

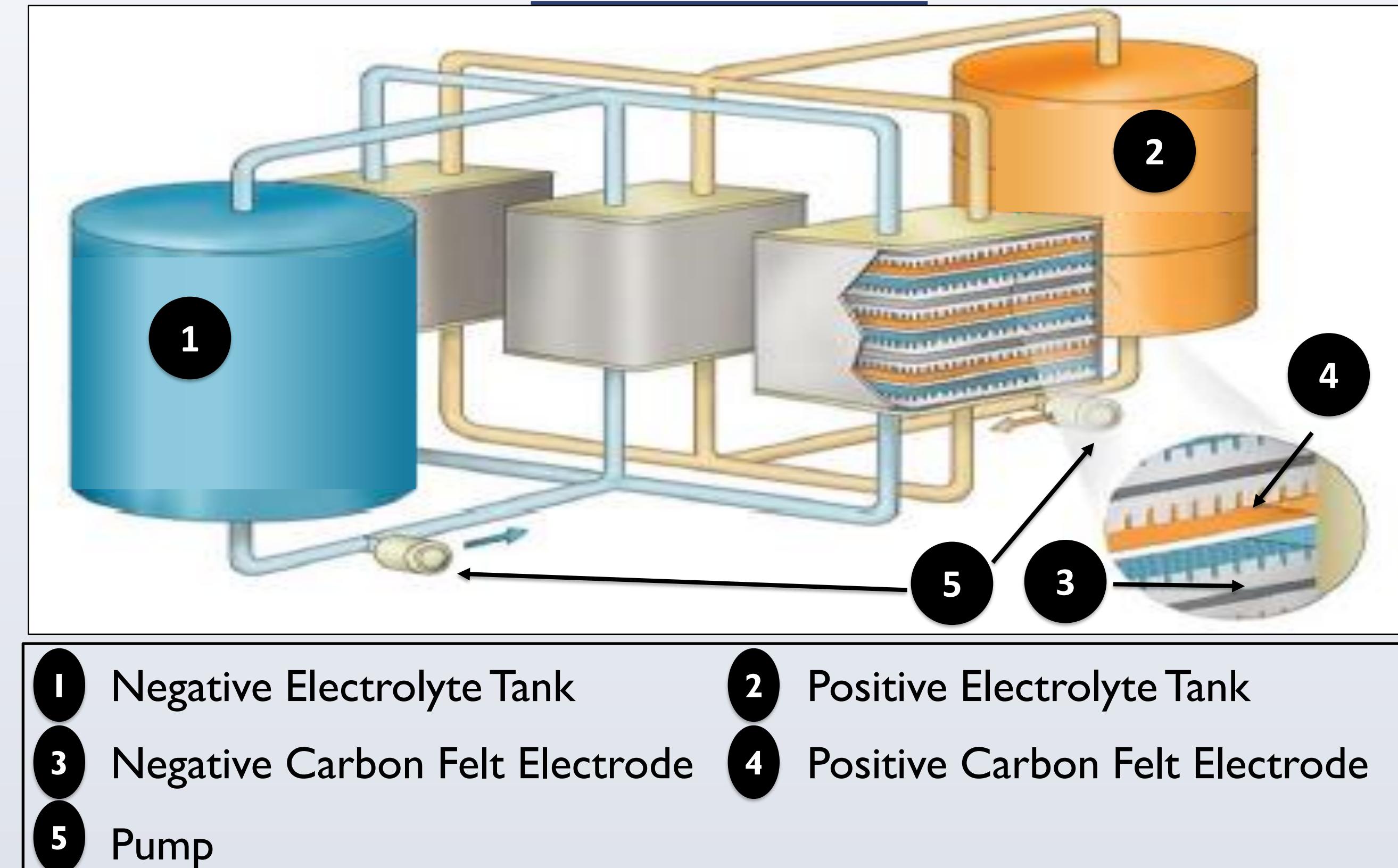
Investigation of the Positive Electrode Kinetics for the Vanadium Redox Flow Battery

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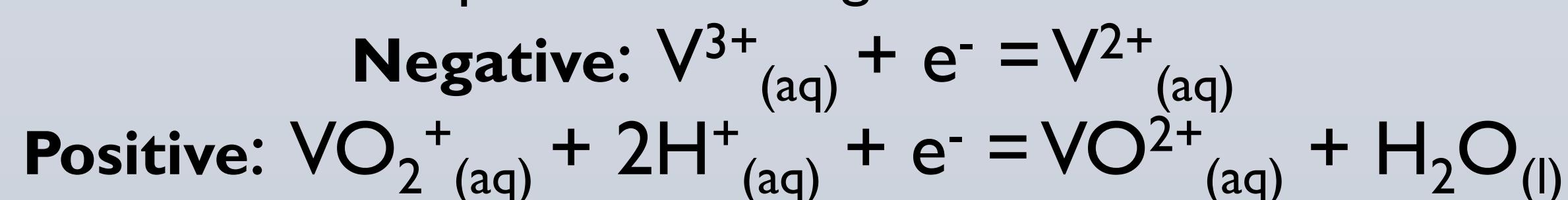
Energy and Mineral Engineering, Electrochemical Engineering

Introduction



As energy demand grows and the number renewable energy farms increase, there is a need for large grid-scale energy storage[2]. Renewable energy systems can produce electricity but are inefficient at storing the energy produced[3]. Electrochemical energy storage methods, such as the Vanadium Redox Flow Battery (VRFB) in figure 1, use large electrolyte tanks and carbon electrodes to store the energy produced from wind or solar systems as chemical energy and release the energy as electricity[4].

The VRFB consists of positive and negative electrode half reactions:



This experiment aims to focus on the reaction kinetics of the positive electrode in a solution of V(IV) / V(V). One improvement for the VRFB energy storage system lies within the functionality of the carbon electrode. Surface treatments to the positive electrode may increase the reaction kinetics for the VRFB, thus improving the energy storage capacity while keeping the size of the VRFB cell small.

Objectives

- Conduct X-Ray Photoelectron Spectroscopy (XPS) on each of the carbon material electrodes and determine microstructure of each electrode.
- Analysis of Linear Sweep Voltammetry to compare exchange current densities and reaction kinetics between electrode materials.
- Create a repeatable testing procedure to yield consistent results.
- Determine if the positive electrode reaction kinetics of the VRFB depend on the electrode material.

Test Procedure

The experiment was conducted using a rotating disk electrode (RDE) consisting of a working electrode, a reference electrode (Ag/AgCl), and a counter electrode (graphite rod). The test solution was made of a 50/50 mixture of 0.005 mol L⁻¹ V(IV) / V(V) and 1 mol L⁻¹ of H₂SO₄ acting as the background electrolyte. The RDE was set to 2000 rpm for each test.

A cathodic and anodic overpotential was applied to the system and through Linear Sweep Voltammetry the current through the carbon electrode was measured. XPS was the surface analysis technique to determine the elemental composition on the surface of each electrode[5].

Results

Table 1. XPS Elemental Composition Comparison as a Percentage

Sample Identifier	C _{total}	C-C	C-O	C=O	O-C=O
PGB	91.0	76.4	8.6	6.1	0.0
PGE	88.8	44.6	23.7	11.5	4.9

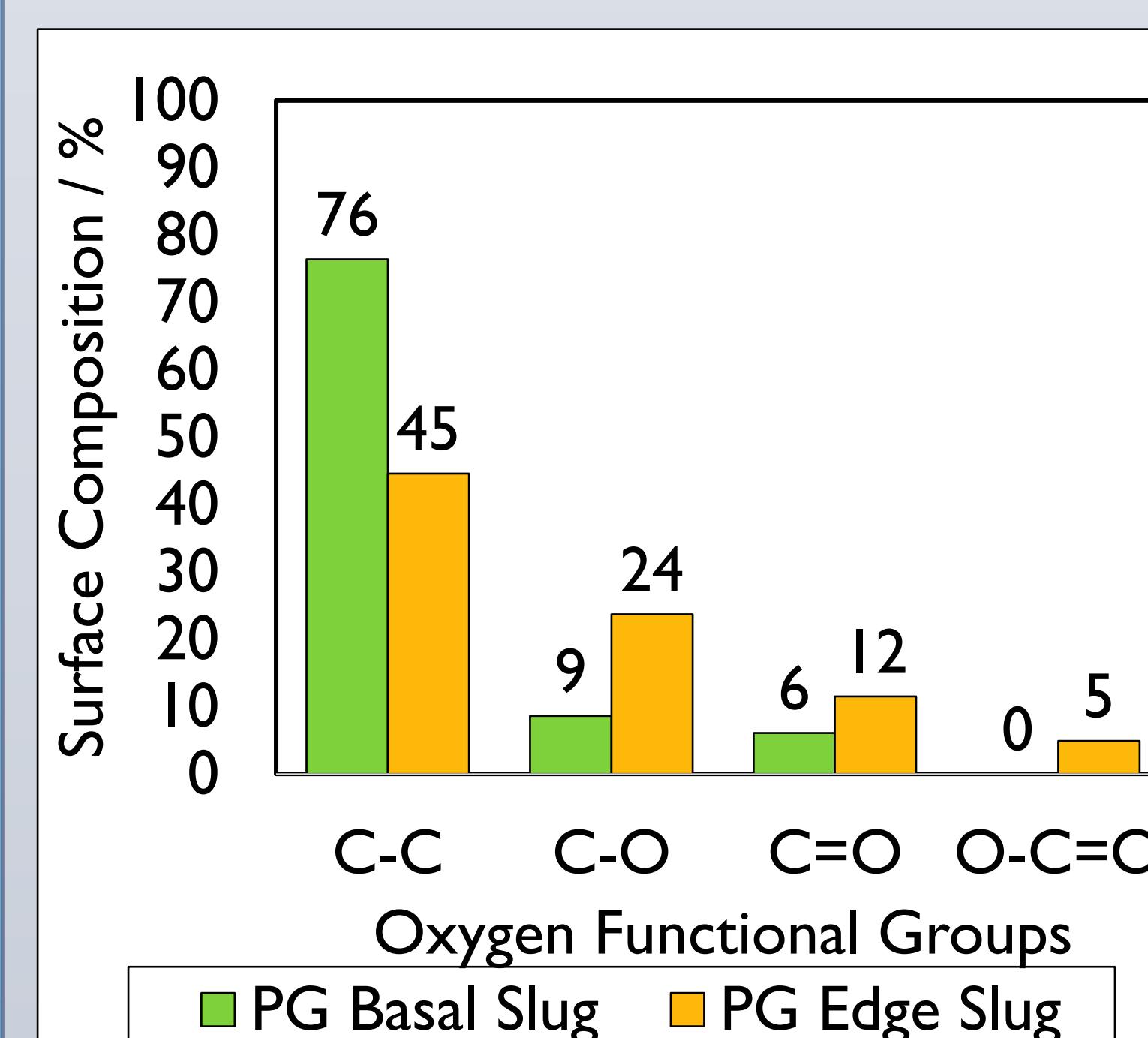
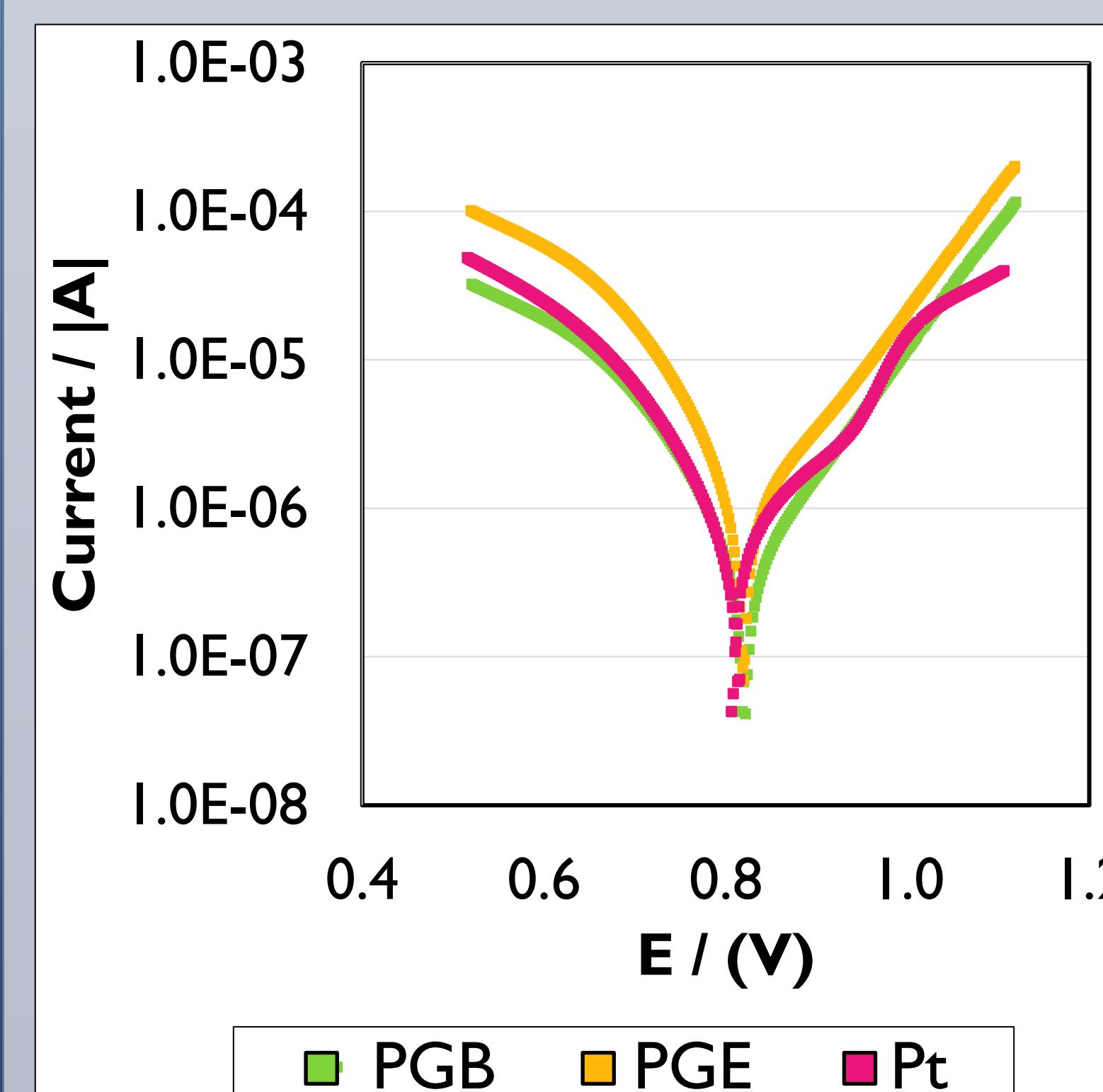


Figure 2. Oxygen Functional Group Comparison



XPS analysis in figure 2 compared the surface compositions for the Edge Plane (PGE) and Basal Plane Pyrolytic Graphite (PGB). The PGB had fewer oxygen functional groups compared to that of PGE. The remaining composition includes 8 % oxygen for PGB and 10 % oxygen for PGE. XPS also showed trace amounts of silicon and nitrogen.

Despite a difference in surface composition, the PGE displayed an exchange current density (j_0) of 4.7 +/- 0.6 μ A/cm². The PGB displayed a j_0 of 2.2 +/- 0.5 μ A/cm². Used as a reference point, Pt was measured to be within the range of j_0 , at 3.1 +/- 0.2 μ A/cm². This small range of j_0 between electrode materials suggests there is minimal impact on the positive electrode half reaction for the VRFB.

Conclusion

Despite the difference in the presence of oxygen functional groups between the edge plane and basal plane pyrolytic graphite electrodes, the electrode material appeared to have minimal impact on the vanadium reaction kinetics. Comparing the rate constant (k_0) values obtained from the exchange current density, the experimental values were within the range of 10⁻⁵ and 10⁻⁶ cm/s found in literature for typical carbon electrodes [6],[7]. Although the experimental carbon values are comparable to those in literature, the preliminary kinetic values for the Pt electrode were lower than what was expected, leading to further investigation into the j_0 and k_0 for Pt. This experiment suggests there is an independent nature between electrode material and the positive electrode reaction kinetics for the Vanadium Redox Flow Battery.

Next Steps

Next steps, with the addition of a glassy carbon electrode, will be to test the electrodes in another batch of the test solution. Once each electrode sample is tested through LSV, Electrochemical Impedance Spectroscopy (EIS), Raman Spectroscopy, and XPS, the electrodes will be modified through surface treatments to increase the number of functional groups. Each of the analysis techniques will be conducted post surface treatment and the results will be compared.

References

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