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Title: Investigation of Oxidative Reduction Reactions in Carbon-Based Electrocatalysts Presentation

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Investigation of Oxidative Reduction Reactions in Carbon-Based Electrocatalysts



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SUMMARY

The premise for this research is the expense of current electrocatalysts such as Platinum and Palladium. By examining the Oxidative Reduction Reactions (ORR) of various Carbon Nanotube (CNT) and Graphene Complexes, this project was able to compare and analyze their relative electrocatalytic properties.

For these tests, all of the samples were drop cast onto a Glassy Carbon Electrode and were analyzed for reactivity using Cyclic and Linear Sweep Voltammetry on an MSR Rotator. These tests showed the current induced with respect to changing voltage and from this the Levich Equation was used to find the number of electrons transferred in each half reaction of ORR for each sample.

The samples were also tested with X-ray Photoelectron Spectroscopy (XPS) to identify their compositions in order to identify any correlation between their electrocatalytic and compositional properties.

Equipment and ORR Theory

The current signal recorded during these ORR tests can be easily influenced by the bulk flow of ions in solution [2]. In cyclic voltammetry (CV), a placid solution is used for short time scales to look at the activity in cyclic voltage changes. However, for longer time trials bulk flow is unavoidable and for consistent results it is necessary to control the solution flow as in linear sweep voltammetry (LV). Tests were conducted at variant RPMs (Revolutions Per Minute) because the spinning rotor produces a steady-state laminar flow adjacent to the RRDE (Rotating Ring Disk Electrode), which assists in producing repeatable results that can be accurately modeled for reaction kinetics.

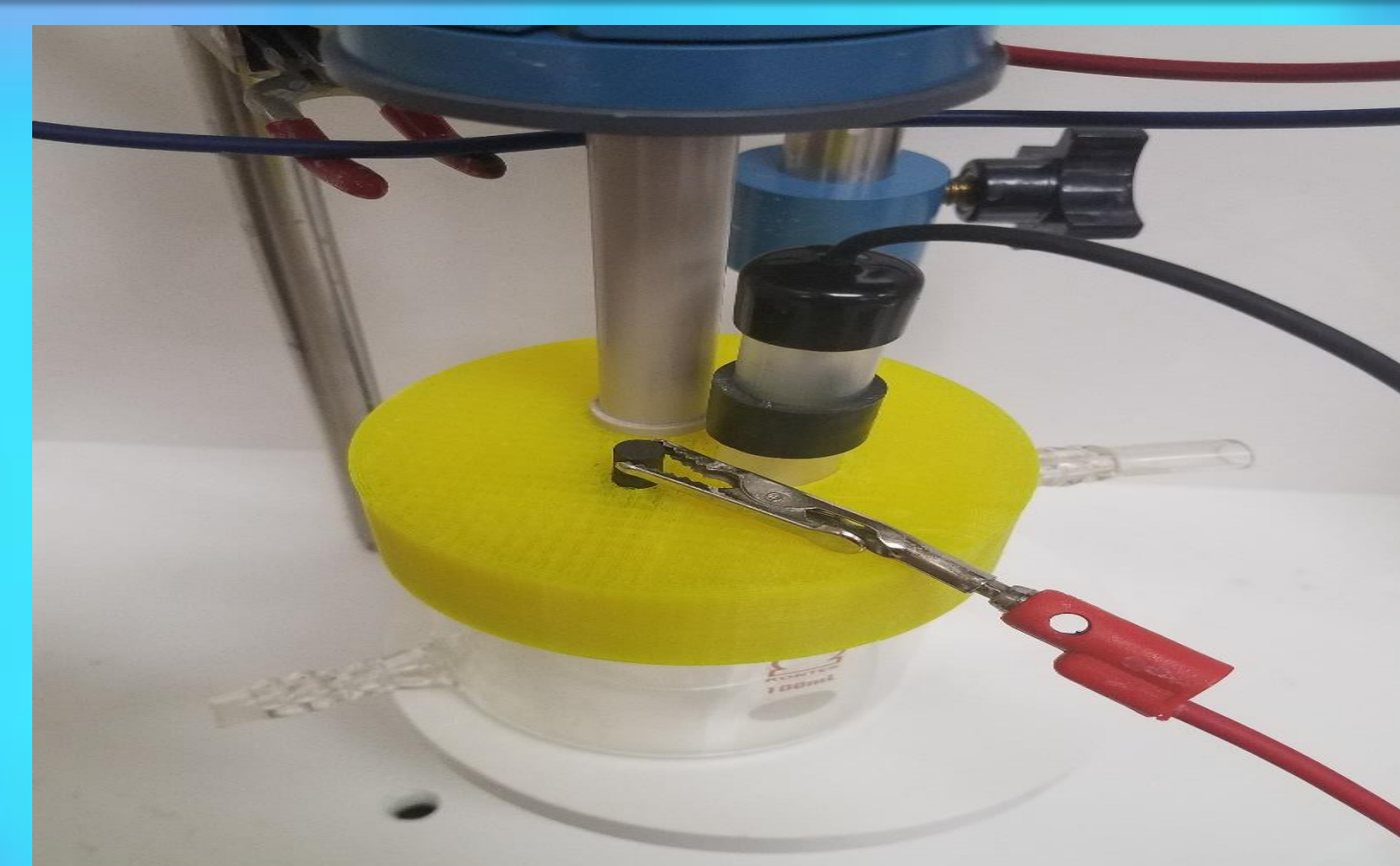


Figure 1. (Right) MSR Rotator from Pine Research Equipment used for CV and LV tests [1]. This was used in conjunction with the Gamry Instruments potentiostat Interface 1000. (Left) Vessel used for ORR testing with 3D printed lid that holds the reference electrode (KOH tube, black), counter electrode (graphite rod, red), and working sense electrode (Glassy Carbon with Sample, tan) in place while testing.

Alkaline Medium

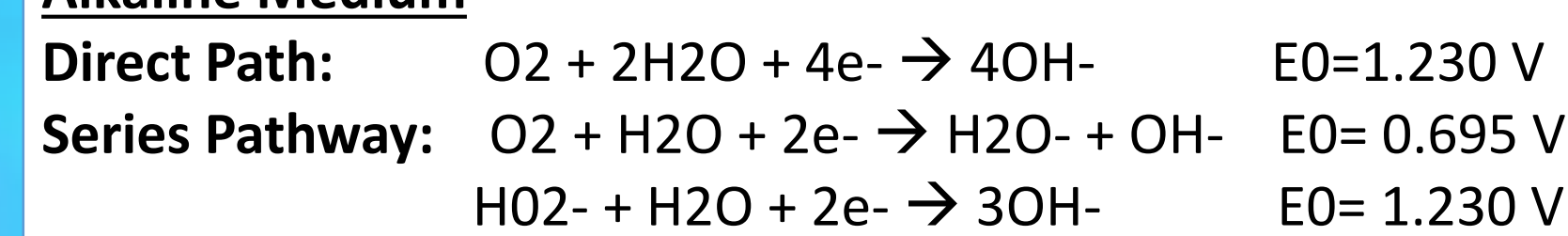


Figure 2. Reductive Half Reaction of KOH solution showing electron transfer [3]

A negative potential was applied to basic 2 M KOH solution, which reduced ions as shown in the reductive half reactions in figure 2. It is also of note that half reactions transfer either 2 or 4 electrons, which indicates the steps completed during ORR.

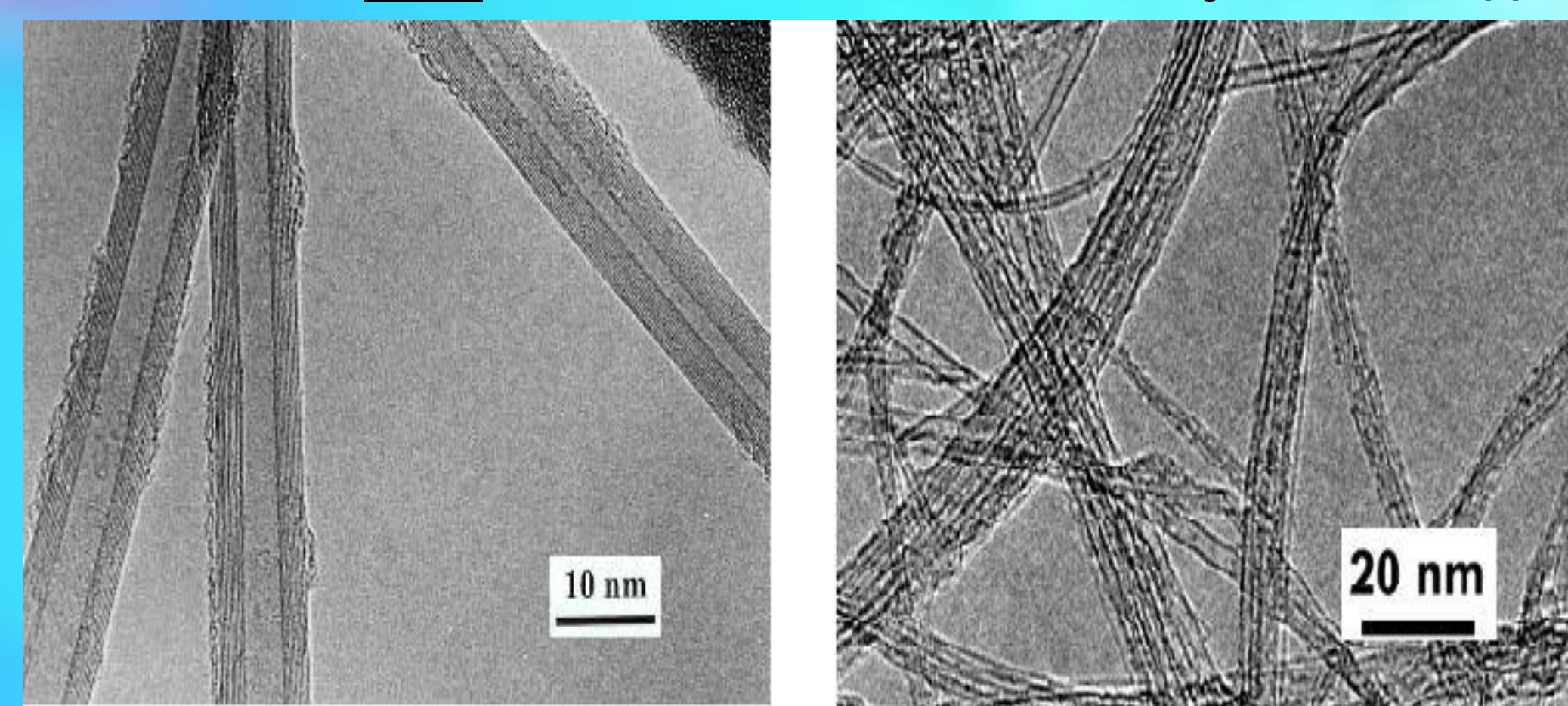


Figure 3. (Above Right) Scanning Electron Microscope image of Multi Walled Carbon Nanotubes [4]

Samples

Preparation of 10 mL increment solutions were in the following ratio (10 mg DDBS, 1 mg EC, 10000mg H₂O). These solutions were then vibrated for 5 minutes to create a homogeneous solution for proper drop casting onto the Glassy Carbon Electrode.

Sample	EC	OD (nm)	Length (μm)	Purity (wt%)	Add Cont (wt%)	Ash (wt%)	Ratio (DDBS:EC:H ₂ O)
1	SW/DWCNT	1-4	5-30	>60	<35	<1.5	10:1:10000
2	SW/DWCNT	1-4	5-30	>90		<1.5	10:1:10000
3	MWCNT	<8	10-30	>95		<1.5	10:1:10000
4	MWCNT	8-15	10-50	>95		<1.5	10:1:10000
5	MWCNT	>50	10-20	>95		<1.5	10:1:10000
6	GMWCNT	30-50	10-20	>99.9		<0.1	10:1:10000
7	DDBS						10:0:10000

Figure 4. (Above) Table of sample solutions. (EC = Electro Catalyst, OD = Outer Diameter, SW/DWCNT = Single Wall/Double Wall Carbon Nanotubes, MWCNT = Multi Walled Carbon Nanotubes, GMWCNT = Graphitized Multi-Walled Carbon Nanotubes, Add Cont = Additional MWNT Content, DDBS = dodecylbenzene sulfonic acid)

Sample 4 and 1 showed the highest oxygen impurity. These impurities are ingrained in the surface chemistry of the samples and changes their electrocatalytic properties. The intense SP Carbon peak also confirms that we measured our Carbon Samples accurately.

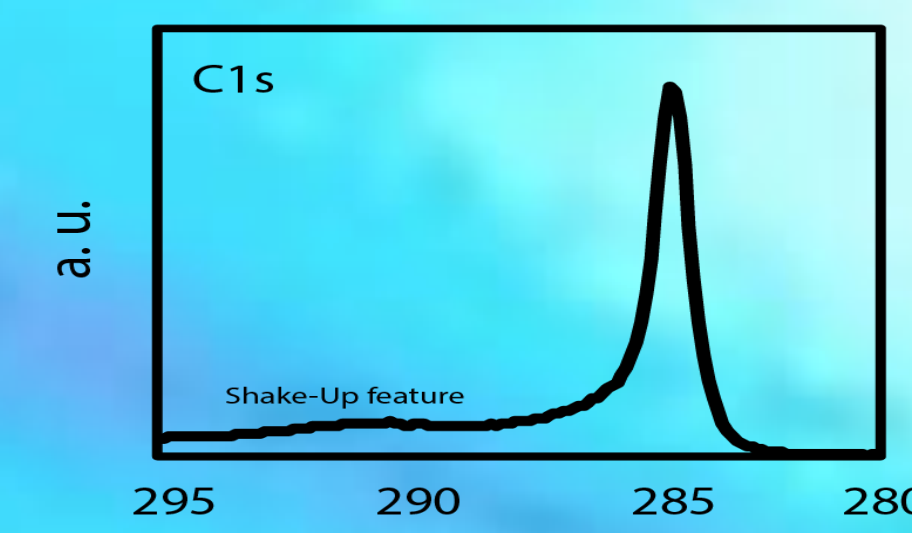


Figure 5. SP Carbon Peak of Sample 1 CNTs

XPS

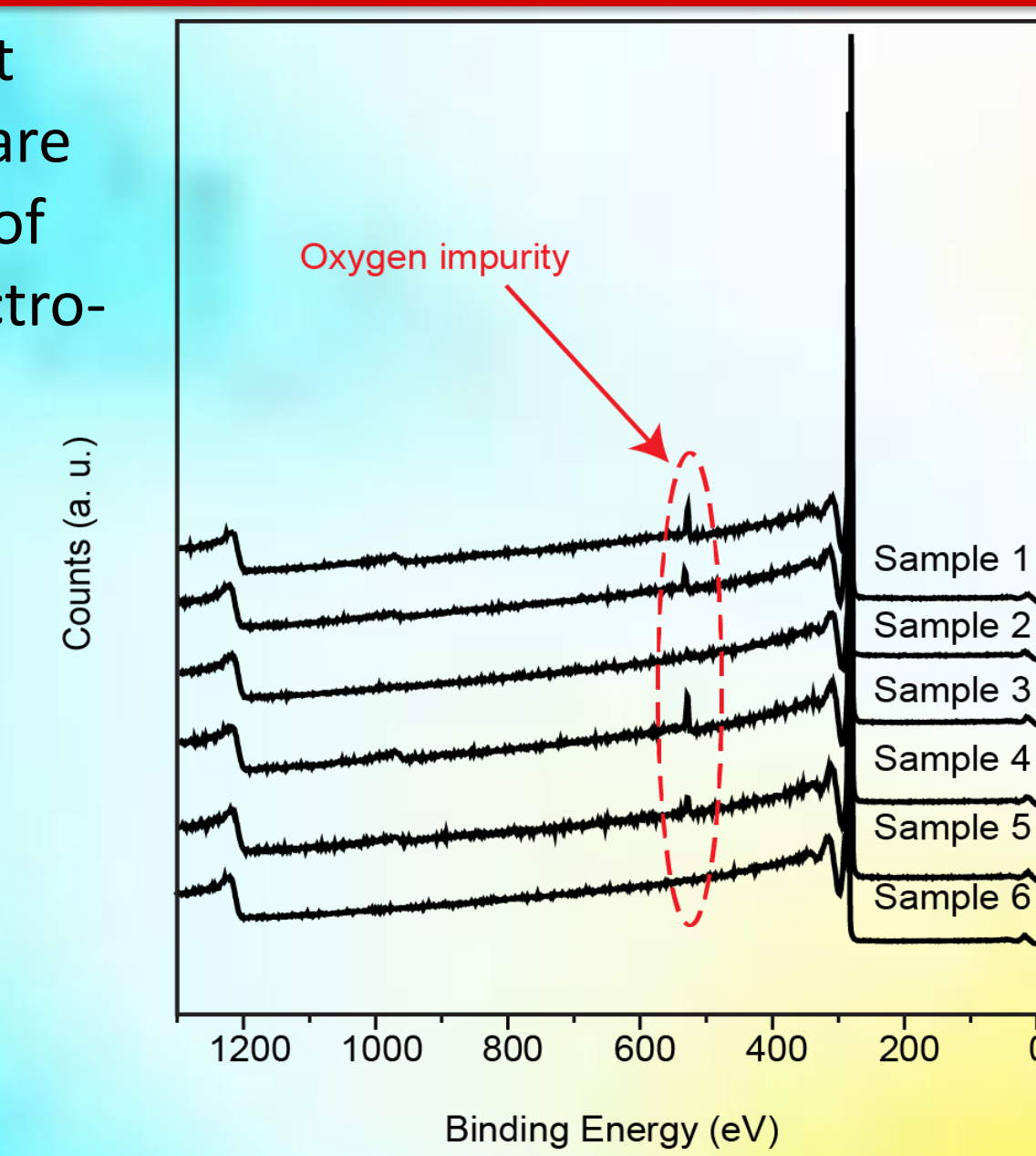


Figure 6. XPS survey spectra of six samples

Sample	Oxygen Impurity (%)
1	3.16
2	2.03
3	0.62
4	3.24
5	1.75
6	0

Figure 7. Table of Atomic Percentage of Oxygen Content

Cyclic and Linear Sweep Voltammetry

CV is where the electrode potential is swept back-and-forth between two extremes, in this case it is swept in the negative (cathodic) direction [2]. The current eventually reaches a maximum value (limiting current) once the applied potential is sufficiently negative relative to the standard electrode potential [2].

Sample 5 and 4 were most reactive towards increasingly negative potentials as is evident in Figure 8. These samples were both longer MWCNT with some impurities. The preserved internal structure and surface impurities of these samples suggest as to making them more conducive to transferring electric current. It is also of note that all the samples have higher reactivity than GC.

In Linear Sweep Voltammetry, the rotation rate (RPM) is held constant as the electrode is swept from one potential to another. Current can be limited by the mass transport ions to the electrode surface, which is directly related to the electrode RPM. Rotating the electrode at a faster rate increases the rate at which material arrives at the electrode surface [2]. Thus, the limiting current decreases with increasing rotation rate. At higher RPM's, the limiting current responses decreases and becomes less chaotic. This indicates that all of the electrocatalysts improve in efficiency as limited mass transport is reduced but the best electrocatalysts seemed to be Samples 5 and 4 as they consistently produced the lowest current peaks.

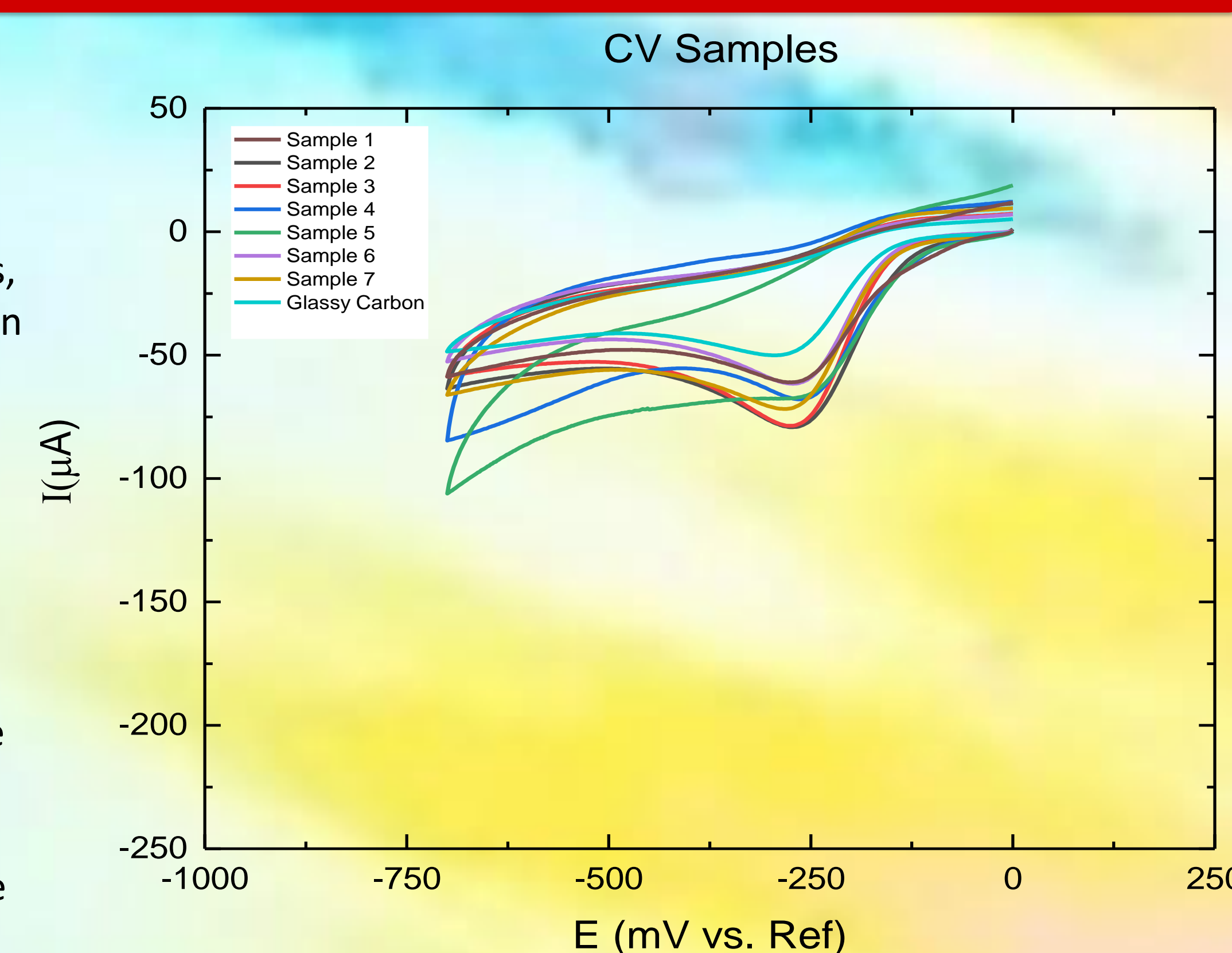


Figure 8. European Convention of Cathodic Sweep on Samples

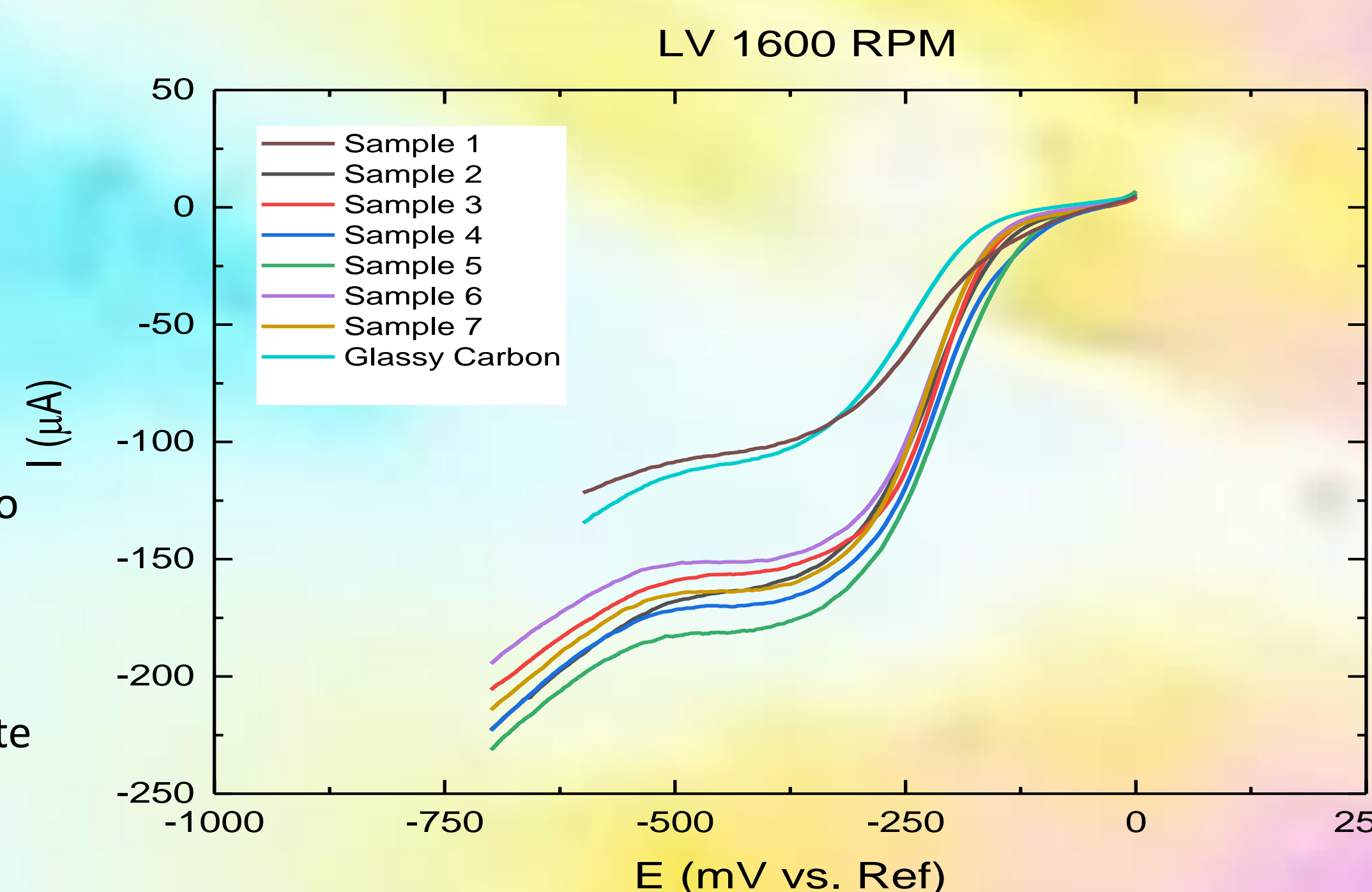


Figure 9. Linear Sweep at 1600 RPM on Samples

Levich

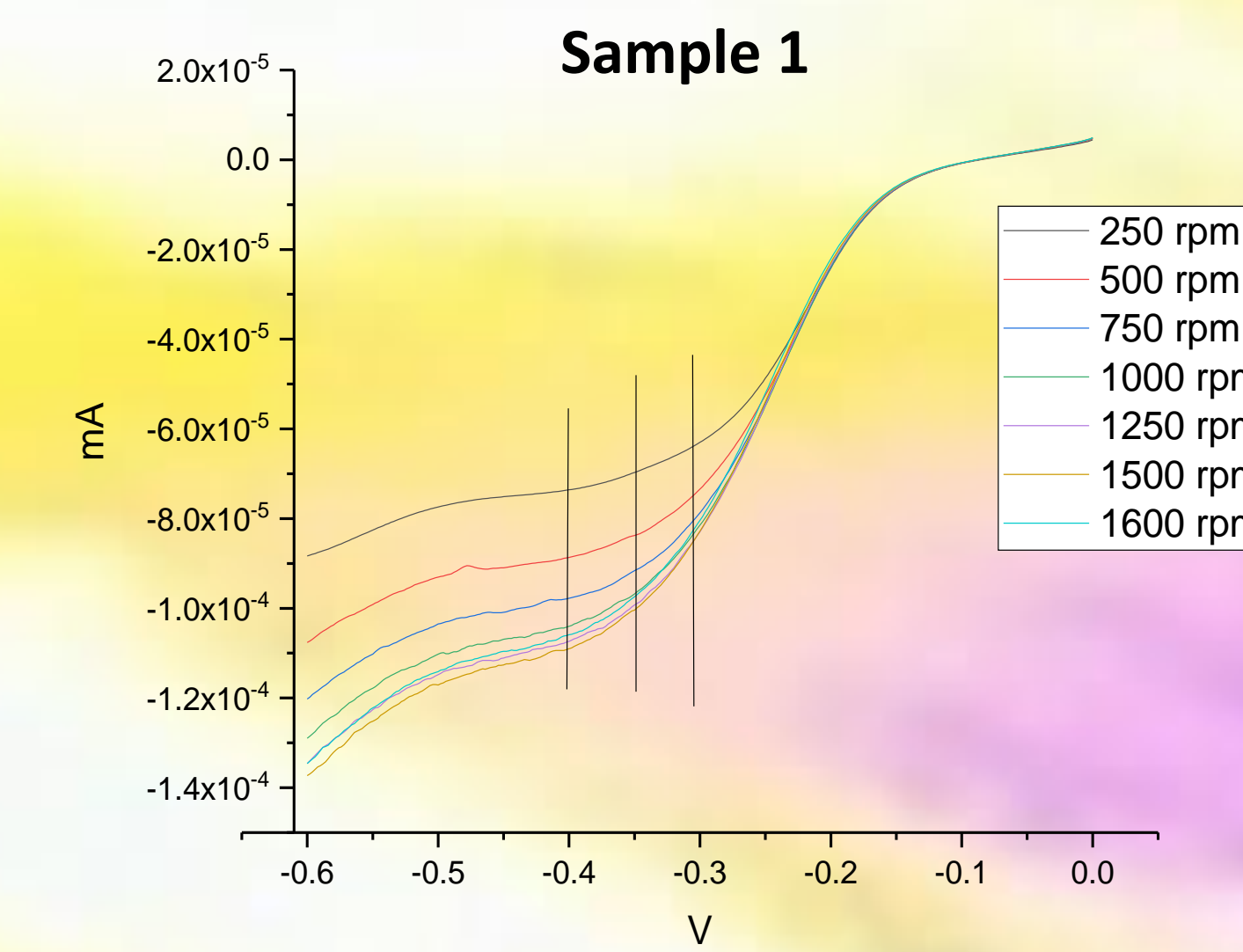


Figure 10. American Convention of Cathodic Sweep with varying RPM tests [3]

Levich Equation

$$i_L = (0.620) \cdot n \cdot F \cdot A \cdot D^{2/3} \cdot \omega^{1/2} \cdot \nu^{-1/6} \cdot C$$

- i_L , is the Levich current
- n , is the number of electrons transferred in the half reaction
- F , is the Faraday constant
- A , is the electrode area
- D , is the diffusion coefficient
- ω , is the angular rotation rate
- ν , is the kinematic viscosity
- C , is the analyte concentration

Figure 11. Levich Equation with Constants Defined

Levich Graphs are a series of voltammograms acquired over a range of different rotation rates. For a simple electrochemical system where the rate of the half reaction is governed by mass transport to the electrode surface. An intercept above zero, however, is an indication that the half-reaction is limited by sluggish kinetics rather than by mass transport. From figure 13, sample one was the only sample to produce 4 electrons in its half reaction. This sample also had the second highest impurity, which is the suspected cause of the greater electron transfer rates.

Levich

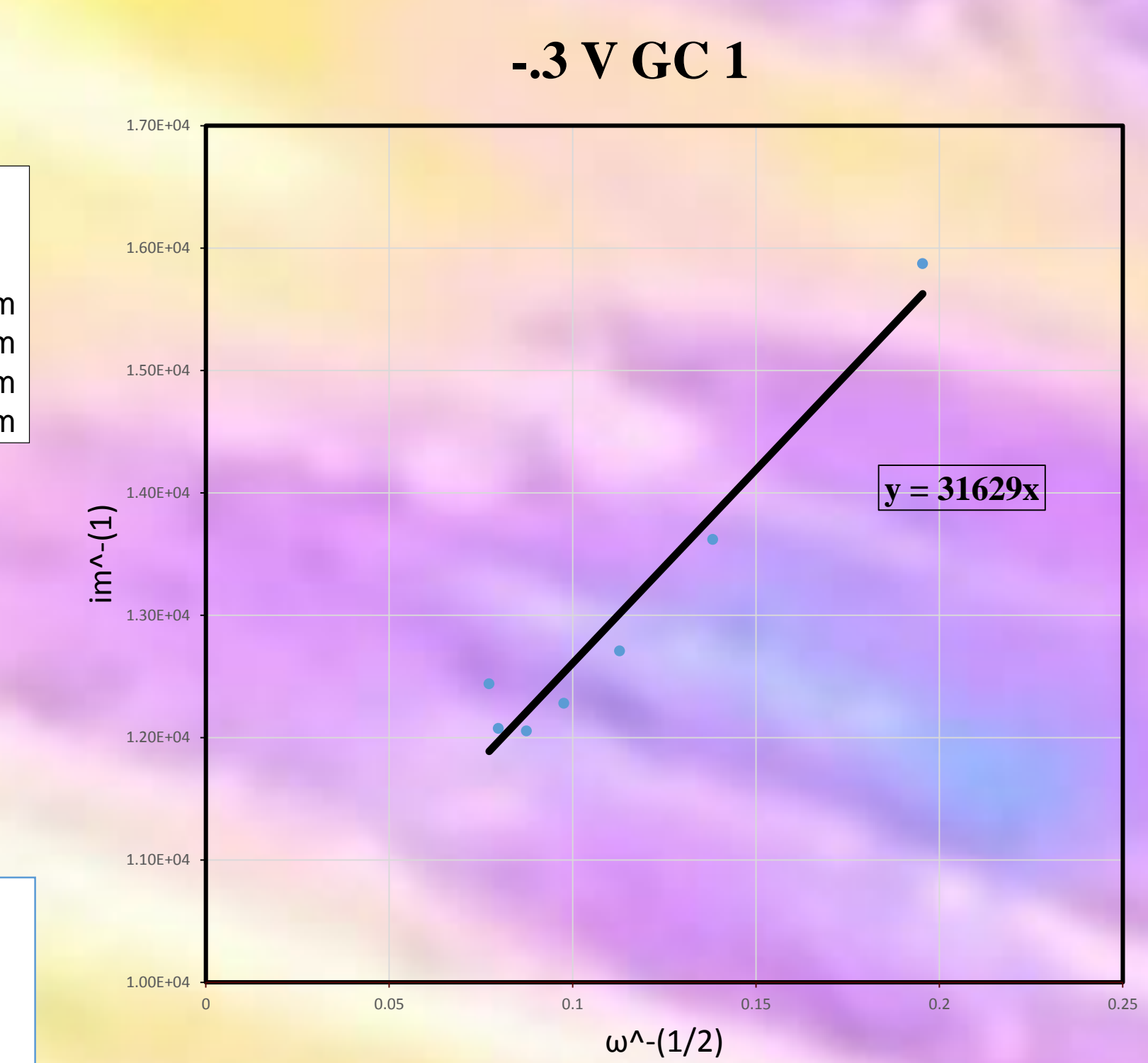


Figure 12. Levich plot of varying currents at constant potentials across multiple RPMs

Sample	Equation	Regression	Electrons Transferred
1	$y = 18042x$	$R^2 = 0.8548$	4.01E+00
2	$y = 33597x$	$R^2 = 0.9965$	2.15E+00
3	$y = 31555x$	$R^2 = 0.9931$	2.29E+00
4	$y = 33468x$	$R^2 = 0.9956$	2.16E+00
5	$y = 35512x$	$R^2 = 0.9903$	2.04E+00
6	$y = 34151x$	$R^2 = 0.9997$	2.12E+00
7	$y = 33762x$	$R^2 = 0.9992$	2.12E+00
GC	$y = 38938x$	$R^2 = 0.9986$	2.01E+00

Figure 13. Table of samples at their limiting currents with their electrons transferred in each half reaction

CONCLUSION

The results of the testing showed that carbon based electrocatalysts are viable options that need further exploration. The tests conducted favored both long MWCNTs and high impurity samples. This gives credence to the theory that surface layers containing impurities are the sites for ORR and that internal structures facilitate the transfer of electrons as current.

The results from XPS, CV, and LV suggest that carbon nanostructure with varying surface chemistry heighten ORR activity given these impurities do not disturb the internal structure. The data also suggests that the surfactant, DDBS, used in the solutions also heightened the reactivity of the electrocatalysts. Sample 7 was approximately the average of the other samples in the LV and CV graphs, but as to why this phenomenon occurred is unknown. To eliminate the possibility of errors, all future experiments will be run multiple times and compared to each trial. Moreover, Sample 4 and 1 had the highest impurity with sample 1 also having the greatest electron rate, but these samples differed in reactivity greatly suggesting that ORR is based upon a combination of impurities and nanostructures.

Future experiments will be aimed at exploring these phenomenon as well as altering the sample's surface chemistry with oxidative Chemical Vapor Deposition and varying types of polymers, as an attempt to improve their ORR activity and longevity. The data presented in this investigation suggests several options to explore as paths to improve the samples ORR and make them better electrocatalysts. Overall, the continued exploration of carbon based electrocatalysts as a viable new option for battery applications is promising.

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