Enhanced activity and stability of Pt catalysts on functionalized graphene sheets for electrocatalytic oxygen reduction

Rong Kou [a], Yuyan Shao [a], Donghai Wang [a], Mark H. Engelhard [a], Ja Hun Kwak [a], Jun Wang [a], Vilayanur V. Viswanathan [a], Chongmin Wang [a], Yuehe Lin [a], Yong Wang [a], Ilhan A. Aksay [b], Jun Liu [a,*]

[a] Pacific Northwest National Laboratory, Richland, WA 99352, USA
[b] Department of Chemical Engineering, Princeton University, Princeton, NJ 08544, USA

ABSTRACT

Electrocatalysis of oxygen reduction using Pt nanoparticles supported on functionalized graphene sheets (FGSs) was studied. FGSs were prepared by thermal expansion of graphite oxide. Pt nanoparticles with average diameter of 2 nm were uniformly loaded on FGSs by impregnation methods. Pt-FGS showed a higher electrochemical surface area and oxygen reduction activity with improved stability as compared with the commercial catalyst. Transmission electron microscopy, X-ray photoelectron spectroscopy, and electrochemical characterization suggest that the improved performance of Pt-FGS can be attributed to smaller particle size and less aggregation of Pt nanoparticles on the functionalized graphene sheets.

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1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) have attracted great attention as alternative clean energy technologies for transportation vehicles, small-scale portable electronics and stationary power supplies [1]. Although considerable progress has been made in developing better PEMFCs electrode materials, the catalytic property and stability of the electrode (e.g. cathode) still need to be improved [2]. Currently, the leading cathode electrocatalysts are Pt and Pt-based alloys supported on carbon black, which are subjected to low pH, high oxygen concentration and high electrode potential conditions in PEMFCs. Under these conditions, Pt nanoparticles on the carbon supports may aggregate or dissolve from the substrate, resulting in decreased activity. Many carbon materials have been investigated as catalyst supports for PEMFCs [3]. It is observed that the structures and properties of the carbon supports, such as surface functional groups [4], graphitizing structure [5–7], and surface area [7], have a large effect on the activity and durability of the catalysts.

Graphene sheets, a two-dimensional carbon material with single (or a few) atomic layer, have attracted great attention for both fundamental science and applied research. The combination of the high surface area (theoretical value of 2630 m^2/g) [8], high conductivity [9], unique graphitized basal plane structure and potential low manufacturing cost [10,11] makes graphene sheets a promising candidate for cathode catalyst support in PEMFCs. Recently, graphene received attention as the catalyst support in methanol oxidation for fuel cell application [12]. In this paper, we investigated the properties of FGS-supported Pt catalysts (Pt-FGS) for electrocatalysis of oxygen reduction. We demonstrate that the new electrocatalysts have good activity and significantly improved stability as compared with the widely used commercial catalysts for PEMFCs.

2. Experiment

Functionalized graphene sheets (FGSs) prepared through a thermal expansion process [10,11] were used in this study since FGSs have high conductivity due to the high temperature treatment. The synthesis process started with chemical oxidation of graphite flakes. The resultant graphite oxides were then split apart by a rapid thermal expansion to yield single but wrinkled graphene sheets. To prepare Pt-FGS, the calculated amount of Pt precursor $H_2PtCl_6 \cdot xH_2O$ was dissolved in 10 ml acetone. The solution was added dropwise into 0.1 g FGS powder under mild stirring. The graphene powder loaded with Pt precursor (20 wt% Pt) was incubated in the oven at 100 °C overnight, and then treated in H_2 at 300 °C for 2 h. Multiwalled carbon nanotube (MWCNT) supported Pt catalysts (Pt-MWCNT) were synthesized following a similar procedure. Commercial catalyst E-TEK (20% Pt supported on Vulcan XC-72 carbon) was purchased from E-TEK company.

* Corresponding author. Tel.: +1 509 375 4443; fax: +1 509 371 6498.
  E-mail address: jun.liu@pnl.gov (J. Liu).

The electrochemical characterization of Pt-FGS, Pt-MWCNT and E-TEK was carried out in a standard three-electrode cell using a Pt wire counter electrode and a Hg/Hg$_2$SO$_4$ reference electrode (0.69 V vs. RHE) at room temperature. Typically, 10 mg Pt-FGS or E-TEK catalyst was dispersed in a solution of 10 ml 2-propanol and 45 μL 5.0 wt% Nafion, and then ultrasonicated to form a uniform black ink. The thin-film rotating-disk electrode (TF-RDE) was prepared by applying 15.0 μL well-dispersed catalyst ink onto pre-polished glassy carbon disk (5 mm in diameter). After drying at room temperature, 15 μL of 0.05 wt% Nafion solution was applied onto the surface of the catalyst layer to form a layer protecting catalyst particles from detaching. The as-prepared TF-RDE was first activated with cyclic voltammetry (CV) between 0 and 1.1 V at 50 mV s^{-1} in N$_2$-saturated 0.5 M H$_2$SO$_4$ solution until a steady CV was obtained. The accelerated durability tests were carried out with CV (0.6–1.1 V) at 50 mV s^{-1} in N$_2$-saturated 0.5 M H$_2$SO$_4$. Oxygen reduction reaction (ORR) was conducted in O$_2$-saturated 0.5 M H$_2$SO$_4$ on the rotating-disk electrode system. All potentials were reported versus reversible hydrogen electrode (RHE).

3. Results and discussion

Fig. 1a shows a transmission electron microscopy (TEM) image of the functionalized graphene sheets. The wrinkles on the graphene sheets are clearly observed. These wrinkles may be important for preventing aggregation of graphene due to van der Waals forces during drying and maintaining high surface area [10,11]. The X-ray photoelectron spectrum (XPS) of FGSs (Fig. 1b) shows a strong C–C bond at 284.6 eV, indicating good sp^2 conjugation. A small bump at 286.6 eV indicates the existence of C–O bonds corresponding to the epoxy and hydroxyl groups on carbon [10]. Fig. 1c is a TEM image of Pt-FGS showing small Pt nanoparticles uniformly distributed on the wrinkled FGSs. A dark field TEM image (inset in Fig. 1c) clearly shows the dispersion of crystalline Pt nanoparticles on the wrinkled FGSs. The size of the Pt nanoparticles is between 1 and 3.5 nm with an average size of 2 nm (Fig. 1d), which is slightly smaller than the average Pt particle size (2.8 nm) of the commercial catalyst (data not shown). The FGSs have a high Brunauer–Emmett–Teller (BET) surface area of 600 m^2/g and a methylene blue surface area of 1850 m^2/g in an ethanol suspension. It should be noted that the measured surface area is usually much smaller than the theoretical value because of restacking of the graphene sheets due to van der Waals forces [11]. Furthermore, the surface groups (epoxy and hydroxyl groups) on FGSs may function as anchoring sites for Pt precursor to prevent the aggregation of the Pt nanoparticles. These two factors might have contributed to the good dispersion of Pt nanoparticles on FGSs.

The durability of both Pt-FGS and commercial catalyst was investigated under cyclic voltammetry (CV) for 5000 cycles in N$_2$-saturated 0.5 M H$_2$SO$_4$. The CV curves of Pt-FGS before and after
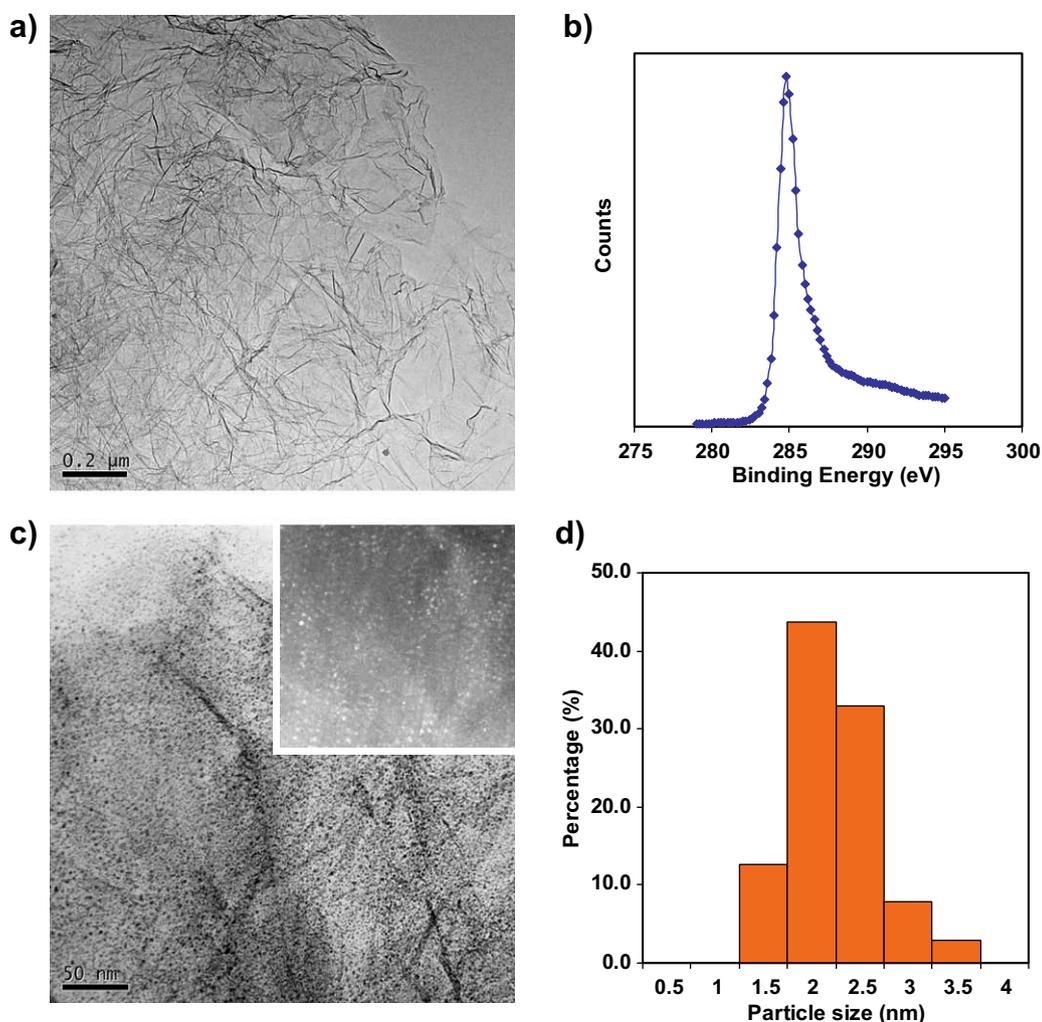
Fig. 1. (a) TEM image of functionalized graphene sheets. (b) High energy resolution photoemission spectra of the C 1s region in FGSs. (c) TEM images of Pt-FGS, Inset shows corresponding dark field TEM image. Scale bar for the inset image is identical to the bright field TEM image. (d) Pt nanoparticle size distribution of Pt-FGS.
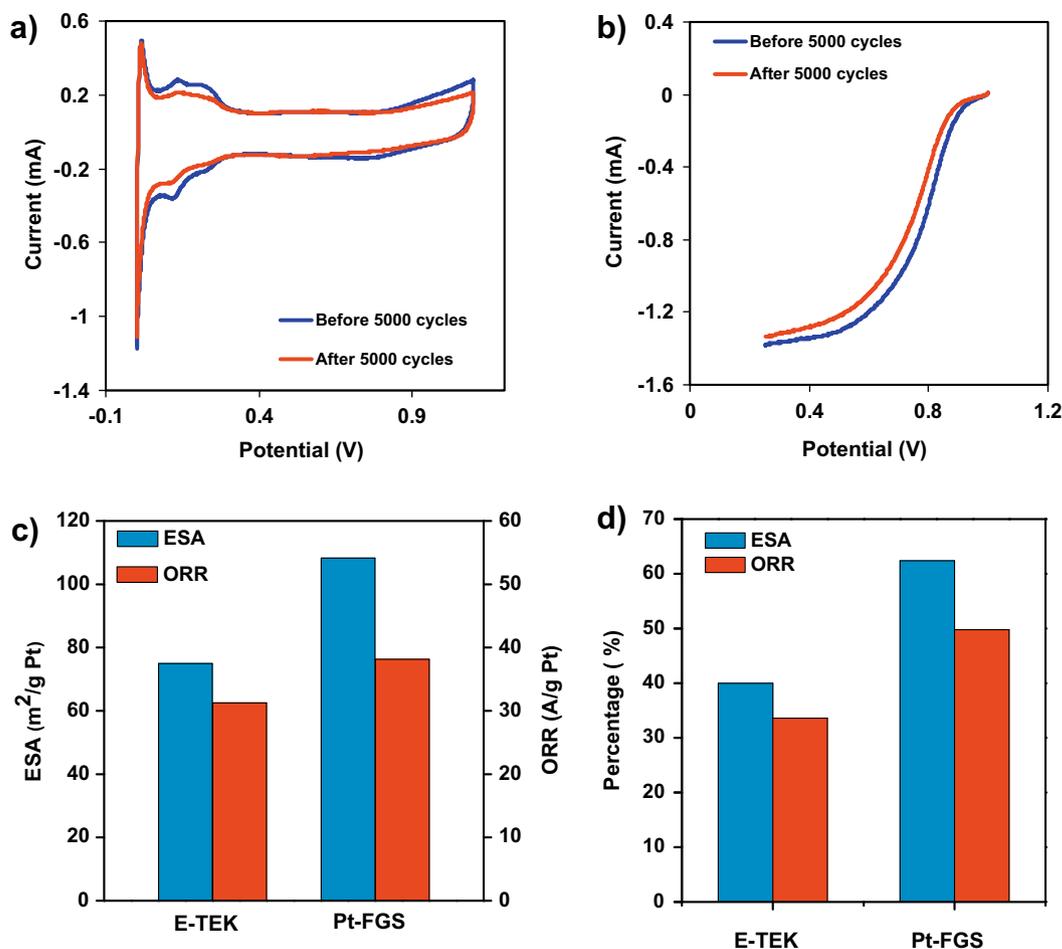
Fig. 2. Electrochemical properties tested in 0.5 M H_2SO_4 aqueous solution. (a) Cyclic voltammograms of Pt-FGS under a scan rate of 50 mV/s before and after 5000 CV degradation; (b) polarization curves for the O_2 reduction (10 mV/s, 1600 rpm) on Pt-FGS catalyst before and after 5000 cycles; (c) original values of ESA and ORR activity at 0.9 V; (d) the percentage of retaining ESA and ORR activity after 5000 CV degradation.

5000 cycles, as shown in Fig. 2a, show standard hydrogen adsorption/desorption peaks between 0.04 and 0.3 V, which is suppressed after 5000 cycle degradation. It indicates that the electrochemical surface area (ESA) estimated from the charge associated with hydrogen adsorption on Pt is decreased after the 5000 cycling.

Fig. 2b shows the representative oxygen reduction reaction (ORR) curves of Pt-FGS before and after 5000 CV cycles. It can be observed that the ORR curve shifts toward more negative potentials after 5000 cycles, which is consistent with previous observation on Pt catalyst supported by other carbon materials [13]. The shifting means that the catalytic activity of Pt-FGS toward ORR slightly decreased. The ORR activity of the electrocatalysts can be evaluated with the kinetic ORR current at 0.9 V on rotating-disk electrodes calculated using Koutecky–Levich equation [14].

Although some loss of the ESA and ORR on Pt-FGS is observed, Pt-FGS shows higher initial value and good retention on both the ESA and ORR activity compared with the commercial catalyst E-TEK. Fig. 2c compares the initial ESA and ORR activity of Pt-FGS and E-TEK samples. The initial ESA of Pt-FGS is 108 m^2/g, which is higher than that of E-TEK (75 m^2/g). The high initial ESA of Pt-FGS is attributed to the smaller particle size of Pt nanoparticles loaded on the FGSs. Based on the average particle diameter of 2 nm for Pt on Pt-FGS, and 2.8 nm on E-TEK, the difference of the ESA values is directly related to the difference in the particle size in inverse proportion. The initial ORR activity of Pt-FGS is also higher than that of E-TEK. After extended cycling, this difference in the ESA and ORR activity is further enhanced. The retained ESA and ORR after the

5000-cycle degradation for both E-TEK and Pt-FGS, compared with initial values in percentage, are shown in Fig. 2d. The ESA of Pt-FGS decreases to 67.6 m^2/g after 5000 CV cycle degradation, i.e. 62.4% of the initial ESA value. In comparison, commercial catalyst E-TEK retains only 40% of the initial ESA. Similarly in ORR activity, Pt-FGS retains 49.8% of the original value while the commercial catalyst only keeps 33.6%. Therefore, Pt on FGSs is much more stable than commercial catalyst under our test condition.

To elucidate difference in the degradation between Pt-FGS and E-TEK, both catalysts after the 5000 CV cycle tests were further investigated by TEM. The particle size of Pt nanoparticles on both Pt-FGS and E-TEK is increased after 5000 CV cycles (Fig. 3a and c), indicating some degree of agglomeration and sintering of the Pt nanoparticles. A comparison of the particle size suggests that the particles on FGSs are much smaller than the degraded E-TEK sample after 5000 CV cycles. In Pt-FGS, the average Pt particle size is increased to 5.5 nm, and more than 75% of the particles remain under 6.9 nm. In E-TEK, the average particle size is increased to 6.9 nm, and more than 45% of the particles are over 6.9 nm. Aggregated Pt nanoparticles larger than 15 nm on E-TEK can also be observed after 5000 CV cycles. These results suggest that the higher ESA and ORR activity of Pt-FGS after degradation are attributed to the smaller particle size. The loss of the ESA and ORR activity is directly related to Pt aggregation. Functionalized graphene sheets, with more π sites and functional groups, may lead to a strong metal-support interaction and resultant resistance of Pt to sintering [6,7,15], and therefore enhanced durability.
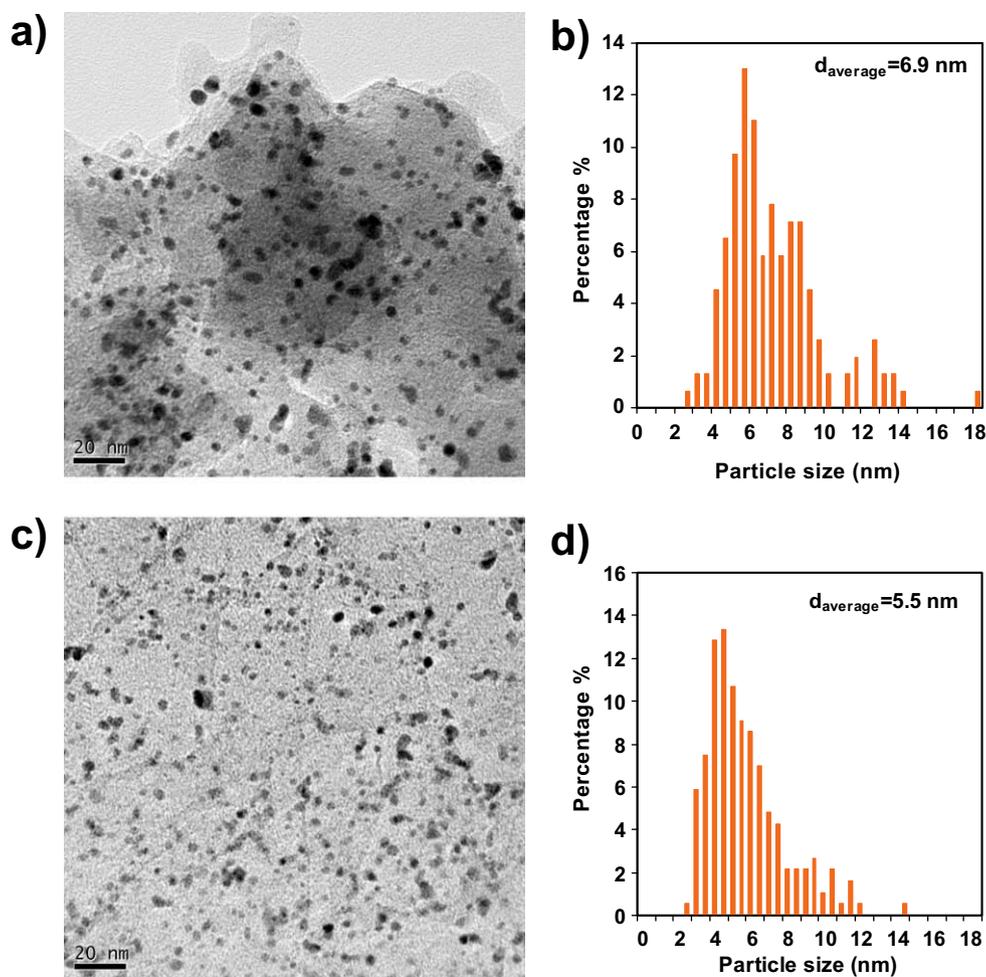
Fig. 3. TEM images of (a) E-TEK and (c) Pt-FGS after 5000 CV degradation, and Pt nanoparticle size distribution diagrams on (b) E-TEK and (d) Pt-FGS after 5000 CV degradation.

We have also tested the performance of Pt catalysts supported on MWCNTs prepared using the same method. Our study shows that 53% ESA and 42% ORR on Pt-MWCNT are retained after 5000 CV cycles at similar condition [16]. The property of Pt-MWCNT is better than that of E- TEK but poorer as compared with Pt-FGS. Higher stability of Pt catalyst on FGSs than MWCNT may be attributed to the functionalized surface groups and the higher surface area of FGSs.

4. Conclusion

In summary, functionalized graphene sheets have been investigated as Pt catalyst supports in oxygen reduction for PEMFCs. Well-dispersed Pt nanoparticles with small particle size were obtained on FGSs. The electrochemical tests showed that the Pt nanoparticles supported on FGSs had good activity and much better stability in both electrochemical surface area and oxygen reduction activity as compared with the commercial catalyst E-TEK. This research raises the possibility of using graphene sheets as a cathode catalyst support in proton exchange membrane fuel cells.

Acknowledgements

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