V.F.14 High Performance and Durable Low PGM Cathode Catalysts

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Overall and Fiscal Year (FY) 2015 Objectives

- Increase mass activity and durability of platinum-based electrocatalysts through three-dimensional (3-D) porous low platinum group metal (PGM) electrocatalysts
- Demonstrate improved performance and durability in fuel cell tests
- Provide pathway to achieve DOE 2020 electrocatalyst target

Technical Barriers

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

(A) Durability

(B) Cost

Technical Targets

This project addresses fuel cell durability and cost (activity) technical barriers through engineering 3-D porous graphene supported nanocomposite platinum catalysts. The goal of this project is to demonstrate that the enhanced durability and performance of our triple-junction stabilized platinum electrocatalysts obtained from ex situ tests can be successfully achieved in fuel cell device test. The specific targets and status are shown in Table 1.

TABLE 1. Project Targets and Status of Electrocatalysts

	RDE test		MEA test	
	Project Target	Project Status	Project Target	Project Status
ORR Activity	80 mA/mg_{Pt}	137 mA/mg_{Pt}	80 mA/mg_{Pt}	On-going
Durability	20% increase	186% (ESA), 275% (ORR)	<20% loss in activity after 1.2 V hold test.	On-going
Carbon Corrosion	NA	NA	2X reduction in carbon corrosion over baseline	On-going

RDE – rotating disk electrode; MEA – membrane electrode assembly; ORR – oxygen reduction reaction; NA – not applicable; ESA – electrochemical surface area

FY 2015 Accomplishments

- Coated platinum nanoparticles uniformly on porous 3-D indium tin oxide (ITO)-graphene nanocomposite using both vapor deposition method and chemical solution method
- Demonstrated enhanced activity (1.5X) and durability (2X) of Pt-ITO-porous graphene in rotating disk electrode (RDE) test
- Improved the durability further of graphene through thermal annealing (transmission electron microscopy [TEM] imaging indicates no sintering of platinum during thermal annealing)
- In situ fuel cell (MEA) tests show much higher performance of 3-D graphene-based electrocatalysts than that of two-dimensional (2-D) graphene that was obtained in our previous project, but also indicate instability of ITO at elevated temperature.

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INTRODUCTION

There is a strong need to decrease the amount of platinum electrocatalyst used in fuel cells and increase its durability for transportation application. Conventional strategies include platinum nanocrystals and platinum alloy with well-controlled structures, durable carbon support, non-carbon support, etc. We have developed the so-called "metal-metal oxide-carbon" triple junction concept to stabilize platinum and protect carbon from corrosion [1]. It also improved the activity of platinum. Good performance was not achieved in fuel cell testing mainly because of the transport issue due to the use of 2-D graphene. In this project, our main goal is to demonstrate the concept in fuel cell

device test using 3-D porous graphene as support so that the transport issue could be addressed.

APPROACH

Our approach includes engineering 2-D graphene into a 3-D architecture and using directly synthesized 3-D porous graphene from a scalable method to address the transport issue in fuel cell tests while maintaining the advantage of our concept of using the triple-junction structure to stabilize platinum electrocatalysts and protect carbon from corrosion. The chemical solution coating processes of metal oxides and Pt catalysts are scalable.

RESULTS

We have intensively studied the porous 3-D Pt-ITO-graphene electrocatalysts. First, we successfully synthesized uniformly dispersed ITO nanoparticles (5─8 nm) on 3-D porous graphene (Figure 1a). Platinum nanoparticles were uniformly deposited onto ITO-graphene using both the chemical solution method (Figure 1b) and the vapor deposition method (Figure 1c). A close inspection of the porous 3-D Pt-ITO-graphene electrocatalyst reveals its detailed structure. Most of the platinum nanoparticles stay around the ITO nanoparticles, indicating a triple-junction structure is formed (Figure 1d). This result is consistent with what we have achieved on the 2-D graphene substrate.

Further investigation reveals that the 3-D porous Pt-ITO-graphene has very high resistance to thermal annealing (Figures 2a and 2b) while the platinum on carbon support without ITO has severe sintering (Figures 2c and 2d). These results indicate that ITO nanoparticles stabilize platinum nanoparticles against thermal sintering. Thermal annealing is a well-known strategy to improve catalyst performance generally (activity and durability). This provides more room to tune the electrocatalysts.

Ex situ RDE electrochemical test results show high oxygen reduction reaction (ORR) performance of Pt-ITO-graphene, particularly the durability (Figure 3). After thermal annealing, the durability of Pt-ITO-graphene was further increased with only a slight decrease in activity. The electrochemical results are consistent with our TEM analysis. These results indicate the concept of using metal-metal oxide-carbon triple-junction structure to stabilize and improve the performance of platinum electrocatalysts is applicable for porous 3-D substrates. This revelation is significant because the porous 3-D architecture is more applicable in fuel cell devices.

From in situ fuel cell (MEA) tests, the 3-D Pt/graphene shows much better performance than the 2-D Pt/graphene that was obtained in our previous project, which was published in Reference 2. In the high current density operating region—for example, at cell voltage of 0.4 V—the Pt/2-D_graphene from the previous project [2] in an H_2/O_2 cell delivered 310 mA/cm$_2$. The Pt/3-D_graphene from this project delivered 710 mA/cm$_2$ in H_2/air cells (with other testing conditions, such as Pt loading, temperature, relative humidity [RH], and pressure remaining exactly the same or similar). This demonstrates the significantly positive effect of graphene structure engineering from 2-D to 3-D; however, Pt-ITO-graphene is less stable than Pt/graphene (Figure 4a). X-ray diffraction (XRD) patterns of Pt-ITO-graphene before and after an accelerated degradation test (ADT) in an MEA reveal the disappearance of ITO patterns after the ADT

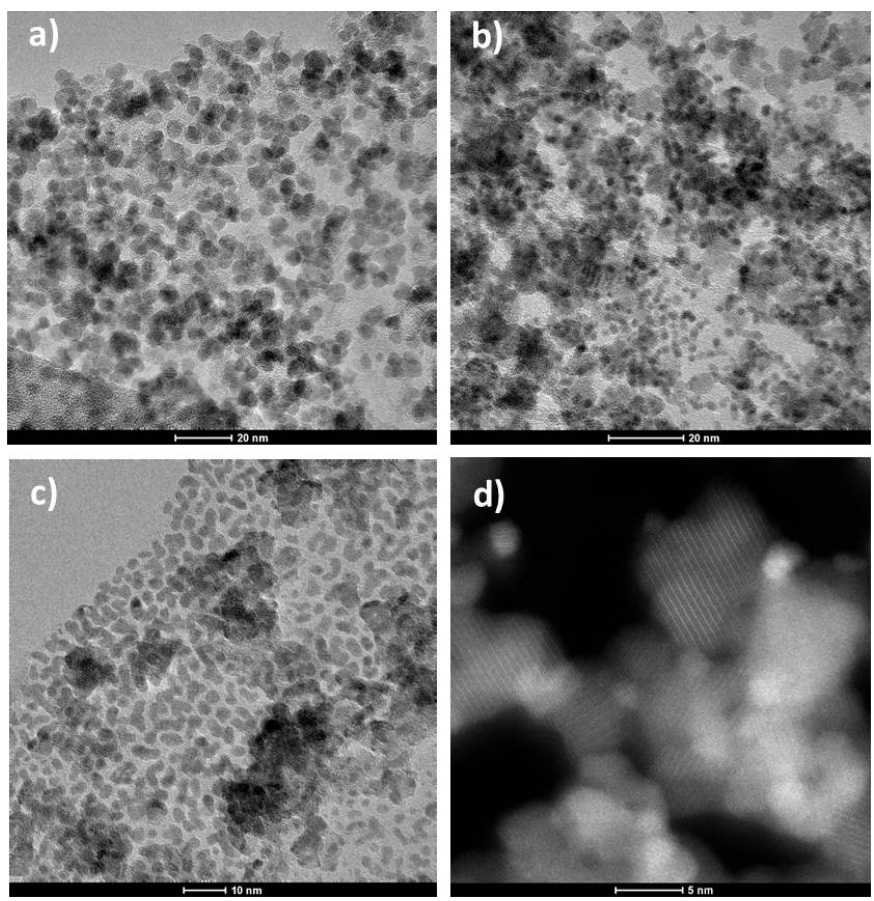

FIGURE 1. TEM images of ITO-graphene (a), Pt-ITO-graphene using chemical solution method (b), Pt-ITO-graphene using vapor deposition method (c), Pt-ITO-graphene using chemical solution method – high resolution dark-field images (d)

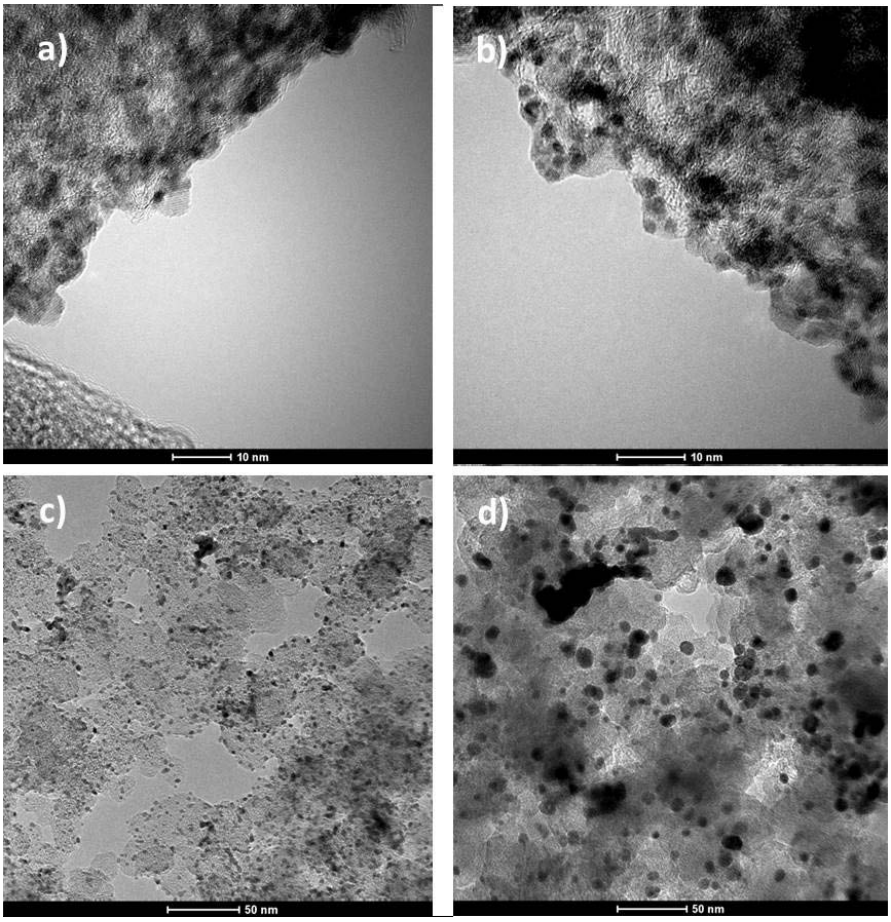

FIGURE 2. TEM images of Pt-ITO-graphene (a, b) and Pt/C (c, d) before (a, c) and after (b, d) thermal annealing

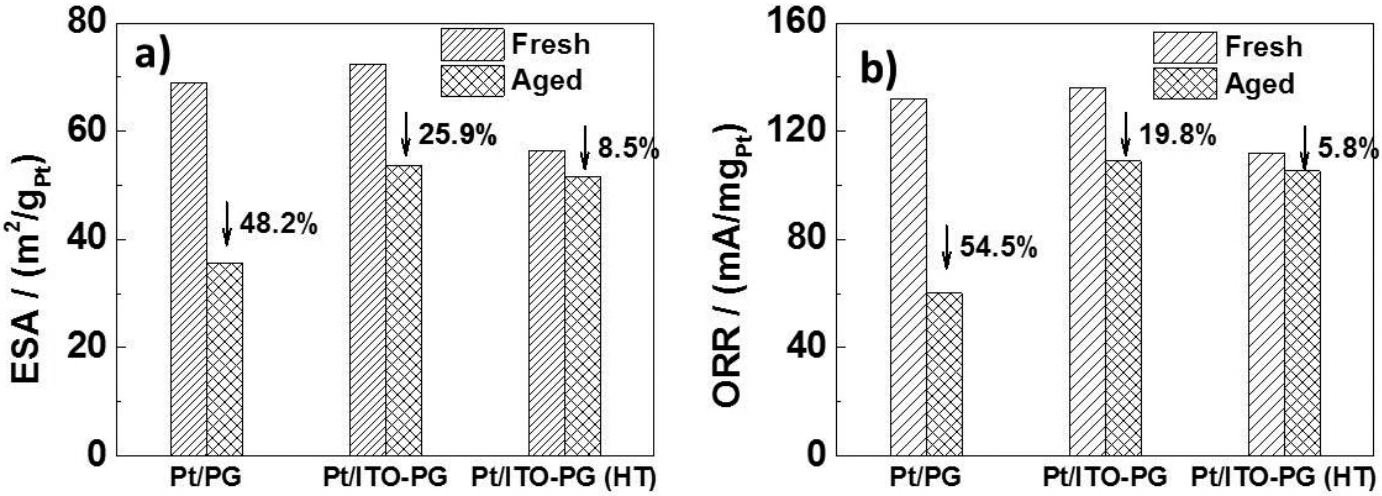

FIGURE 3. Electrochemical surface area (ESA) and ORR activity before and after accelerated degradation test (ADT). ESA1 and ORR1 are values before ADT; ESA2 and ORR2 are values after ADT (PG = porous graphene, HT = heat-treatment/thermal annealing).

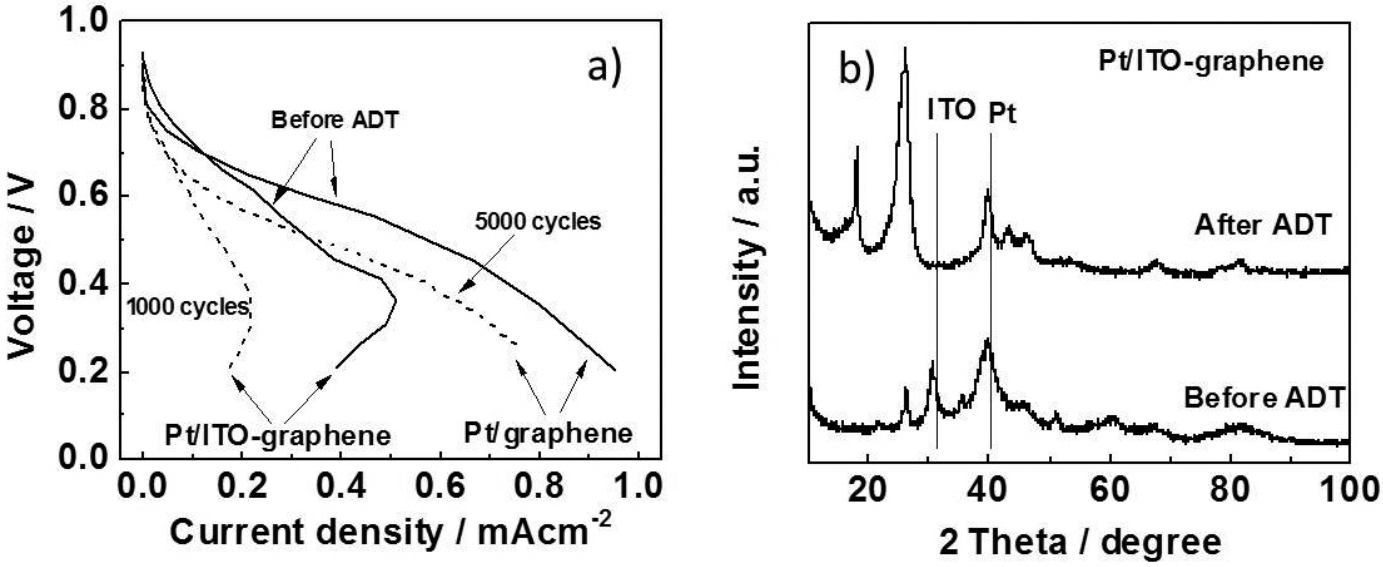

FIGURE 4. a) In situ fuel cell testing results of 3-D Pt/graphene and Pt-ITO-graphene; b) XRD patterns of Pt-ITO-graphene before and after ADT. Testing conditions: 1) Current-voltage curves: A/C: 0.28/0.23 mg Pt/cm$_2$, 80°C, 100% RH, 150 kPa, H_2/air: 200/600 sccm, SGL 25BC; 2) ADT electrochemical stressing protocol: 1.0-1.5 V cyclic voltammetry at 500 mV/s. (a.u. = arbitrary units).

(Figure 4b). This indicates the possible dissolution of ITO during MEA testing (at 80°C) and the urgency of developing alternative metal oxide nano coatings with high stability. In the future, if the well-developed nano-alloys and core-shell electrocatalysts are integrated into the metal oxide coated 3-D graphene, both the performance and durability will be further improved.

CONCLUSIONS AND FUTURE DIRECTIONS

The concept of using metal-metal oxide-carbon triple-junction structure to stabilize and improve the performance of platinum electrocatalysts that we developed previously on a 2-D graphene substrate was successfully demonstrated on a 3-D porous substrate.

- Uniformly dispersed platinum and ITO nanoparticles were successfully deposited on a 3-D porous graphene substrates. TEM characterization revealed that it forms a Pt-ITO-graphene junction structure.
- This junction structure stabilizes platinum nanoparticles and provides high resistance against thermal annealing that can be used to tune electrocatalyst performance.
- Electrochemical test results show enhanced performance of Pt-ITO-graphene, particularly the durability.
- Alternative metal oxides will be investigated to replace ITO so that the instability issue of ITO can be addressed.
- Advanced nano-alloys and core-shell electrocatalysts will be integrated into the metal oxide coated 3-D graphene to further improve both the performance and durability.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Y. Shao, Y. Cheng, R. Kou, Y. Wang, J. Liu. "Durable Nanostructured Electrocatalysts for Oxygen Reduction Reaction: Materials Design and Testing Protocol." 2015 MRS Spring Meeting & Exhibit April 6–10, 2015, San Francisco, California.

2. Y. Shao, Y. Wang, J. Liu. "Porous nanocomposite from scalable synthesis for electrocatalytic applications." Invention Report filed on December 9, 2014.

3. Y. Shao, Y. Cheng, W. Duan, W. Wang, Y. Lin, Y. Wang, J. Liu. "Nanostructured Electrocatalysts for PEM Fuel Cells and Redox Flow Batteries: a Selected Review." Accepted for publication in ACS Catalysis.

4. Y. Shao, Y. Wang, J. Liu. "Support solution for PEM fuel cell cathode." Invited paper by Nano Energy, to be submitted.

REFERENCES

1. Kou, R.; Shao, Y.Y.; Mei, D.H.; Nie, Z.M.; Wang, D.H.; Wang, C.M.; Viswanathan, V.V.; Park, S.; Aksay, I.A.; Lin, Y.H.; Wang, Y.; Liu, J., Stabilization of Electrocatalytic Metal Nanoparticles at Metal-Metal Oxide-Graphene Triple Junction Points. J. Am. Chem. Soc. 2011, 133 (8), 2541–2547.

2. Park, S.; Shao, Y.Y.; Wan, H.Y.; Rieke, P.C.; Viswanathan, V.V.; Towne, S.A.; Saraf, L.V.; Liu, J.; Lin, Y.H.; Wang, Y., Design of graphene sheets-supported Pt catalyst layer in PEM fuel cells. Electrochem. Commun. 2011, 13 (3), 258–261.