

IV.C.7 Non-Precious Metal Electrocatalysts

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Objectives

- Develop a non-precious metal cathode electrocatalyst for polymer electrolyte fuel cells
 - Promotes the direct four-electron transfer with high electrocatalytic activity (comparable to that of Pt)
 - Chemically compatible with the acidic polymer electrolyte
 - Low cost

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- O. Stack Material and Manufacturing Cost
- P. Component Durability
- Q. Electrode Performance

Approach

- Investigate complex oxides containing transition metals with multiple oxidation states (e.g., spinels and perovskites)
 - Oxides of metals with multiple oxidation states (e.g., Co, Ni, Fe, Mn) contain oxygen vacancies or defects that may facilitate oxygen binding and dissociation
 - Host oxide is chosen to be stable in the acidic environment (e.g., titanium and chromium oxide)
- Investigate transition metal carbides and nitrides
 - Contain surface vacancies and defects
 - Isoelectronic with platinum (e.g., tungsten carbide), catalytically active in hydro-treating and dehydration reactions
 - Resistant to acidic corrosion and electronically conducting
- Investigate metal centers attached to an electron-conducting polymer backbone
 - Allows easy control of spacing between metal centers
 - Electron conductor in close proximity to reaction site can promote high catalyst utilization

Accomplishments

- Established capability to evaluate the kinetics of oxygen reduction without the influence of mass transfer effects and verified technique using standard Pt/C electrocatalyst

- Evaluated the oxygen reduction reaction (ORR) activity and stability of nickel, iron, and cobalt complex oxides
- Initiated evaluation of the ORR activity and stability of carbides and nitrides

Future Directions

- Investigate methods for stabilizing complex transition metal oxides
- Test the ORR activity of select transition metal carbides and nitrides
- Continue to explore transition metal carbide/nitride-based materials, especially mixed transition metal carbides/nitrides (e.g., M_1M_2N , $M_1N_xC_y$, M = transition metal)
- Begin synthesis of metal centers attached to polymer backbones
- Incorporate higher-temperature ORR kinetic measurements
- Begin theoretical work (e.g., density functional theory calculations) to guide choice of candidate materials
- Fabricate and test a membrane-electrode assembly using newly-developed cathode electrocatalyst

Introduction

One of the main barriers to commercialization of polymer electrolyte fuel cell power systems is cost. The cost of the membrane-electrode assembly constitutes approximately 84% of the total fuel cell stack cost (~\$180/kW), with the anode and cathode contributing ~\$82/kW. This high cost is largely due to the use of platinum-containing electrocatalysts.¹ In the past decade, there have been significant advances in reducing the platinum metal loading of both the anode and cathode. However, any further substantial cost reductions will require the replacement of platinum with a less costly electrocatalytic material.

Approach

Based on stability diagrams and past cathode electrocatalyst work, we identified several materials that may be active for oxygen reduction and stable in the acidic fuel cell environment. These are complex oxides containing transition metals (e.g., spinels and perovskites) with multiple oxidation states (e.g., Co, Ni, Fe, Mn). The host oxide was chosen to be stable in the acidic environment, such as chromium oxide and titanium oxide. The metals were chosen to have multiple oxidation states, which are known to promote oxygen vacancies and surface defects to facilitate oxygen binding and dissociation. Two other classes of materials with desirable properties are transition metal nitrides and carbides. These materials are known to contain surface vacancies and

defects, to be isoelectronic with platinum and catalytically active in hydro-treating and dehydration reactions, resistant to acidic corrosion, and electronically conducting. The oxygen reduction kinetics of the candidate materials were determined using the thin-film rotating ring-disk electrode technique. This technique allows determination of the reaction kinetic parameters (exchange current density and transfer coefficient) independent of mass-transfer effects and the detection of the presence of reaction intermediates (e.g., H_2O_2).

Results and Conclusions

During this first year of the project, we constructed a rotating ring-disk electrode apparatus for evaluating the kinetics of the ORR on potential electrocatalyst materials supported in a Nafion[®] matrix. We verified the operation of this apparatus and technique using state-of-the-art carbon-supported platinum dispersed in a Nafion[®] matrix. The Tafel plots^a derived from these experiments, Figure 1, were used to determine the kinetic parameters. The kinetic parameters showed excellent agreement with literature values.^{2,3} We evaluated the oxygen reduction activity and stability of complex oxides containing transition metals with multiple oxidation states (spinel and perovskites) and transition metal carbides and nitrides. These

^aA plot of the log of the current density for an electrochemical reaction versus the over potential for the reaction - i.e., the relationship between the measured rate of the electrochemical reaction and the potential of the electrode.

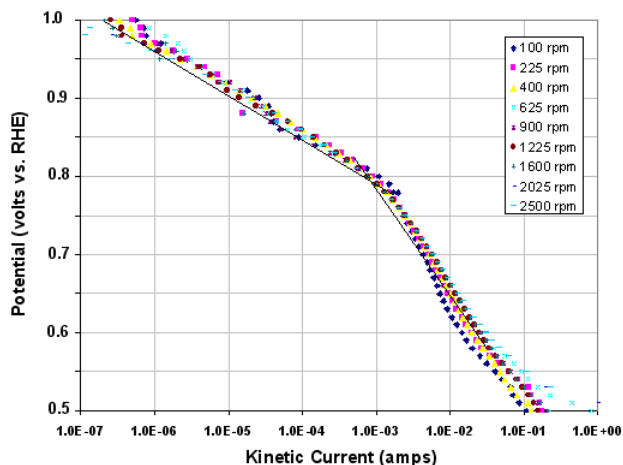


Figure 1. The Tafel plot for the ORR on the standard Pt/C cathode electrocatalyst material was determined to verify the validity of the rotating ring-disk electrode technique for determining the ORR kinetics. The kinetic parameters derived from this plot agree well with literature values.

materials were either not stable in the acidic Nafion[®] environment (oxides) or showed no activity for the ORR at useful potentials (carbides and nitrides). The cyclic voltammetry of the cobalt chromium oxide material, Figure 2, with and without the presence of oxygen in the electrolyte, showed that the material has oxygen reduction activity at low potentials (0.0 to 0.3 volts vs. RHE). However, this activity decreases with cycling of the potential, as is evidenced by disappearance of the oxygen reduction peak. We will continue to explore transition metal carbide/nitride-based materials, especially the mixed transition metal carbides/nitrides (e.g., M_1M_2N , $M_1N_xC_y$, M = transition metal). We will also develop electrocatalysts with well-controlled spacing

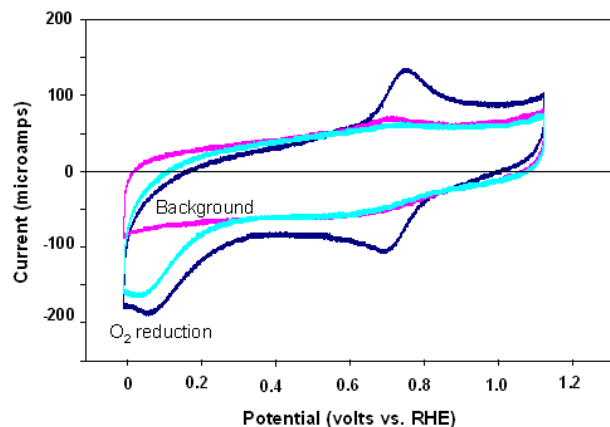


Figure 2. The voltammetry of Co-Cr-O/Carbon/Nafion[®] shows ORR activity, but instability in acidic environment.

between catalytic sites and close proximity to an electron conductor by attaching active metal centers to an electron-conducting polymer backbone.

References

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3. U.A. Paulus, T.J. Schmidt, H.A. Gasteiger, and R.J. Behm, *J. Electroanal. Chem.*, **495** (2001) 134.