



A solvent approach to the size-controllable synthesis of ultrafine Pt catalysts for methanol oxidation in direct methanol fuel cells



Feng Ye^a, Hui Liu^{a,b}, Yan Feng^{a,b}, Jianling Li^c, Xindong Wang^c, Jun Yang^{a,*}

^a State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China

^b University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing, 100049, China

^c State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, No. 30 College Road, Beijing, 100083, China

ARTICLE INFO

Article history:

Received 2 September 2013

Received in revised form

26 November 2013

Accepted 29 November 2013

Available online 11 December 2013

Keywords:

Pt/C catalyst

Nanoparticle

Methanol oxidation reaction

Membrane electrode assembly

Direct methanol fuel cell

ABSTRACT

An ethylene glycol (EG)-based approach has been developed for the synthesis of Pt/C catalysts with uniform Pt nanoparticles. A number of characterization techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electrochemical measurements are used to characterize the as-prepared Pt catalysts. The well-dispersed Pt nanoparticles with average size of approximate 2 nm could be obtained in the EG/water mixture with volume ratio of 1/1, which display higher activity for methanol oxidation than that of the Pt/C products prepared at other EG/water volume ratios (0:1, 2:1, and 1:0). In particular, the performance of the Pt nanoparticles prepared at EG/water volume ratio of 1/1 in the membrane electrode assembly for direct methanol fuel cells has also been evaluated and benchmarked by commercial Pt/C catalysts. This study offers a vivid example to synthesize Pt nanoparticles with fine size and good catalytic activity by simply tuning the solvent ratio in colloidal chemistry methods.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Direct methanol fuel cells (DMFCs) have been recognized as one of the most promising power sources for portable electronic devices because of a variety of advantages, such as high specific energy, ease in the handling of liquid fuel, and low operating temperatures [1–8]. The excellent catalytic activity of platinum for the electrooxidation of methanol especially below 80 °C makes this metal preferable to be used as electrocatalysts both at anode and cathode of DMFCs [9,10]. The Pt nanoparticles supported on carbon (Pt/C) have good catalytic activity for DMFC reactions primarily owing to the better dispersion and larger surface area, which is usually associated with the fine size of Pt nanoparticles [11]. For decades, a number of synthesizing techniques, including colloidal chemistry methods [12–16], reverse micelle methods [17–20], and electrochemical deposition methods [21–23], have been used to prepare Pt nanoscale catalysts. In comparison with the electrochemical deposition methods, although the colloidal chemistry methods are more complex, they are promising to prepare nanoparticles with controllable size and morphology [24]. For colloidal chemistry methods, to prepare nanoparticles with uniform distribution and small size, an alcoholic solvent is usually used preferentially because its lower surface tension and better intrinsic viscosity are favorable for the

preparation of finer particles via the diffusion control of ions/atoms [25], which might be the rate determining step for nucleation and growth of nanoparticles in the solution [26–29]. In addition, the concentration of metal precursors in alcoholic solvent could be much higher than that in aqueous phase for the preparation of well-dispersed metal nanoparticles, and this is very important for the large-scale production of nanoscale catalysts. For example, Yang et al. successfully prepared Pt and Ru nanoparticles with average size of approximate 1.5 nm in ethylene glycol (EG) using 300 W microwave radiation at 160 °C [30]. Notwithstanding the disadvantage of using high operating temperature, the preparation in EG should be recognized for its ability to produce metal nanoparticles with smaller sizes.

Herein, we present an EG-based approach for the synthesis of Pt/C catalysts with uniform Pt nanoparticles well dispersed on carbon supports. In this strategy, the chloroplatinic (IV) acid is reduced in a physical mixture of EG and water, and the size and morphology of Pt nanoparticles are controlled by simply tuning the volume ratio of EG and water in their mixture. The prepared Pt/C catalysts are characterized by SEM and TEM. The performance of the as-prepared Pt/C catalysts at the optimal EG/water volume ratio (1:1) for methanol oxidation reaction is examined and compared with that of Pt/C catalysts synthesized at other EG/water volume ratios (i.e. 0:1, 2:1, and 1:0). Furthermore, the property of the membrane electrode assembly (MEA) with the as-prepared Pt/C catalysts at anode is used to evaluate the performance of the fuel cell. This study might be a vivid example to use colloidal chemistry

* Corresponding author. Tel.: +86 10 8254 4915; fax: +86 10 8254 4915.
E-mail address: jyang@mail.ipe.ac.cn (J. Yang).

methods for the synthesis of metal nanoparticles with controllable size and enhanced catalytic property.

2. Experimental

2.1. Preparation of Pt/C catalysts

In a typical procedure, 174 mg of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 260 mg of Vulcan XC-72 carbon supports were added to 50 mL of EG/water mixture with volume ratio of 1:1, respectively. The two solutions were then completely mixed by vigorously stirring to form homogeneous slurry in a round bottom flask. The pH of the mixture was adjusted to 12 by adding NaOH. Next, the solution was heated at 90 °C for 2 h under Ar flow with constant stirring. Subsequently, 20 mL of 0.038 M HCOOH was added to the mixture, and it was stirred at 90 °C for 6 h. The final products were washed with 1 L of de-ionized water and filtered. The catalyst powders after filtration were dried at 80 °C for 12 h in a vacuum oven. The catalyst thus obtained was labeled as Pt/C-01.

The Pt/C catalysts labeled as Pt/C-02, Pt/C-03, and Pt/C-04 were also prepared using the same protocol, corresponding to the EG/water volume ratio at 0:1, 2:1, and 1:0, respectively. The nominal loadings of Pt on carbon support in these four prepared catalysts were 20 wt%.

2.2. Characterization of Pt/C catalysts

SEM observations were carried out on ZEISS and LEO-1530 FESEM instruments. TEM characterizations of the catalysts were performed on a JEOL JEM-2100FX microscope operated at 200 kV. For SEM and TEM measurements, a drop of the nanoparticle solution was dispensed onto a 3 mm carbon-coated copper grid. Excessive solution was removed by an absorbent paper, and the sample was dried under vacuum at room temperature.

The thin film electrode used as working electrode in the electrochemical measurements was manufactured as follows: 50 mg of the catalyst was dispersed ultrasonically in a mixture consisting of 10 mL of ethanol and 500 μL of Nafion (5 wt%). 100 μL of the dispersed catalyst was pipetted on a graphite carbon substrate to form the electrode (8 mm in diameter). Then the electrode was dried at 75 °C in a vacuum oven. Potentiostat of Bio-logic VMP3 (with EC-lab software version 9.56) was used for all the electrochemical experiments in the conventional three-electrode cell at 30 °C. A Pt sheet and a saturated calomel electrode SCE were used as the counter electrode and reference electrode, respectively. All potentials in this work are quoted in reference to SCE.

The electrochemically active surface areas (ECSAs) of the Pt/C-01, Pt/C-02, Pt/C-03, and Pt/C-04 were calculated from cyclic voltammograms (CVs), which were recorded in 0.5 M H_2SO_4 between -0.25 and 1.1 V with a scan rate of 100 mV s^{-1} . Meanwhile, the electrocatalytic oxidations of methanol on Pt/C catalysts were also determined by the CVs recorded between 0 and 0.85 V with the scanning rate of 10 mV s^{-1} . The electrolyte was 1.0 M methanol in 0.5 M H_2SO_4 . All electrolyte solutions were deaerated by pure argon for 20 min before the electrochemical measurement. In addition, the stability of Pt/C catalysts as-prepared at different EG/water volume ratios was evaluated by chronoamperometry curves obtained at a given potential of 0.65 V vs SCE.

2.3. Preparation and evaluation of membrane-electrode assembly (MEA)

The preparation of microporous layer and MEA followed a protocol reported previously [31]. The catalyst for the anode was the prepared Pt/C with the loadings of 3.0 mg cm^{-2} . The catalyst for the cathode was Pt black (Johnson Matthey) with the loadings of

2.0 mg cm^{-2} . Catalyst slurries were prepared by mixing catalysts, Nafion ionomer, isopropyl alcohol, and deionized water. The slurries were dispersed and then uniformly sprayed onto the Teflon blank to form a thin catalyst layer. The catalyst coated membrane was obtained by transferring the catalyst layers from Teflon blanks to the Nafion 115 by hot-pressing the electrodes at 135 °C under pressure of 750 N cm^{-2} for 3 min. A 5 cm^2 MEA was prepared. For comparison, a MEA composed of commercial Pt/C (20% Pt, Johnson Matthey) with the loadings of 3.0 mg cm^{-2} at anode and commercial Pt black (Johnson Matthey) with the loadings of 2.0 mg cm^{-2} at cathode was also fabricated and evaluated.

Polarization tests were carried out by a VMP3 system using a single cell at 50 °C. Methanol solutions (2.0 M, 2.5 mL min^{-1}) and air (0.1 MPa, 670 mL min^{-1}) were fed to the anode and cathode, respectively.

3. Results and discussion

The SEM images of the as-prepared Pt particles on carbon XC-72 by the EG-based methods were shown in Fig. 1. As indicated, at EG/water volume ratios of 1:1 (Fig. 1a), 0:1 (Fig. 1b), and 2:1 (Fig. 1c), tiny Pt nanoparticles with similar sizes were formed and observed on carbon supports. However, as shown in Fig. 1a, the Pt nanoparticles synthesized at EG/water ratio of 1:1 were more uniform and better dispersed on the surface of carbon support, while the Pt nanoparticles synthesized at other EG/water ratios (0:1 and 2:1) were only distributed sparsely on the surface of carbon support (Fig. 1b and Fig. 1c). In the absence of water (i.e. the EG/water volume ratio of 1:0), as manifested by Fig. 1d, larger Pt particles were generated as dominant product and they were randomly distributed on the carbon supports in separate or aggregated forms.

The Pt/C products as-prepared at different EG/water volume ratios were further characterized by TEM. In the TEM images, the Pt nanoparticles exhibit a dark contrast as compared with the carbon support (Fig. 2). In accordance with the characterization by SEM images, the TEM images further revealed that Pt nanoparticles prepared at EG/water volume ratio of 1:1 have uniform size and better distribution on the surface of carbon support.

In colloidal chemistry method, the nanoparticle could be formed via two processes, i.e. nucleation and crystal growth [28,32]. The nucleation mainly determined by the supersaturation and temperature is the starting point of crystallization, while the particle growth is a process of the assembling of atoms on the surface of nuclei. The growth is controlled by the diffusion of atom to the growing surface followed by the incorporation into the lattice. The incorporation process might be associated with the formation of chemical bond, which could be regarded as the reaction step. Therefore, the particle growth might be regulated by diffusion step and reaction step. Both the diffusion step and the reaction step can be the rate determining step for the particle formation. The compromise of diffusion step and reaction step might be an important prerequisite to facilitate the formation of nanoparticles with uniform size and narrow size distribution [26]. The water in EG/water mixture could affect the diffusion of Pt atoms generated from the reduction of H_2PtCl_6 by effectively regulating the viscosity and dielectric constant of ethylene glycol. At an appropriate EG/water volume ratio (e.g. 1:1), the viscosity (3.39 $\text{mPa}\cdot\text{s}$ at room temperature) of the mixture and the dielectric constant may sufficiently balance the diffusion step and reaction step in the colloidal chemistry method, thus offering an optimal condition for the formation of Pt nanoparticles. At other EG/water volume ratios (i.e. 0:1, 2:1, and 1:0), the viscosity and the dielectric constant of the mixture might be far from the optimal balance, resulting in the formation of Pt nanoparticles with less uniform or larger diameter.

Download English Version:

<https://daneshyari.com/en/article/186752>

Download Persian Version:

<https://daneshyari.com/article/186752>

[Daneshyari.com](https://daneshyari.com)