

Development of Platinum Embedded in Reduced Graphene Oxide (Pt@rGO) for Fuel Cell Applications

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Introduction:

For the past century, researchers have been searching for an environmentally friendly alternative energy conversion device to replace the antiquated 18th-century internal combustion system. One of the most promising and emerging alternative energy conversion devices is the polymer electrolyte membrane fuel cell (PEMFC). The hydrogen fuel cell essentially converts hydrogen gas and oxygen gas into water while producing electrical energy, rendering this system significantly more environmentally attractive [1]. Some of the reasons that this system is not implemented today include its high cost and relatively low efficiencies from its catalyst layer, compared to its combustion system counterpart. Conventionally, the catalyst layer is composed of a supporting matrix of porous carbon black and platinum (Pt). Platinum serves the pivotal role as the catalyst, converting the incoming hydrogen gas into its hydronium ions and electrons. Once the platinum is embedded within the carbon black, some of carbon black's pores close during synthesis, rendering the platinum nanoparticles inside the pores useless.

Instead of using a porous carbon material, we will be employing reduced graphene oxide (rGO), a planar carbon structure, to maximize the efficiencies of Pt in fuel cell's catalyst layer. The aggregation of Pt particles on the carbon composite is still one of the imminent obstacles for hydrogen fuel cell integration; this

conglomeration decreases the catalyst efficiencies in the catalyst layer [2]. Different concentrations of stabilizers, such as Nafion ionomer and polyvinylpyrrolidone (PVP) were employed to prevent aggregation of Pt nanoparticles. Nafion ionomer is a sulfonated tetrafluoroethylene based fluoropolymer with a hydrophobic backbone and with hydrophilic side chains. In solution, Nafion ionomer forms micelles due to its amphiphilic property. PVP is a water soluble polymer with the ability to quickly form thin films. Because of this property, PVP can coat other molecules. These two dispersing agents lower the tendency for Pt nanoparticles to conglomerate. An increase Pt nanoparticle conglomeration would in turn lower the effective surface area of Pt and hence decrease catalytic activity in the hydrogen fuel cell.

Experimental Procedure:

We added 33 wt% PVP, 60 wt% PVP, and 33 wt% PVP and 2.5 vol% Nafion in Sample 1, 2 and 3 respectively. The solutions underwent catalytic vapor diffusion and heat treatment at 500°C. The composites were then observed under the scanning electron microscope (SEM), x-ray diffraction (XRD), and cyclic voltammetry (CV).

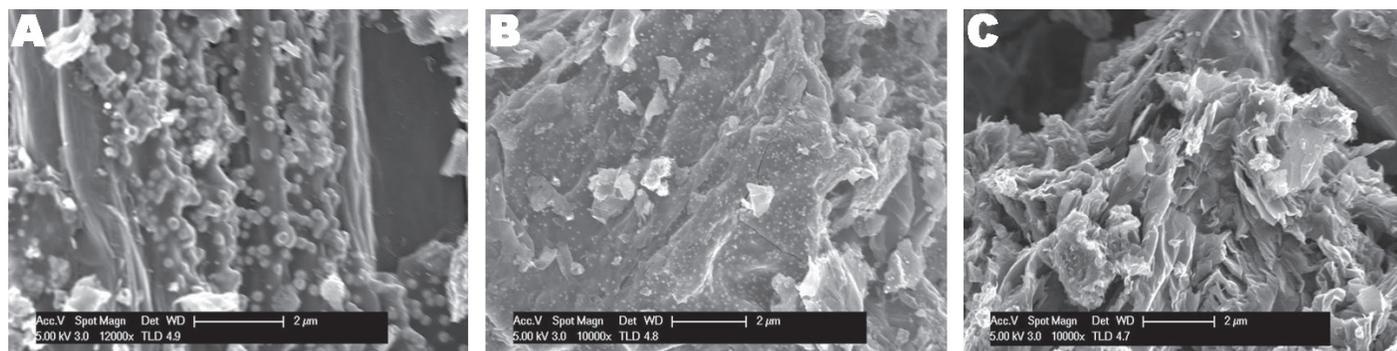


Figure 1: a) Scanning electron microscope (SEM) of Sample 1 containing 33 wt% PVP; b) SEM of Sample 2 containing 60 wt% PVP; c) SEM of Sample 3 containing 33 wt% PVP and 2.5 vol% Nafion ionomer.

Results and Conclusions:

The samples were observed through the SEM to visually understand the Pt behavior in each of the samples. In Figure 1 a), Sample 1 displayed Pt aggregation on rGO surface. With 2 μm as the resolution, the aggregated particles were estimated to be ~ 100 nm average in diameter. In Figure 1 b), the SEM image displayed significantly less Pt aggregation on the rGO surface for an increase of PVP. In Figure 1 c), an inclusion of a low concentration of Nafion depicted no visible Pt nanoparticle aggregation at a 2 μm resolution.

Each aggregated Pt particle was composed of the amalgamation of Pt nanoparticles. The average crystalline size of the aggregated particles can be calculated using the Scherrer equation for XRD data. From the summarized data in Figure 2, the Pt crystal size ranges from 5 nm to 9 nm in diameter of the Pt embedded in rGO (Pt@rGO) composites. The ACS amongst the three samples was relatively similar despite the different concentrations of stabilizing agents.

The efficiencies of the Pt in each sample were also observed with cyclic voltammetry (CV). CV was ramped from potentials of -0.4 V to 1.6 V with sweep rate of 10 mV/s. At negative potentials, the hydrogen oxidation reactions ($\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$) were measured. The total charge accumulated (proportional to the area underneath the cathodic peak) was converted into the amount of Pt surface area useful for oxidation purposes. A low concentration of PVP proved to have the lowest performance as it yielded the lowest effective surface area (ESA) of Pt. The inclusion of a low concentration of Nafion and PVP drastically increased Pt ESA. PVP was hypothesized to act as a coating layer over the Pt nanoparticles, sterically stabilized Pt nanoparticles from aggregating. Likewise, the behavior of Nafion ionomer at low concentrations could account for dramatic increase in performance. Nafion was composed of a hydrophobic backbone with hydrophilic side chains. In water-based solutions, Nafion ionomer formed micelles. These structures physically prevented Pt nanoparticles from aggregating. At a 2.5 vol% Nafion concentration, Nafion cluster size was large enough to prevent Pt conglomeration.

Sample	ACS ^[a] (d.nm)	ESA ^[b] (m ² /g)
Sample 1 (33 wt% PVP)	8.61	24.14
Sample 2 (60 wt% PVP)	5.45	28.50
Sample 3 (2.5 vol% Nafion + 33 wt% PVP)	6.76	40.85

Figure 2: Summary of results. Average crystal size (ACS) calculated from XRD data. Effective surface area (ESA) of Pt calculated from CV data.

Future Work:

The parameters are not yet optimized as these results are still preliminary results. Carbon black showed better performance than the current results, ranging from 40 m²/g - 100 m²/g as the Pt ESA. In the future, we will explore the efficiencies of platinum embedded in different carbon supporting matrix or varying the concentration of multiple dispersing agents to maximize the performance in rGO.

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References:

- [1] "Fuel Cells." Fuel Cell Technology Program. U.S. Department of Renewable Energy, Nov. 2010. Web. 25 August 2013.
- [2] Nice, Karim; Strickland, Jonathan; "How Fuel Cells Work." How Stuff Works. Web. 25 August 2013.