L3 Milestone: Discover, synthesize, measure activity, and characterize new electrolyte media or electrode coatings that promote CO_2RR

Immobilized Electrocatalysts on Graphitic Supports

Thomas Chan, Clifford P. Kubiak

University of California, San Diego

Abstract

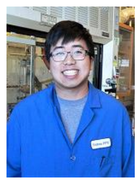
Graphitic materials such as carbon nanotubes, and reduced graphene oxide offer a inexpensive, stable, porous, and conductive support for electrocatalysts. The graphitic support enables the electrocatalysts to turnover in an aqueous environment where it would have normally been limited by its insolubility. We are interested in studying the underlying mechanisms and characterize these electrocatalyst/graphitic hybrid electrodes. By immobilizing Ferrocene, a well-studied redox active species, we are able to determine that merely 12% of the Ferrocene is electroactive, which can be improved upon. Additionally, we found that the immobilized Ferrocene behaves as a freely diffusing species as described by the Randles- Sevcik equation. From cyclic voltammetry, we can see that these graphitic films cause a mass transport limitation to the surface, where ions are unable to rearrange quickly. SEM was performed to study the topography of these hybrid electrodes.

Introduction

CO_2RR electrocatalysts are excellent at reducing CO_2 to CO, but as molecular catalysts, they are limited in their commercial use due to solubility. By exploring graphitic supports like carbon nanotubes (CNT) and reduced graphene oxide (rGO), we are able to immobilize these CO_2RR electrocatalysts to enable them to be used in aqueous environments. To improve upon these hybrid electrocatalyst/graphitic electrodes, we conducted a series of experiments to understand the mass transport at the electrolyte/electrode interface and to increase the percent electroactive species.

Team

Prof. Kubiak



Thomas Chan

Outlook

We have learned that our hybrid electrodes are experiencing mass transport limitations through studying a model redox active species, ferrocene. We have shown that a layer of multiwalled carbon nanotubes (MWCNT) can cause mass transport limitations through cyclic voltammetry in an aqueous $Ru(NH_3)_6Cl_3$ solution. Additional characterization will be performed to understand the underlying mechanisms, such as CO_2 and N_2 surface adsorption. Future plans include developing a CO_2 electrolyzer flow cell with these electrocatalyst/graphitic electrodes.

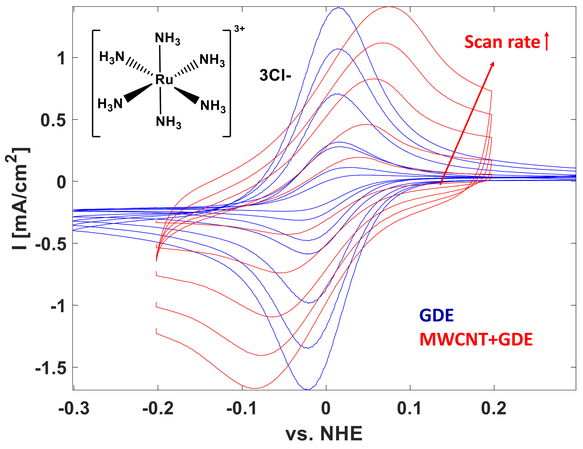
Acknowledgements

This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993

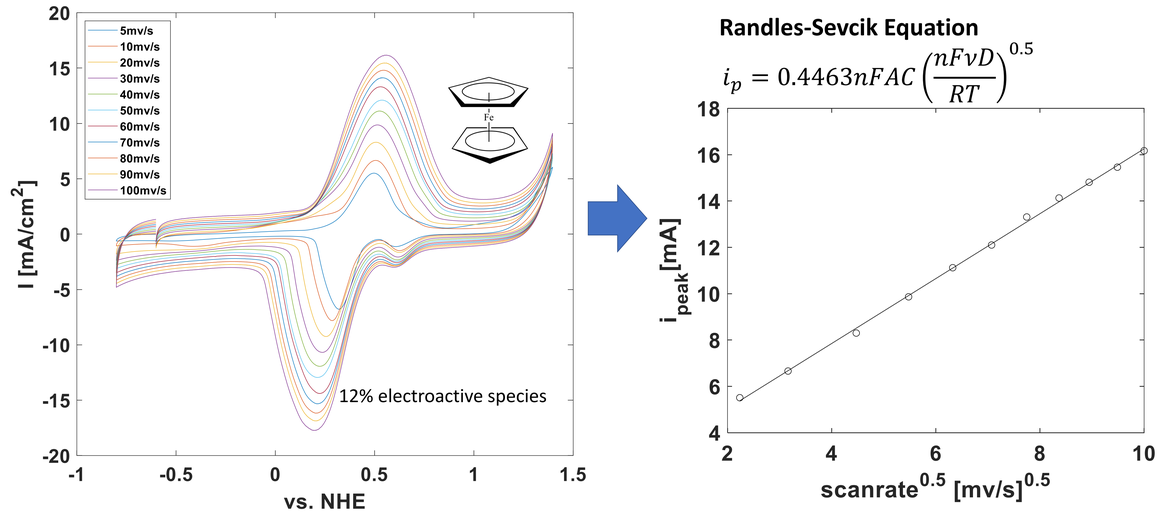
Results, Discussion

Characterization of Electrocatalyst/graphitic Hybrid Electrodes

To improve these hybrid electrodes, we aim to develop our understanding of their underlying mechanisms, which is suggested to be attributed to the aromaticity of the graphitic support and catalyst. Controlling the mass transport at the catalytic sites is crucial to ensure there that the catalysts are not reactant limited. We have found that the immobilized species behave similar to that of a mass transport limited freely diffusing system as described by the Randles-Sevcik equation. Additionally, we probed into studying and improving the percent of electroactive species on the electrode. Using SEM, we look at the surface morphology to adjust our fabrication methods.

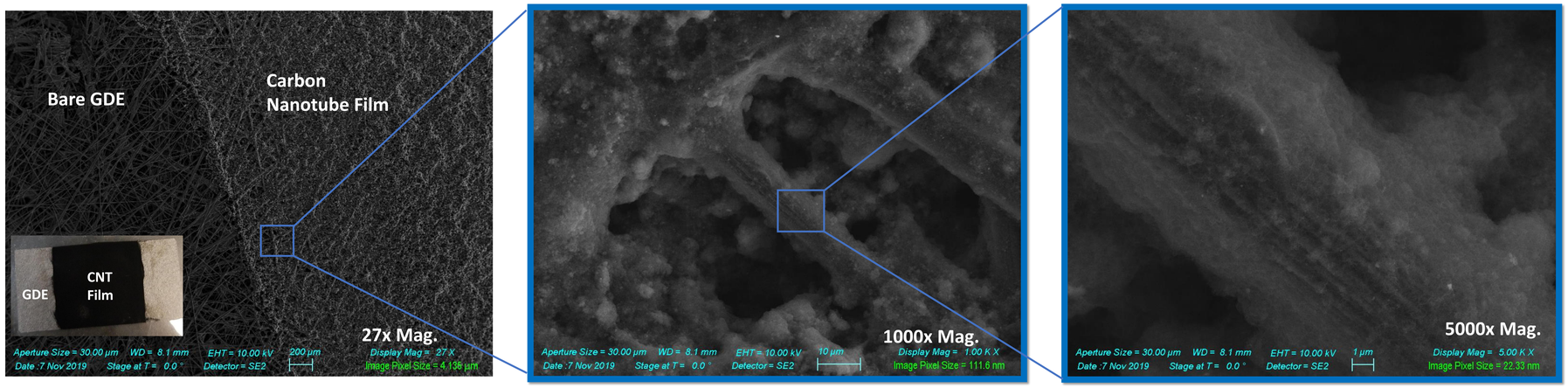


A series of cyclic voltammograms (CV) with increasing scan rates, 10, 25, 50, 75, 100mv/s were performed with bare gas diffusion electrode(GDE) and a coated GDE with MWCNTs in a 5mM $Ru(NH_3)_6Cl_3$ aqueous solution. The CV's show mass transport limitations from the MWCNT films, which is inferred from the peak to peak separation in the red traces (MWCNT).



A series of CV's with increasing scan rates, 10,20,30,40,50,60,70,80,90,100 mv/s were performed with a GDE coated with ferrocene, MWCNT, and Nafion 117. By integrating the cathodic peak to get the total charge which can be converted to moles of ferrocene, we determined that 12% of the ferrocene that went into the ink was electroactive. Additionally, we plotted the cathodic peak current, I_{peak} vs. scan rate$^{0.5}$ to see that the relationship follows the Randles-Sevcik equation. The Randles-Sevcik equation is used to describe a system of freely diffusive species, which is interesting because the Ferrocene is on immobilized on the surface of the MWCNT.

SEM of Hybrid Electrode Topography



SEM images were taken of a GDE coated with multi-walled carbon nanotubes (MWCNT) at the edge of the coated area. The first SEM image is at 27x magnification shows that the carbon fibers are completely coated with MWCNTs and the morphology is changed with the coating, The blue square is the area where the second SEM at 1000x magnification is taken also showing the microscopic film covering the carbon fibers. Again the blue square is the area where the third SEM image at 5000x magnification was taken which shows MWCNT clumps on the surface of these carbon fibers.