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Project Entitled: Nanostructured Catalyst Systems for Fuel Cells: Synthesis and Characterization of Low Platinum Content Electrocatalysts for O₂ Reduction

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Nanostructured Catalyst Systems for Fuel Cells: Synthesis and Characterization of Low Platinum Content Electrocatalysts for O₂ Reduction

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Background

Despite considerable advances in recent years, existing fuel cell technology has two drawbacks: the inadequate efficiency of energy conversion and the high Pt content in electrocatalysts.^{i,ii} The slow kinetics of the electrocatalytic oxygen reduction reaction (ORR) can be identified as the principal cause of these problems. For this reason, practical current densities require a large number of reaction sites, i.e. a large Pt content in oxygen cathodes. Consequently, the ORR has been the focus of considerable attention.^{iii, iv, v} Despite progress achieved over the last several years, further improvements are necessary. Decreasing the Pt content and increasing its activity are the requirements that have to be satisfied to achieve a competitive cost and long-term fuel cell performance stability.

Objective

The objective of this project is to synthesize and characterize new O₂ reduction catalysts with enhanced activity and ultra low Pt loading, and to test them in membrane electrode assemblies (MEAs) to determine their performance under fuel cell cathode operating conditions.

Experimental

Membrane Electrode Assembly Fabrication.

Three-layer MEAs were fabricated with electrocatalyst loadings, types, metals fractions, binders, binder/carbon ratios, and binder/(carbon+metals) ratios as shown in Tables I-III.¹ Catalyst inks were prepared with a 5 weight percent Nafion[®] 1100 EW solution (ElectroChem, Inc.) and proprietary diluting agents.

MEAs were fabricated as described in references 1 and 2. Five (5) cm² transfer decals were prepared from glass-reinforced polytetrafluoroethylene (PTFE) films (Saint-Gobain). Each catalyst ink coat / layer was painted on one side of each decal with a flat brush (Winsor Newton) with the appropriate catalyst ink under infrared heat to a final dry weight. Nafion[®] 112 (Aldrich) was converted to the salt form, then MEAs were fabricated using the following procedure on a Carver hydraulic press: (1) Place MEA assembly into pre-heated (210 C) press and compress at 400 psig for 10 minutes. (2) Cool under pressure to room temperature. (3) Remove from press. (4) Peel decals away from the MEA assembly one at a time leaving only the electrodes fused to the membrane.

All MEAs were protonated in a 1.5M H₂SO₄ acid mixture at room temperature (23 C) for 18 hours followed by a deionized water rinse at room temperature for 2 hours to remove residual acid prior to fuel cell testing. SGL 25BC materials (SGL Carbon Group) were used as gas diffusion media.

¹ Three-layer, catalyst-coated membranes are referred to as a 3-layer MEA. Once gas diffusion layers are added, it is termed a 5-layer MEA. With seals/gaskets, it is termed a 7-layer MEA.

Table I. 51433-51-22 MEA Conditions Table

Anode	Reactant	H ₂
	Catalyst loading (mg metals per cm ²)	0.2
	Electrocatalyst type	20 weight% Pt on Vulcan XC-72 C black (E-tek DeNora)
	Metals fraction	0.200
	Binder (B)	Nafion® 1100 EW
	B/C	0.5
	B/(metals+C)	0.4
Cathode	Reactant	Air
	Catalyst loading (mg metals per cm ²)	0.4
	Electrocatalyst type	20 weight% Pt on Vulcan XC-72 C black (E-tek DeNora)
	Metals fraction	0.200
	Binder (B)	Nafion® 1100 EW
	B/C	0.5
	B/(metals+C)	0.4
Membrane		N112
Membrane thickness		50.8µm
Cell area		5cm ²
Gas diffusion layer (GDL)		SGL 25BC
Acidification		1.5M H ₂ SO ₄ , 23C, 18hr

Table II. 51433-46-22 MEA Conditions Table

Anode	Reactant	H ₂
	Catalyst loading (mg metals per cm ²)	0.2
	Electrocatalyst type	20 weight% Pt on Vulcan XC-72 C black (E-tek DeNora)
	Metals fraction	0.200
	Binder (B)	Nafion® 1100 EW
	B/C	0.5
	B/(metals+C)	0.4
Cathode	Reactant	Air
	Catalyst loading (mg metals per cm ²)	0.4
	Electrocatalyst type	BNL Pt/Pd/C
	Metals fraction	0.255
	Binder (B)	Nafion® 1100 EW
	B/C	0.5
	B/(metals+C)	0.4
Membrane		N112
Membrane thickness		50.8µm
Cell area		5cm ²
Gas diffusion layer (GDL)		SGL 25BC
Acidification		1.5M H ₂ SO ₄ , 23C, 18hr

Table III. 51433-50-14 MEA Conditions Table

Anode	Reactant	H ₂
	Catalyst loading (mg metals per cm ²)	0.2
	Electrocatalyst type	20 weight% Pt on Vulcan XC-72 C black (E-tek DeNora)
	Metals fraction	0.200
	Binder (B)	Nafion® 1100 EW
	B/C	0.5
	B/(metals+C)	0.4
Cathode	Reactant	Air
	Catalyst loading (mg metals per cm ²)	0.4
	Electrocatalyst type	BNL IrPt/Pd/C
	Metals fraction	0.255
	Binder (B)	Nafion® 1100 EW
	B/C	0.5
	B/(metals+C)	0.4
Membrane		N112
Membrane thickness		50.8µm
Cell area		5cm ²
Gas diffusion layer (GDL)		SGL 25BC
Acidification		1.5M H ₂ SO ₄ , 23C, 18hr

Fuel Cell Testing

Single-cell fuel cell testing was performed using a 600 W Fuel Cell Technologies, Inc. test station with Poco graphite flow fields and glass-reinforced PTFE seals/gaskets. The flow fields were single-serpentine, 800 μm -wide channels with a channel: land width ratio of 1:1 and a 5 cm^2 active area. This station is equipped with an Agilent Technologies 120 A load module, digital mass flow controllers, an automated back pressure system, 5 cm^2 fuel cell hardware, an on-board AC impedance system and humidity bottle assemblies. The on-board electrochemical impedance spectroscopy system was used to measure the in situ high frequency resistance (HFR) of each MEA at a frequency of 1 kHz. (The HFR is the sum of the membrane, interfacial and electrode resistances.).

All MEAs were conditioned at 80 C, 100% relative humidity (RH) at 0.50 V until the in situ HFR and load achieved stable values before polarization curves were collected. Short-term polarization curves were collected from OCV to 0.30 V at 0.10 V increments with a 5 minute delay.

Results

In this testing, the Pt and Ir-Pt monolayer on Pd cathode catalysts had improved current density per mg Pt compared to standard E-tek Pt/C cathode catalyst controls on Nafion® 112 at 80 C, 100% RH, 7.5 psig in H_2 -air, as shown in Figure 1. Ir-Pt/Pd/C polarization curves also appeared to have improved stability at high current densities where mass transport losses dominate. This improved current density occurred despite the fact that both BNL electrocatalysts had higher HFR values than the E-tek control, as shown in Figure 2.²

Transmission electron microscopy (TEM) was used to characterize the electrode morphology. Figures 3-5 show the unique structures of each cathode studied. It is seen from these figures that the BNL electrocatalysts agglomerated more than the E-tek control.

² Additional polarization curves and MEA conditions tables can be found in BNL Nanocat Preliminary Report III Rev. 2, located in the Appendices. Additional reports and a joint white paper can also be found in the Appendices.

Figure 1. Specific Polarization Curves; Conditions: 80 C, 100% RH, 7.5 psig, 200 sccm H₂, 500 sccm air, 5.00 cm² cell area.

Figure 2. HFR Plots; Conditions: 80 C, 100% RH, 7.5 psig, 200 sccm H₂, 500 sccm air, 5.00 cm² cell area.

Figure 3. TEM Image of 51433-51-22 Pt/C Control Cathode

Figure 4. TEM Image of 51433-46-22 Pt/Pd/C Cathode

Figure 5. TEM Image of 51433-50-14 IrPt/Pd/C Cathode

Promising Observations

1. Pt and Ir-Pt monolayer on Pd cathode catalysts show improved current density per mg Pt compared to standard E-tek Pt/C cathode catalyst controls.
2. Ir-Pt/Pd/C polarization curves appear to have improved stability at high current densities where mass transport losses dominate.
3. Based on TEM, BNL electrocatalysts agglomerate more than E-tek control.

Recommendations

1. Eliminate BNL electrocatalyst agglomeration.
2. Perform optical microscopy to determine electrode thickness and quality.
3. Generate Tafel plots to evaluate kinetic parameters.
4. Down select and evaluate performance as a function of temperature and relative humidity.
5. Evaluate effect of catalyst type on hydrogen crossover and durability.
6. Study the binder/catalyst interaction.

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