

V.C.5 Novel Non-Precious Metal Catalysts for PEMFC: Catalyst Selection through Molecular Modeling and Durability Studies

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Objectives

- Synthesize carbon-based metal-free catalysts and carbon-composite catalysts for oxygen reduction reaction (ORR).
- Optimize catalytic active reaction sites as a function of carbon support, surface oxygen groups, nitrogen content, surface modifiers, pyrolysis temperature, porosity, and the concentration of the non-metallic additive "X" in the catalyst matrix.
- Evaluate catalyst stability under various conditions to demonstrate the potential of carbon-based catalysts to substitute conventional Pt catalysts currently used in the membrane electrode assembly (MEA).

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:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

- Non-Pt catalyst activity per volume of supported catalyst (Year 2010) : $>130 \text{ A/cm}^3$ (stack) at $0.8 \text{ V}_{\text{IR-free}}$
- Cost: at least 50% less than a target of $0.2 \text{ g (Pt loading)/peak kW}$
- Durability: $>2,000 \text{ h}$ operation with less than 10% power degradation

Accomplishments

- Carbon-based metal-free catalysts
 - Accomplished the catalytic activity as high as 288 A/cm^3 at 0.2 V for 6 mg/cm^2 catalyst loading in the fuel cell.
 - No irreversible loss of catalytic activity during 200 h of continuous operation.
- Metal-free CN-X and C-X catalysts
 - Optimized "catalyzed pyrolysis" conditions to increase the concentration of the active reaction sites.
 - Accomplished the catalytic activity as high as 2.0 A/cm^2 at 0.2 V for 4 mg/cm^2 catalyst loading in the fuel cell.
 - No significant performance degradation was observed for 480 h of continuous operation.
- Corrosion resistant carbon support
 - Tested the high corrosion resistant carbon-composite as cathode catalyst support according to the DOE test protocol.
 - USC Pt/CC showed lower performance degradation than the one reported for the General Motors (GM) Pt/C catalyst.



Introduction

Pt and Pt based alloy catalysts are widely used in proton exchange membrane fuel cells (PEMFCs) because of their high catalytic activity and selectivity as

well as high corrosion resistance. In the last few years, several transition metal compounds such as macrocycle-based metal porphyrin system, chevrel phase-type compounds and other transition metal chalcogenides have been proposed as selective catalysts for ORR. However, significant increase in activity and stability of the catalyst is still essential for PEMFC applications. The objective of this project is to develop highly active and stable carbon-based metal-free catalysts and carbon-composite catalysts with strong Lewis basicity (π electron delocalization) to facilitate ORR.

Approach

Carbon-based metal-free catalysts were synthesized by modifying the surface functional groups on the porous carbon black with low-cost organic precursors. As a next step, highly active carbon-composite catalysts were developed using a metal-free catalyst as a catalyst support through the following steps: (i) the deposition of Co-N or Co-Fe-N chelate complex on the support, and (ii) the high-temperature pyrolysis, and (iii) the chemical post-treatment (acid leaching). In a separate study, the carbon-composite catalyst was used as the support for the preparation of Pt/CC catalysts and the stability of the catalyst/catalyst support was evaluated using DOE test protocol.

Results

Highly active and stable carbon-composite catalysts for oxygen reduction in PEMFCs were developed through the high-temperature pyrolysis of Co-Fe-N chelate complex, followed by the chemical post-treatment. A carbon-based metal-free catalyst developed by us was used as the support. The carbon-composite catalyst showed an onset potential for oxygen reduction as high as 0.87 V in H_2SO_4 solution, and generated less than 1% H_2O_2 . The PEMFC exhibited a current density as high as 288 A/cm^2 at 0.2 V for a catalyst loading of 6.0 mg/cm^2 . No significant performance degradation was observed for 480 h of continuous fuel cell operation. Materials characterization studies indicated that the metal-nitrogen chelate complexes decompose at high pyrolysis temperatures above 800°C, resulting in the formation of the metallic species. During the pyrolysis, the transition metals facilitate the incorporation of pyridinic and graphitic nitrogen groups into the carbon matrix, and the carbon surface doped with nitrogen groups is catalytically active for oxygen reduction. Figure 1 compares the powder X-ray diffraction (XRD) patterns for the metal-free support and the carbon-composite catalyst. The XRD pattern for the carbon-composite catalyst shows the characteristic diffraction peaks that can be assigned to a mixture of the metallic phases (i.e., Co, Fe and Co_xFe_y) and to the cementite phase (Fe_3C).

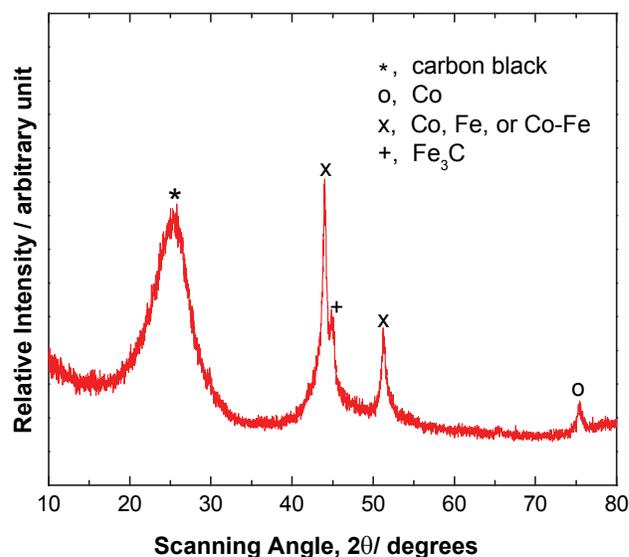


FIGURE 1. Powder XRD patterns of the metal-free carbon support and the carbon-composite catalyst. The carbon-composite catalyst was subjected to the chemical leaching.

In order to study the role of transition metals in facilitating the incorporation of nitrogen functional groups during the pyrolysis, the catalyst was prepared without using any transition metals as follows: ethylene diamine was adsorbed on the metal-free carbon support, followed by the pyrolysis at 900°C and the chemical leaching in 0.5 M H_2SO_4 solution at 90°C. The X-ray photoelectron spectroscopy (XPS) data are presented in Figure 2. It was found (data not shown) that the catalyst prepared without metal-nitrogen complexes showed no improvement in the activity in comparison to the metal-free carbon support. As indicated in Figure 2, the surface nitrogen concentration increased from 1.9 to 3.9 wt%, when the pyrolysis was performed in the presence of transition metals.

Figure 3 demonstrates the cell voltage transient and the polarization behavior measured for the fuel cell with the carbon-composite cathode catalyst for stability test. The tests were run at 50 mA/cm^2 using H_2 and O_2 without applying the back pressure. The cathode catalyst loading was 2.0 mg/cm^2 . The test result showed an initial increase of potential to ca. 0.35 V, followed by a very slight decay with time (the decay rate $\approx 80 \mu\text{V h}^{-1}$). Note that only ca. 10% performance decrease was observed for 480 h of continuous operation. Figure 4 compares the XPS spectra of N 1s region for the catalysts taken from the fresh MEA and the MEA tested for 480 h. Two dominant peaks are observed at 398.5 and 401.0 eV that can be assigned to pyridinic nitrogen and graphitic nitrogen, respectively, for both samples. This result confirms that catalytically active nitrogen functional groups remain stable on the carbon matrix during long-term fuel cell operation.

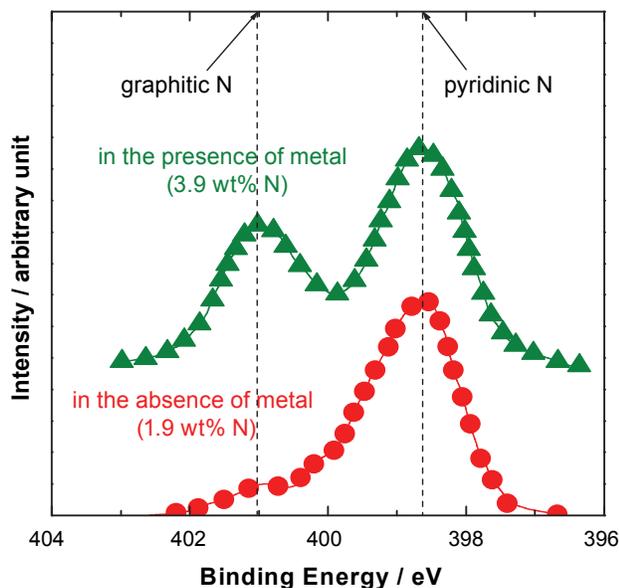


FIGURE 2. XPS spectra of N 1s region obtained for the catalysts pyrolyzed in the absence and presence of transition metals (Co and Fe). The carbon-composite catalysts were subjected to the chemical leaching.

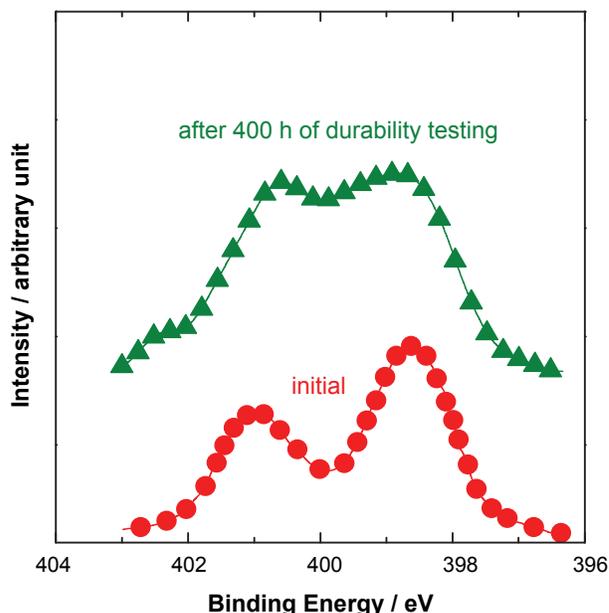


FIGURE 4. XPS spectra of N 1s region for the catalysts taken from the fresh MEA and the MEA tested for 480 h.

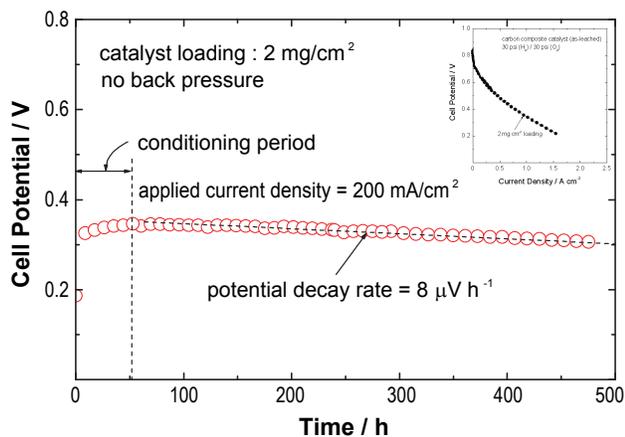


FIGURE 3. Galvanostatic potential transient measured on the carbon-composite catalyst for stability test. The cathode catalyst loading was 2.0 mg/cm². The tests were run at 50 mA/cm² using H₂ and O₂ without applying the back pressure. The polarization behavior is also given in the inset.

Figure 5 summarizes the percentage of potential loss at 0.5 A/cm² for GM, Pt/CC1, and USC Pt/CC2 catalysts as a function of corrosion times ranging from 0 to 50 h. The GM fuel cell data presented in this figure was obtained from General Motors Fuel Cell Activities, “Accelerated test protocols to demonstrate 5,500 hr catalyst durability”, Part 2 of 2, for presentation to the FreedomCAR Fuel Cell Tech Team and DOE, 15 June 2005. Figure 6 presents the percentage of potential loss at 0.5 A/cm² on Pt/CC1 and Pt/CC2 catalysts as a function of corrosion times ranging from 0 to 100 h.

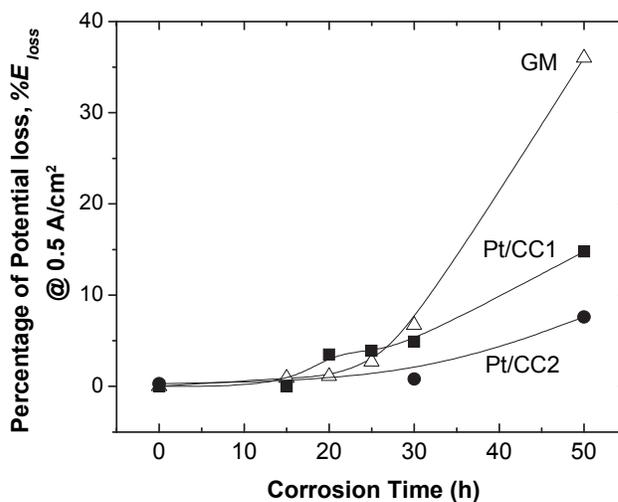


FIGURE 5. Comparison of the percentage of potential loss at 0.5 A/cm² on GM, Pt/CC1, and Pt/CC2 catalysts as a function of corrosion times ranging from 0 to 50 h.

The durability studies of both the Pt/CC catalysts demonstrated much slower decrease of the catalyst activities when polarized at 1.25 V than those observed in the GM report. At 0.5 A/cm² the observed decrease of the catalyst activity prepared with USC composite support was 7.6% - 14.8 % compared with a loss of activity of 36% observed by GM. The results indicated more than 50% better performance of the USC supported platinum catalyst than the activity observed by GM after 50 h of testing. After 100 h at 1.25 V, it was not possible to compare the results of the USC

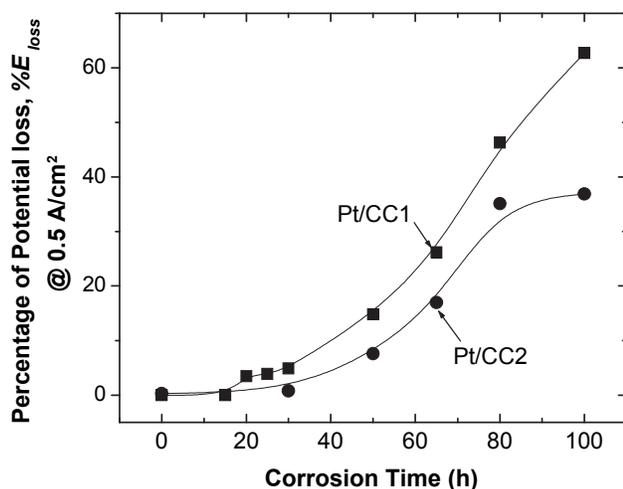


FIGURE 6. Comparison of the percentage of potential loss at 0.5 A/cm² on Pt/CC1 and Pt/CC2 catalysts as a function of corrosion times ranging from 0 to 100 h.

supported catalysts because the GM data were not available. It is necessary in the future further to improve the stability of the support. Development of nano-structured conductive polymer as a support with high stability is currently carried out at USC.

Figure 7 presents the polarization curves of the Pt/CC catalyst subjected to load cycling (step change between 0.7 V/30 s and 0.9 V/30 s) using H₂/N₂ with an relative humidity (RH) of 100% and back pressure of 150 kPa. The polarization curve was obtained using H₂ and air. As can be seen from the figure, the activity of the catalyst remained unchanged at 0.8 A/cm² over 30,000 cycles. The DOE target is ≤30 mV loss at 0.8 A/cm². The stability test indicates that the carbon-composite catalyst developed at USC can be an alternate high corrosion resistant catalyst support for PEMFCs.

Conclusions

Carbon-composite catalysts were developed using a metal-free catalyst as a catalyst support through catalyzed pyrolysis followed by chemical post-treatments. Pt/CC catalysts were synthesized using the carbon-composite catalyst as the catalyst support and the stability test was performed according to DOE test protocol. XPS studies revealed the increase of nitrogen content in carbon-composite catalysts when pyrolyzed in the presence of transition metals. A stability test of the carbon-composite catalyst with a loading of 2 mg/cm² at 50 mA/cm² using H₂ and O₂ without applying the back pressure showed an initial increase of potential to ca. 0.35 V, followed by a very slight decay with time (the decay rate ≈80 μV h⁻¹). Only ca. 10% performance decrease was observed for 480 h of continuous operation. The durability studies of both the Pt/CC

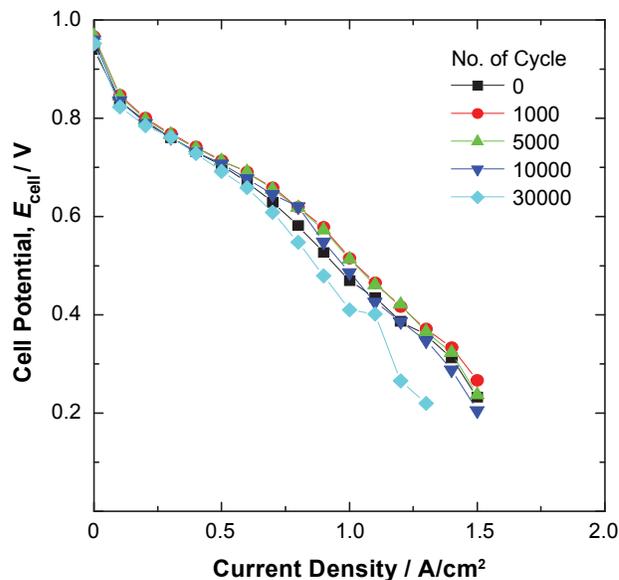


FIGURE 7. Comparison of polarization curves of Pt/CC catalyst after load cycling test.

catalysts synthesized in this study demonstrated much slower decrease of the catalyst activities when polarized at 1.25 V than those observed in the GM report. At 0.5 A/cm² the observed decrease of the catalyst activity prepared with USC composite support was 7.6%–14.8% compared with a loss of activity of 36% observed by GM. The results indicated more than 50% better performance of the USC supported platinum catalyst than the activity observed by GM after 50 h of testing. Load cycle test performed under 100% RH did not show any loss in potential at 0.8 A/cm².

Future Directions

University of South Carolina

- Prepare carbon-composite catalyst using mesoporous carbon support.
- Improve water management by controlling hydrophobicity of catalyst layer and by reducing catalyst layer thickness.
- Increase the fuel cell durability by improving the integrity of the carbon-composite catalyst layer in the MEA.
- Reduce the MEA resistance by decreasing the catalyst layer thickness and by increasing the specific gravity and activity of the catalyst.

Northeastern University and Case Western Reserve University

- No additional work.

Special Recognitions & Awards/Patents Issued

1. Crystal Flame Innovation Award in Research from FuelCell South was presented to Dr. Popov's research group for research work in the field of non precious catalyst development and preparation thin film assemblies with nano-structured catalysts and the development of the pulse deposition technique for preparation of membrane electrode assemblies.
2. B. N. Popov, J. W. Lee, N. P. Subramanian, S.P. Kumaraguru, H. Colon, V. Nallathambi, V, X. Li, G. Wu, Carbon-based composite electrocatalysts for low temperature fuel cells. *U.S. Patent Appl.* (2008).
3. B. N. Popov, N.P. Subramanian, H. Colon, Composite catalysts supported on modified carbon substrates and methods of making the same. *U.S. Patent Appl.* (2008).

FY 2008 Publications/Presentations

1. X. Li, L. Liu, J.W. Lee, B.N. Popov, Development of tellurium-modified carbon catalysts for oxygen reduction reaction in PEM fuel cells. *J Power Sources* 182, 18 (2008).
2. V. Nallathambi, J.W. Lee, X. Li, N.P. Subramanian B.N. Popov, Development of Highly Active Metal-Free Carbon-Based Catalysts for Oxygen Reduction in PEM Fuel Cells, *J. Electrochem. Soc.*, (Under Review July 2008).

3. J.W. Lee, B.N. Popov, Ruthenium-based electrocatalysts for oxygen reduction reaction-a review. *J Solid State Electrochem.*, 11, 1355 (2007).
4. V. Nallathambi, G. Wu, N.P. Subramanian, S.P. Kumaraguru, J.W. Lee, B.N. Popov, Highly active carbon-composite electrocatalysts for PEM fuel cells. *ECS Transactions* (2007), 11, 241 (2007).
5. X. Li, H. Colon, G. Wu, J.W. Lee, B.N. Popov, Development of stable Pt-Co cathode catalysts for PEM fuel cells. *ECS Transactions* (2007), 11, 1259 (2007).
6. X. Li, V. Nallathambi, H.R. Colon-Mercado, J.-W. Lee, B.N. Popov, "Development of Stable Pt-Co Cathode Catalysts for PEM Fuel Cells," *212th Meeting of the Electrochem. Soc.*, Washington DC, October, 2007.
7. V. Nallathambi, G. Wu, N.P. Subramanian, S.P. Kumaraguru, J.-W. Lee, B.N. Popov, "Highly Active Carbon-Based Electrocatalysts for PEM Fuel Cells," *212th Meeting of the Electrochem. Soc.*, Washington, D.C., October, 2007.