Preparation and Electrochemical Properties of Pt@C Nanocomposites

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(Received November 17, 2008; CL-081078)

By using maize as the carbon source, well-dispersed Pt nanoparticles embedded in carbon matrix (Pt@C) are prepared by soaking corn in K_2PtCl_6 solutions followed by calcination in nitrogen atmosphere. Linear sweep voltammograms exerted on the Pt@C nanocomposites reveal a good current response to methanol oxidation.

Highly dispersed Pt@C nanocomposites are known to be an efficient electrocatalyst for the methanol oxidation reaction in DMFCs.[1] The properties of composites are greatly influenced by several aspects, such as particle sizes, the contents and dispersion of Pt nanoparticls, and the surface area of carbon substrate. As well-known, the higher surface area relates to an increase in the active sites for reaction and may reduce the load of expensive Pt. Extensive attention has been payed to using various carbon nanomaterials to enlarge the surface area of carbon matrix, such as nanotubes, nanocoils, and nanofibers, to enhance the electroactivity.[2] Also, much effort has been exerted on reducing the size of metal particles to increase the electrochemical active surface. Conventionally, carbon-based composites are fabricated by loading metal on carbon matrix. This route usually results in poorly dispersed metal particles with wide size distribution.[3] Recently, many new methods have been developed to prepare carbon composites to achieve materials with high porosity of carbon, reduced sizes, and narrow size distribution of metal. The main documented methods are chemical reduction in aqueous solutions, organic sol, electrochemical deposition, vapor deposition, thermal decomposition, impregnation, microemulsion, and microwave technology.[4] However, the preparation of highly dispersed supported platinum nanoparticles with uniform sizes still remains a challenge. While the impregnation process is by far the most attractive preparation route owing to its feasibility, it is also limited by the large average particle size, agglomerate of nanoparticles, broad size distribution, and poor reproducibility.[5] If metal cations or anions are highly dispersed in carbon precursers, controlled heat treatment may produce well-dispersed Pt nanoparticles in the carbon substrate. From this view, maize granules were selected as the carbon source to adsorb metal species. Nearly monodispersive Pt nanoparticle loaded carbon composites were readily prepared by calcinating the metal anion impregnated maize granules. Herein, we report the facile preparation and electrochemical characterization of Pt@C nanocomposites.

The Pt@C nanocomposites were prepared by soaking maize granules in K_2PtCl_6 solution followed by calcination. Typically, 10 g of maize groats were merged in 50 mL of 0.05 M aqueous K_2PtC1_6 solution and layed statically at room temperature for 15 days. Afterward, the maize groats were washed with deionized water and dried at 50 °C. Then the maize groats were carbonized under nitrogen atmosphere at various temperatures for 2 h. The products obtained at 700, 800, 900, and 1000 °C are denoted as Pt@C-700, Pt@C-800, Pt@C-900, and Pt@C-1000, respectively. The black products were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TG), X-ray photoluminicence spectroscopy (XPS), and electrochemical measurements.

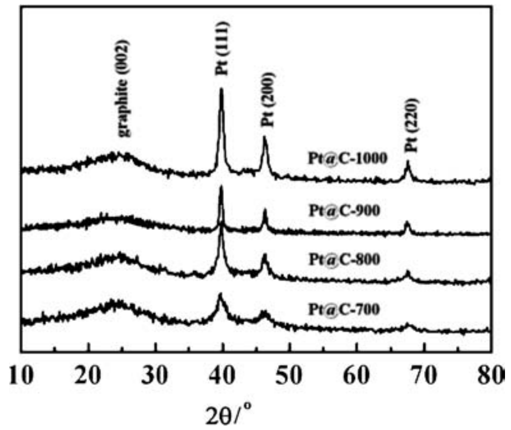

Figure 1. XRD patterns of the Pt@C nanocomposites obtained at different temperatures.

Figure 1 shows the XRD patterns of Pt@C nanocomposites prepared at various temperatures. The practical data well match the documented data and are indxed into face-centered cubic phase of Pt (JCPDS card No. 70-2057). The difference of the peak width indicates the size difference between various samples. The broad peak aroud 25° corresponds to the 002 reflection of graphite. To further confirm the presence of Pt, XPS measurements were exerted on the Pt@C samples (Supproting Information Figure S1).[6] The binding energy of Pt (71.38 eV) is very close to that of metallic Pt (71.3 eV), confirming the presence of metallic Pt in the carbon substrate. The content of Pt is determined by TG analysis (Figure S2). The loading amounts of Pt are greatly related to the calcination temperature. The contents of Pt are sequentially 4.32, 4.78, 6.4, and 7.9 wt % for Pt@C-700, Pt@C-800, Pt@C-900, and Pt@C-1000, respectively.

The microstructures of Pt@C nanocomposites were studied by TEM observation. TEM images reveal that Pt nanoparticles are highly dispersed in the carbon matrix with a relatively narrow particle size distribution (Figure 2). Calcination temperature greatly affects the sizes of Pt nanoparticles and the porosity of carbon. The particle sizes are 4–8 nm ($D_{av} = 5.65$ nm) for Pt@C-700 and 5–12 nm ($D_{av} = 7.8$ nm) for Pt@C-800. The particle sizes greatly enlarged when the heating temperature was over 900 °C. The composites obtained at 900 °C are embedded with 12–29 nm ($D_{av} = 22.6$ nm) nanoparticles. Pt nanoparticles in the sample heated at 1000 °C are 10–28 nm ($D_{av} = 18.3$ nm) in diameters. TEM images also implies that Pt@C-900 and

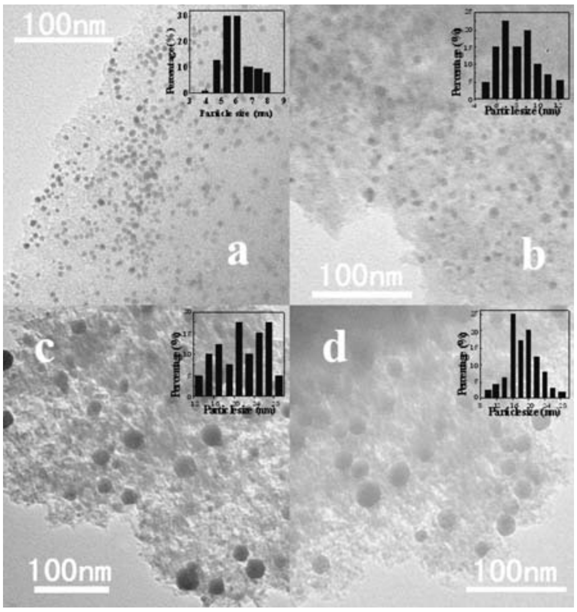

Figure 2. TEM images of the nanocomposites prepared at different temperatures: (a) Pt@C-700, (b) Pt@C-800, (c) Pt@C-900, (d) Pt@C-1000.

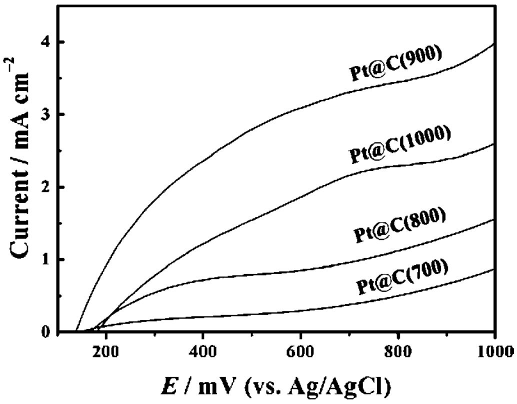

Figure 3. Linear sweep voltammograms of Pt@C nanocomposite electrodes in 0.5 M H_2SO_4 and 1 M MeOH at a scan rate of 50 mV s^{-1}.

Pt@C-1000 are more porous than the other two samples. Nitrogen adsorption isotherms (Figure S3) reveal BET surface areas of 523.8 m^2 g^{-1} for Pt@C-900 and 371.3 m^2 g^{-1} for Pt@C-1000 with broad pore size distributions. Attempts to measure the surface area for Pt@C-700 and Pt@C-800 failed.

To examine the activity for electrochemically oxidizing methanol, linear sweep voltammetry was performed on Pt@C nanocomposite electrodes (Figure 3). The current densities in 0.5 M sulfuric acid and 1 M methanol are much higher than that in bare sulfuric acid solution (Figure S4) for all nanocomposite electrodes. The current densities at 0.7 V for methanol oxidation were sequentially 0.0384, 0.0959, 3.309, and 2.159 mA/cm^2 (Figure S5). The largest current of Pt@C-900 exhibits the highest activity. The onset potential for methanol oxidation occurs at 0.14 V by using Ag/AgCl electrode as the reference, which is the most negative among the composite electrodes in this work. The low activity, compared to the documented data, may stem from the low loading amount of Pt. Combined with the nitrogen adsorption data and previous work in the documents, the large surface area of Pt@C-900 affords more active sites and shows better catalytic behavior, although Pt@C-900 contains larger Pt nanoparticles. No visible oxidation peaks are displayed except for Pt@C-1000. The present data also implies an electron-transfer-controlled mechanism of electrooxidizing methanol on our Pt@C nanocomposite electrodes.

In a summary, Pt@C nanocomposite electrocatalysts are prepared via a facile route by using maize as the carbon source. The particle sizes and porosity relate to the calcination temperature. The nanocomposites are active for electrooxidizing methanol. Pt@C-900 exhibits the highest activity. Ongoing work focused on increasing the loading amount and enlarging the porosity.

This work was supported by NSF of Tianjin (Grant No. 05YFJMJC13500), STDFU of Tianjin (Grant No. 2006ba47).

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6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) February 14, 2009; doi:10.1246/cl.2009.260