

## **Four electron selective O<sub>2</sub> reduction by a tetranuclear vanadium(IV/V)/hydroquinonate catalyst: Application on the operation of a Zn-air battery**

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**Figure S1.** Cyclic voltammogram of O<sub>2</sub> in aqueous solution of 0.2 M KNO<sub>3</sub> at 273 K recorded at pHs 5.8. Scan Rate 25 mV/s. Working electrode=glassy carbon. Page S3

**Figure S2.** Cyclic voltammograms of the complex **1** (2.5 mM) in A) deoxygenated and oxygenated aqueous solutions (red and black lines respectively) at pH=4.6 at scan Rate 25 mV/s. The solutions contained 0.2 M KNO<sub>3</sub> and measured at 273 K. Working electrode=glassy carbon. Page S4

**Figure S3.** A) RDE voltammetry curves of aqueous solution of **1** under Ar and O<sub>2</sub> in pH=4.9 at various rotation rates. B) Koutecky-Levich plots at 0.110 V under Ar and under O<sub>2</sub>, Scan rate: 25 mV s<sup>-1</sup>. Page S5

**Figure S4.** <sup>51</sup>V NMR spectra of an D<sub>2</sub>O solution of **1** (2.50 mM) and V<sup>IV</sup>OSO<sub>4</sub> (2.50 mM) at pD=3.0 and 4.6. Page S6

**Table S1.** RDE data of compound **1** at pH=2.5 under N<sub>2</sub>. Potentials vs Ag/AgCl.

Page S7

**Table S2.** RDE data of compound **1** at pH=2.5 under O<sub>2</sub>. Potentials vs Ag/AgCl.

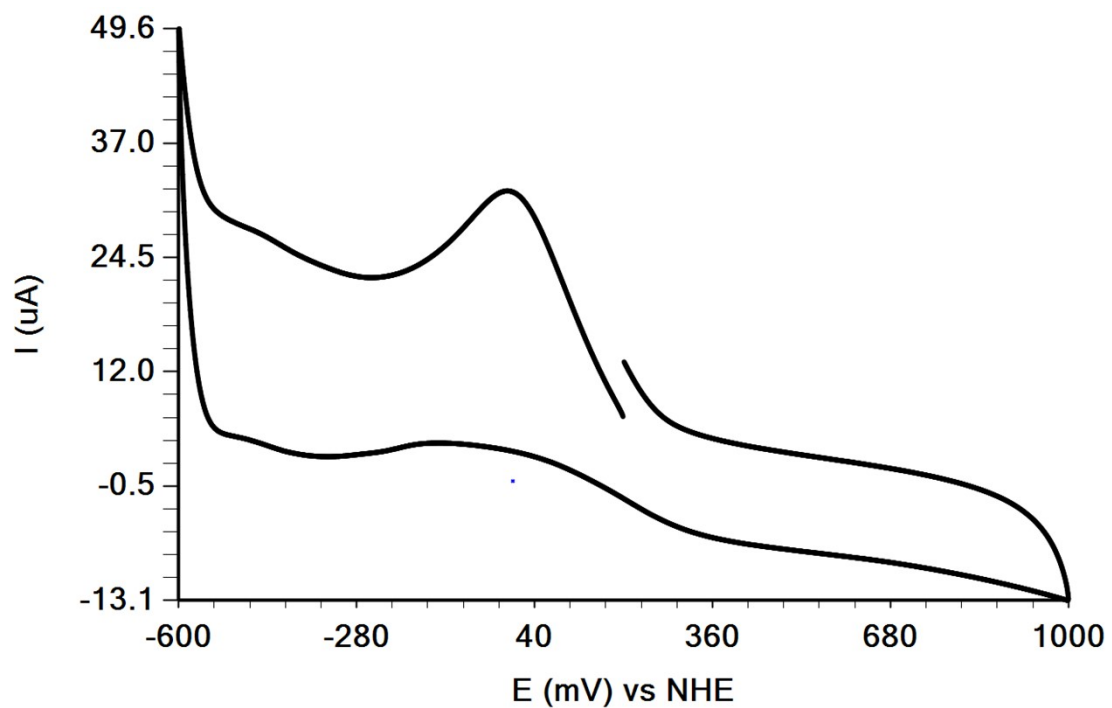
Page S129

**Table S3.** RDE data of compound **1** at pH=4.9 under N<sub>2</sub>. Potentials vs Ag/AgCl.

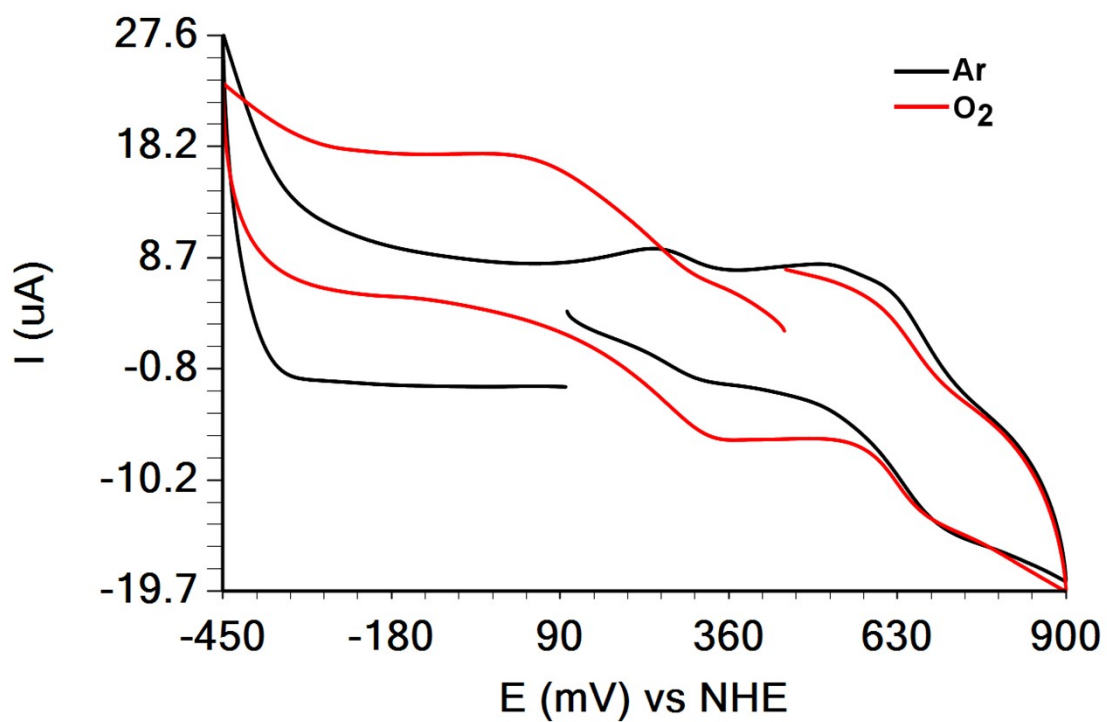
Page S251

**Table S4.** RDE data of compound **1** at pH=4.9 under O<sub>2</sub>. Potentials vs Ag/AgCl.

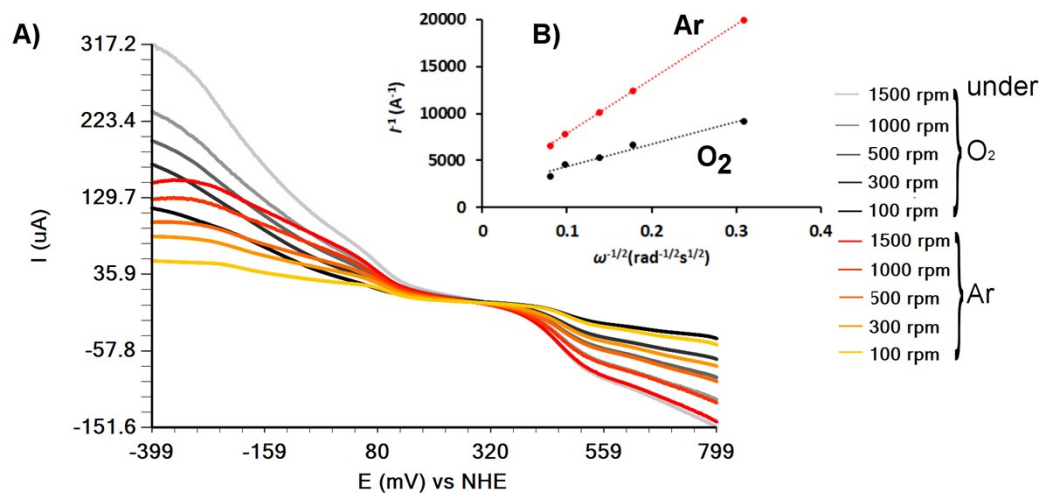
Page S373



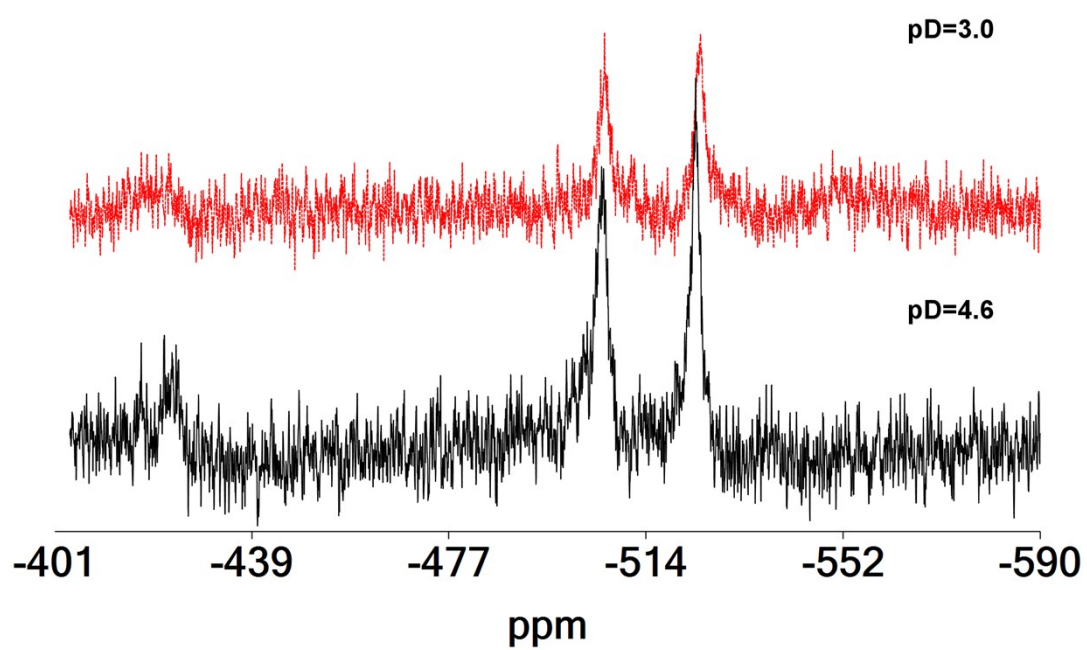
**Figure S1.** Cyclic voltammogram of O<sub>2</sub> saturated aqueous solution of 0.2 M KNO<sub>3</sub> at 273 K recorded at pHs 5.8. Scan Rate 25 mV/s. Working electrode=glassy carbon.



**Figure S2.** Cyclic voltammograms of the complex **1** (2.5 mM) in A) deoxygenated and oxygenated aqueous solutions (red and black lines respectively) at  $\text{pH}=4.6$  at scan Rate 25  $\text{mV/s}$ . The solutions contained 0.2 M  $\text{KNO}_3$  and measured at 273 K. Working electrode=glassy carbon.



**Figure S3.** A) RDE voltammetry curves of aqueous solution of **1** under Ar and  $\text{O}_2$  in pH=4.7 at various rotation rates. B) Koutecky-Levich plots at -0.130 V under Ar and under  $\text{O}_2$ , Scan rate:  $25 \text{ mV s}^{-1}$ .



**Figure S4.**  $^{51}\text{V}$  NMR spectra of an  $\text{D}_2\text{O}$  solution of **1** (2.50 mM) and  $\text{V}^{\text{IV}}\text{OSO}_4$  (2.50 mM) at pD=3.0 and 4.6.

**Table S1.** RDE data of compound **1** at pH=2.5 under N<sub>2</sub>. Potentials vs Ag/AgCl.

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Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\29032021\complex 6 sweep scan under nitrogen ph 2.5\100 rpm.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 100 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.01

Potential/V, Current/A

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Mar. 29, 2021 05:06:49

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\29032021\complex 6 sweep scan under nitrogen ph 2.5\300 rpm.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 300 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.01

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Mar. 29, 2021 05:09:51

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\29032021\complex 6 sweep scan under nitrogen ph 2.5\500 rpm.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 500 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.01

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Mar. 29, 2021 05:13:25

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\29032021\complex 6 sweep scan under nitrogen ph 2.5\1000 rpm.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 1000 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.01

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Mar. 29, 2021 05:18:33

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\29032021\complex 6 sweep scan under nitrogen ph 2.5\1500 rpm.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 1500 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.01

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**Table S2.** RDE data of compound **1** at pH=2.5 under O<sub>2</sub>. Potentials vs Ag/AgCl.

Mar. 29, 2021 04:12:38

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\29032021\sweep scan under oxygen ph 2.5\100 rpm.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 100 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.001

Potential/V, Current/A

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Mar. 29, 2021 04:18:51

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\29032021\sweep scan under oxygen ph  
2.5\300 rpm.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 300 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.001

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Mar. 29, 2021 04:22:45

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\29032021\sweep scan under oxygen ph  
2.5\500 rpm.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 500 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.001

Potential/V, Current/A

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Mar. 29, 2021 04:26:16  
Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\29032021\sweep scan under oxygen ph  
2.5\1000 rpm.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 1000 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.01

Potential/V, Current/A

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Mar. 29, 2021 04:29:17

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\29032021\sweep scan under oxygen ph  
2.5\1500 rpm.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 1500 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.01

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-0.398, 7.795e-4  
-0.399, 7.816e-4

**Table S3.** RDE data of compound **1** at pH=4.9 under N<sub>2</sub>. Potentials vs Ag/AgCl.

Mar. 30, 2021 03:52:00

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\30032021\complex 6 sweep experiment under n2\100 rpm\_25 mv rate.txt

Data Source: Experiment

Instrument Model: CHI650E

Header: 100 rpm

Note:

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.001

Potential/V, Current/A

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Mar. 30, 2021 03:55:33

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\30032021\complex 6 sweep experiment under n2\300 rpm\_25 mv rate.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 300 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.001

Potential/V, Current/A

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Mar. 30, 2021 03:58:02

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\30032021\complex 6 sweep experiment under n2\500 rpm\_25 mv rate.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 500 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.001

Potential/V, Current/A

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Mar. 30, 2021 04:01:03

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\30032021\complex 6 sweep experiment under n2\1000 rpm\_25 mv rate.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 1000 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.001

Potential/V, Current/A

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Mar. 30, 2021 04:04:03

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\30032021\complex 6 sweep experiment under n2\1500 rpm\_25 mv rate.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 1500 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.001

Potential/V, Current/A

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-0.397, 1.478e-4  
-0.398, 1.477e-4  
-0.399, 1.476e-4

**Table S4.** RDE data of compound **1** at pH=4.9 under O<sub>2</sub>. Potentials vs Ag/AgCl.

Mar. 30, 2021 03:28:07

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\30032021\complex 6 sweep experiment inder o2\100 rpm\_25 mv rate.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 100 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.001

Potential/V, Current/A

0.800, -4.296e-5

0.799, -4.264e-5

0.798, -4.238e-5

0.797, -4.218e-5

0.796, -4.200e-5

0.795, -4.181e-5

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0.772, -3.910e-5

0.771, -3.902e-5

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0.769, -3.885e-5

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0.735, -3.679e-5  
0.734, -3.676e-5  
0.733, -3.671e-5  
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Mar. 30, 2021 03:30:31

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\30032021\complex 6 sweep experiment inder  
o2\300 rpm\_25 mv rate.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 300 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.001

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Mar. 30, 2021 03:32:51

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\30032021\complex 6 sweep experiment inder  
o2\500 rpm\_25 mv rate.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 500 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.001

Potential/V, Current/A

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Mar. 30, 2021 03:35:28

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\30032021\complex 6 sweep experiment inder  
o2\1000 rpm\_25 mv rate.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 1000 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.001

Potential/V, Current/A

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Mar. 30, 2021 04:18:09

Linear Sweep Voltammetry

File: c:\users\shadji04\desktop\sofia cv\30032021\complex 6 sweep experiment under  
o2\1500 rpm\_25 mv rate

o2\_n2\_o2.txt

Data Source: Experiment

Instrument Model: CHI650E

Header:

Note: 1500 rpm

Init E (V) = 0.8

Final E (V) = -0.4

Scan Rate (V/s) = 0.025

Sample Interval (V) = 0.001

Quiet Time (sec) = 2

Sensitivity (A/V) = 0.001

Potential/V, Current/A

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