Synthesis of Organic Electroactive Polymers for Energy Applications

NEBRASKA CENTER FOR ENERGY SCIENCES RESEARCH

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Summary

Electroactive and conformal coatings of conjugated polymers were achieved by oxidative chemical vapor deposition and spin coating techniques. These coatings were used to catalyze oxygen reduction reaction (ORR) as well as carbon dioxide reduction reaction (CO2RR). Cyclic Voltammetry (CV) was performed to observe the capacitance of the material and their activity during these reactions.

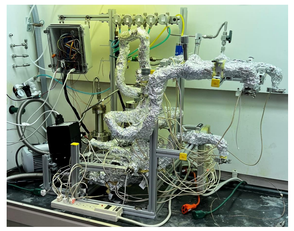


Figure 1. Picture of an oxidative chemical vapor deposition (oCVD) reactor. Foil and fiber glass insulation are required to maintain a constant temperature.

Motivation

CO2RR and O2RR are promising reactions in pursuit of sustainable energy solutions. Currently, most of the energy production around the world is generated via combustion and thus produces unwanted CO2 emissions. CO2RR has the potential to decrease our pollution output while O2RR is a key reaction in alternative energy conversion devices, such as metal-air batteries[1]. The catalysts required for these reactions tend to be costly metals. Therefore, the development of cheap, abundant and effective catalyst material is needed. Considering the relatively low cost of the materials used for polymer synthesis, we expect polymeric materials to become alternative building blocks in catalyst design.

Materials & Methods

Oxidative Chemical Vapor Deposition (oCVD) is a liquid-free, single-step approach to synthesize, dope and coat conjugated polymers[2].

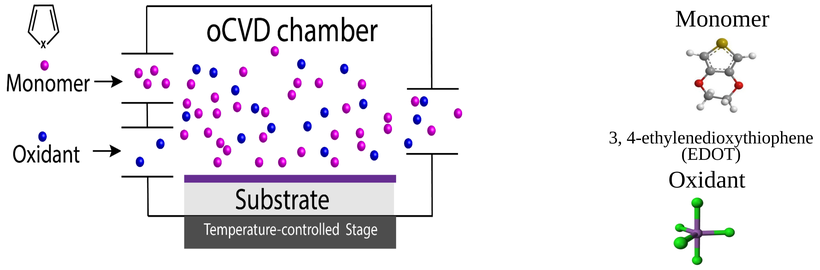


Figure 2. Schematic of an oxidative chemical vapor deposition (oCVD) reactor. Reactants are fed to a vacuum chamber where they deposit onto a temperature-controlled substrate.

Monomer

3, 4-ethylenedioxythiophene (EDOT)

Oxidant

Antimony pentachloride ($SbCl_5$)

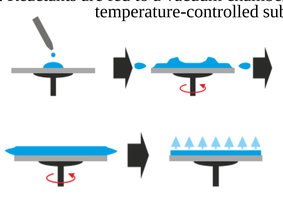


Figure 3. Schematic of spin coating technique. Polymer containing solution is dropped onto the substrate surface then evaporates and is sheered away during the rotation

Spin coating is a solvent-based technique to synthesize thin films that is Common in the industry of microelectronics. Utilizing a solution of PEDOT:PSS 2.8% wt in H2O and 99% IPA in a volumetric ratio of 1:5 respectively, thin films were fabricated by rotating at 1500rpm for 1 minute.

Materials & Methods cont.

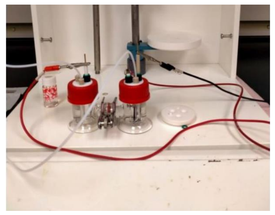


Figure 4. Picture of H-Cell used for CO2RR. CO2 is fed to each chamber. The chambers are separated by an ionomer membrane.

For CO2RR, a H-Cell was set up to allow constant flow of CO2. A Nafion membrane was utilized as the ionomer within the cell. In one half there is the working and reference electrode, the other half holds the counter electrode. In this case the counter electrode was platinum

Results

Capacitance Measurements:

Iridium Tin Oxide (ITO) glass was coated and used in CV test to determine capacitance.

The oCVD sample had the highest charging capacitance. The oCVD PEDOT sample had a charging capacitance of 4.583mC, the spin coated sample was 282.3µC and the control was 1.253mC.

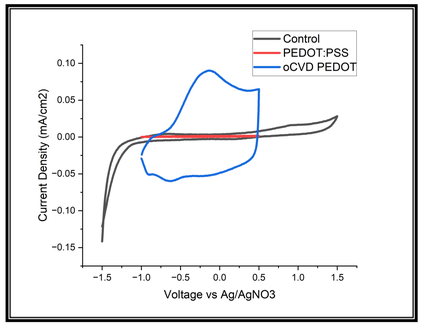
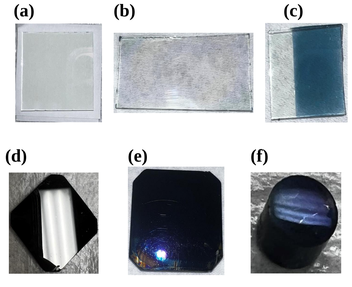


Figure 5. CV scan of 50mV/s for coated ITO samples in 0.1M TBAPF6 in Acetonitrile electrolyte. oCVD PEDOT sample displays a significantly higher charging capacity.



O2RR Measurements:

Glassy Carbon was coated and used in CV to determine the overpotential at which O2RR begins and the associated discharge capacitance.

The oCVD PEDOT sample displayed the least negative overpotential as well as the smallest discharge capacitance. The oCVD PEDOT sample had a discharge capacitance of -130.5µC,. the PEDOT:PSS sample was -11.60mC and the control was -31.36mC.

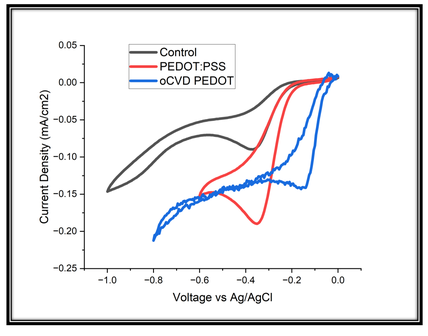


Figure 6. CV scan of 50mV/s of coated Glassy Carbon samples in 0.1M KOH electrolyte that was saturated in O2. oCVD PEDOT sample displays the smallest overpotential to initiate the reduction.

Figure 7. a)Uncoated ITO sample. b) Spin Coated PEDOT:PSS ITO sample. c) oCVD coated PEDOT ITO sample d) Uncoated Glassy Carbon plate sample. e) Spin Coated PEDOT:PSS Glassy Carbon plate sample. f) oCVD coated PEDOT Glassy Carbon disk sample. The disk is utilized for O2RR as rotating ring disk electrode experiments are planned in the future.

Future Work

CO2RR Measurements:

Polished Copper was coated and used in CV test to determine activity during CO2RR

Copper control outperformed both coated samples with a discharge capacitance of -137.2mC. The oCVD PEDOT and PEDOT:PSS samples were relatively the same with values of -608.2µC and -578.8µC respectively

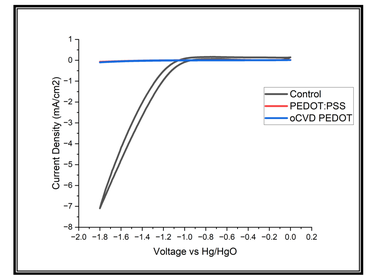


Figure 8. CV scan of 50mV/s of coated Copper samples in 0.1M KOH electrolyte that was under CO2 gas. Unexpectedly the control had the best performance. Future improvement to synthesis procedure is necessary.

(a) (b) (c)

Figure 9. a) Uncoated Copper Sample. b) Spin coated PEDOT:PSS Copper sample. c) oCVD coated PEDOT Copper sample. The color bands on the oCVD sample indicate a nonuniform coating

Conclusion

The ITO sample that was coated in PEDOT via oCVD had the largest charging capacitance, however the glassy carbon and copper samples that were coated in the same manner did not reach nearly the same current densities. This displays that the electrochemical properties of the latter two films were possibly impeded by things like nonuniformity in film thickness and impurities within the films.

Previous research on PEDOT and PEDOT:PSS's O2RR[3] and CO2RR[4] activity displays much greater discharging capacitances than observed in this project.

Further improvement to synthesis parameters are necessary to fully understand the potential capabilities of PEDOT's CO2RR and O2RR activity.

The capacitance recorded from the oCVD PEDOT coated ITO sample shows promise in the materials ability to improve electrochemical properties of the substrate it is deposited on.

Acknowledgement

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References

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[2] Kaviani, S., et al., Electroactive and Conformal Coatings of oCVD Polymers for Oxygen Electroreduction. ACS Applied Polymer Materials, 2019

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