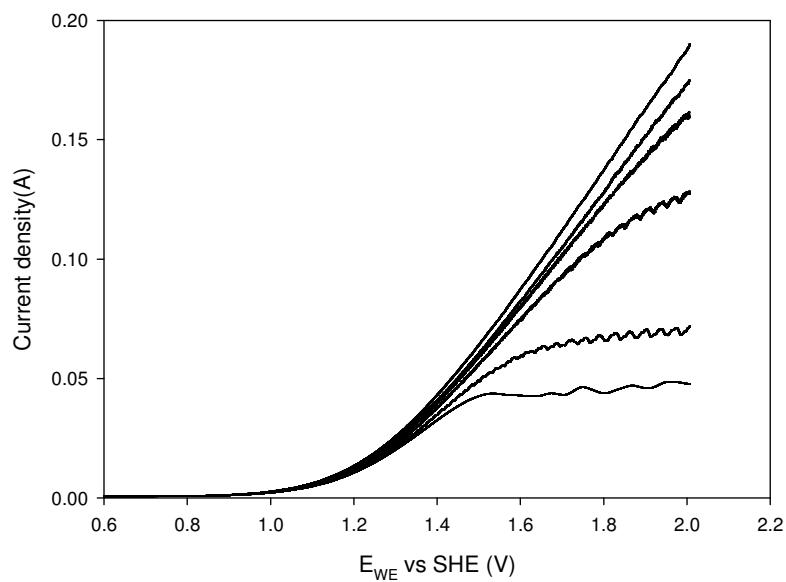


Figure F.23 LP scan of Pt/Ta₂O₅-C at different rotation speeds in 1.5M H₂SO₄ at 30°C

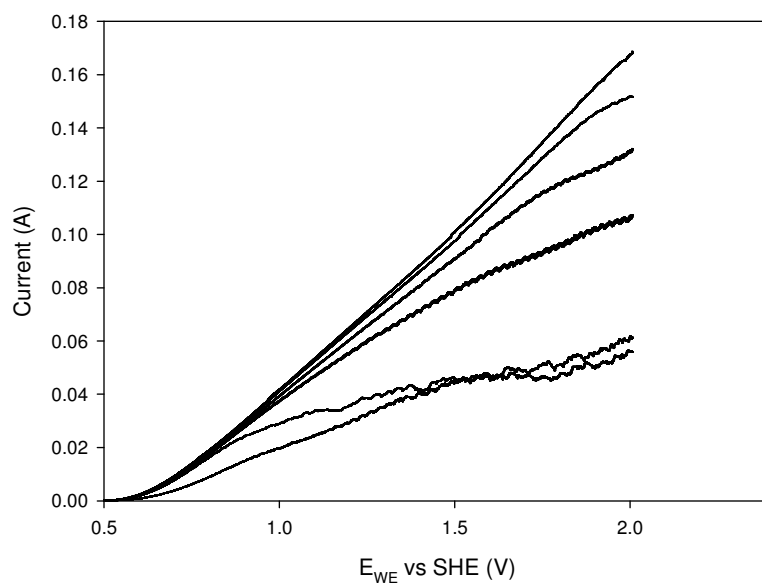


Figure F.24 LP scan of Pt/Nb₂O₅-C at different rotation speeds in 1.5M H₂SO₄ at 30°C