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Preparation of high loading Pt supported on carbon by on-site reduction

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The fuel cell, as one of the efficient, pollution free power sources, is approaching the commercialization stage [1, 2] after more than 160 years development [3], though the applications remain largely for aerospace and military use at present. This is benefited from breakthroughs of key technologies and materials [2, 4]. Electrode catalysts are especially crucial to the low temperature fuel cells (proton exchange membrane fuel cell, PEMFC, and direct methanol fuel cell, DMFC), which dominate the fuel cell performance and the cost as well. Apart from the discovery of new catalysts, it is important to invent catalyst preparation techniques since this directly relates to the catalyst properties and the cost.

It is well known that commercially available carbon supported catalysts (M/C, where M = precious metal or alloy, C = carbon) are prepared by chemical methods [5–11]. Multi-step procedures and long-time treatments were needed to prepare high metal loading ($M >$ 40 w%) catalyst. Otherwise, large metal clusters easily formed (favorable metal cluster size is around 4 nm [12] used in fuel cells). Another intrinsic problem is that the catalyst aggregates during the drying process when using conventional drying methods. The lumped catalyst should be re-broken by mechanical methods or ball milling to make fine powders. In that case, even the precious metal clusters attached on carbon were in nanometer scale, whereas the aggregated particle size would be in sub-micron scale. The utility of the catalyst dramatically reduced under such circumstances since catalytic reaction is a surface reaction. Highly dispersed (higher surface area) catalyst will provide higher activity. Several methods are now available for the preparation of carbon-supported catalysts [13–16]. The surfactant stabilized method and separate step absorption is an alternative to control small cluster size and make high precious metal loading [17]. However, the removal of surfactant added to the complexity. Therefore, the preparation of highly dispersed, nanometer sized catalysts remains a challenge. We report here a recently invented novel method that can avoid the weaknesses mentioned above. Simply regulating the procedure can control the size of Pt clusters. The advantages presently known and the experimental conditions are explained.

An X-ray diffratometer D/Max-IIIA (Rigaku Co., Japan) using Cu $K\alpha 1$ ($\lambda = 0.154056$ nm) as radiation source was used for identification of the catalyst crystallites. Transmission electron microscopy (TEM) was performed on a Philips CM-300 high resolution system operating at 200 keV. Surface area measurements were performed on a ASAP 2010 surface area and porosity analyzer at a bath temperature of 77.23 K using nitrogen gas as the adsorbate. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a VG ESCALAB MKII spectrometer using an Al $K\alpha$- ray source. Energy dispersive X-ray spectroscopic analysis was performed on a LEO 1530 VP, Germany. A microwave oven of 2.45 GHz, 850 W was used to prepare catalysts.

The Pt/C catalysts were prepared by the following procedure. Vulcan XC-72 (Cabot, USA) was mixed with acetone under ultrasonic agitation for 10 min. H_2PtCl_6 that had been previously dissolved in acetone was slowly added into the carbon containing flask with mechanical stirring. After evaporation of acetone the sample was heated in a microwave oven in a 5 s on/off duration for several times to remove residual acetone. H_2PtCl_6 is now uniformly attached on carbon after this process. X-ray photon spectroscopic (XPS) measurement revealed that platinum existed on carbon as Pt(IV) Oxide, Pt(II) Oxide and Pt. Therefore, the following reaction might have occurred in this stage:

$$H_2PtCl_6 + x/2O_2 \rightarrow PtO_x + 2HCl + 2Cl_2 \qquad (x = 1\text{–}2)$$

At the same time carbon monoxide formed under heating and it subsequently acted as a reducing agent to reduce PtO_x:

$$C + O_2 \rightarrow CO$$

$$PtO_x + xCO \rightarrow Pt + xCO_2$$

No matter what products formed, they were strongly stuck on to the carbon and resisted washing. The decomposing of H_2PtCl_6 in this step was possibly

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due to an elevated temperature at the local reaction site that induced localized enhancements of reaction rate [18].

The further reduction of platinum oxide was performed by addition of formic acid and then the solution was adjusted to pH = 9 by ammonia. This reductive reaction hardly proceeded at room temperature and remarkable reaction started at temperatures over 60 °C. Therefore, the solution was put into a microwave oven and heated under continuous argon gas flow at a schedule of 20 s on and 15 s off until the sample was completely dried. X-ray diffraction proved that the second step was necessary (Fig. 1). Fig. 1a is the XRD pattern before reduction. A distinctive peak at a d-value of 0.22684 nm (2theta 39.700 degrees) corresponded to Pt. However, the identification of the peak at the d-value of 0.25551 nm (2theta 35.09 degrees) was ambiguous. The standard d-value of PtO_2 is 0.25800 nm (2theta 34.74 degrees) and Pt_3O_4 is 0.24980 nm (2theta 35.92 degrees). It is believed that the peak at 35.09 degrees resulted from the overlap of peaks at 34.74 degrees and at 35.92 degrees respectively since the position of these two peaks are so close. It is easy to understand that Pt_3O_4 could be identified as the mixture of PtO and PtO_2 and, therefore, the peak at 35.09 degrees further proved the existence of Pt(II) Oxide or/and Pt(IV) Oxide. The lower peak intensity implied the platinum compounds were in the amorphous form before the reduction and higher temperature heating under argon atmosphere. One remarkable advantage is that the chloride ions can be spontaneously removed during the second step of the process. No chloride ions were determined by chemical analysis using silver nitrate titration. The result was further conformed by energy dispersive X-ray spectroscopy (EDX) since no chloride ions were detected.

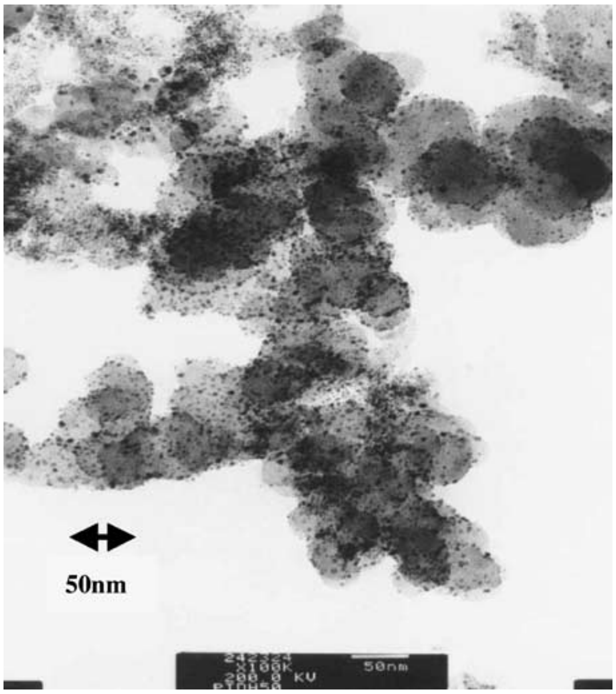

Figure 2 TEM image of a 50% Pt/C catalyst.

Comparing with the method reported by Boxall and coworkers [15, 19] the present method has the following distinguished features. The preparation process could be done in one flask with one transference. The two step procedure provided on site reduction of the target catalyst which had uniformly dispersed onto the supporting matrix instead of reduction in solution. Additionally, the dried sample spontaneously existed as fine powders. The following experimental results evidenced these features. Fig. 2 shows the transmission electron micrograph (TEM) of a typical sample of 50% platinum on carbon (50%Pt/C). It is obvious that platinum was uniformly dispersed on the carbon and that the distribution of clusters was accounted as in Fig. 3. The histogram shows that the average platinum cluster diameter was 3.5 nm and more than 90% of platinum clusters were in the range 2.5 nm to 4.5 nm in diameter. The data are better than those for commercially available products in terms of platinum cluster size. Chen and coworkers showed the particle size between 3.5–4.0 nm for Pt loading less than 20% catalysts by microwave-assisted method [16]. Boxall and Lukehart prepared 20%Pt/C catalysts by a multi-step microwave irradiation method that gave the average platinum clusters of 8 nm in diameter [15]. However, 20%Pt/C

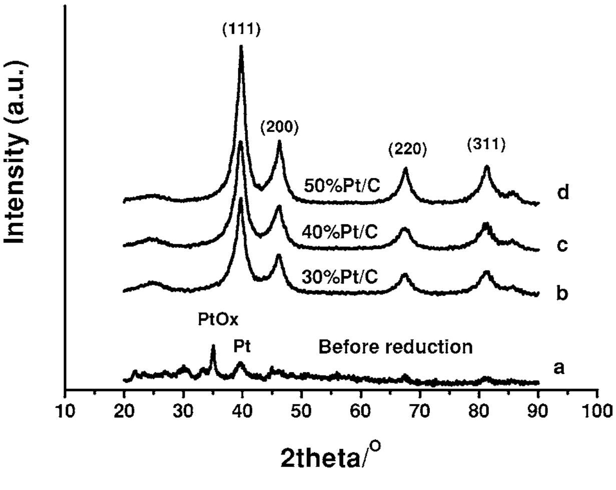

Figure 1 XRD patterns of Pt/C catalysts with different Pt loadings as indicated.

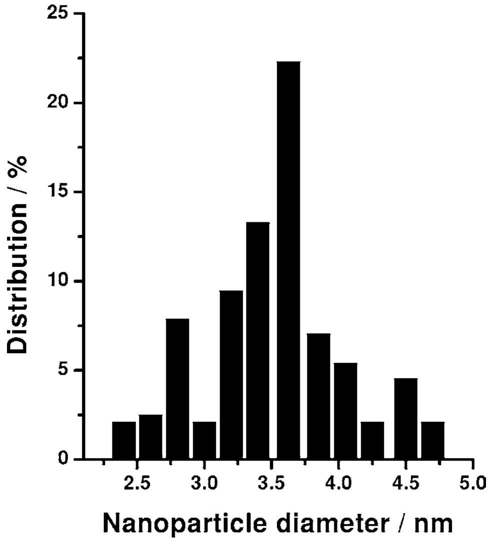

Figure 3 Histogram of Pt nanocluster diameters of a 50% Pt/C catalyst.

TABLE I Surface area of Pt/C catalysts (BET)

Catalyst	VulcanXC-72	20%Pt/C	30%Pt/C	40%Pt/C	50%Pt/C
SA · m^2 g^{-1}	236	128	119	92	80
E-Tek	250	112	88	72	–

catalyst prepared by the present method gave the average cluster size as small as 2 nm (TEM micrograph is not presented here). Inspecting the surface area of various platinum loading samples, it was found that the surface areas (SA) were larger than commercially available products as well. Table I summarized the results.

The principle of microwave drying is that the changing electrical field interacts with the molecular dipoles and charged ions. The heat generated by the molecular rotation is due to friction of this motion. Heat transfer advantages when applying microwave power into the bulk of a material include: faster energy absorption, reduced thermal gradients, and selective heating. Contrasted with conventional drying methods, microwave drying heats the sample bulk evenly, making every particle reach the same temperature immediately. In this case, the fast evaporation of moisture broke the lumped sample into powder due to the internal pressure formed by the expansion of moisture. The smaller the particle the higher the surface area is. It is clear that the catalyst made by the present method avoided the procedure of mechanical disintegration, resulting in smaller particles and subsequently gave higher surface area. This is very important since catalytic reaction in a fuel cell is a surface reaction and the reaction activity is proportional to the surface area of the catalyst.

It should be recognized that the formation of platinum clusters has two distinct phases. The first phase is the formation of nuclei of the new phase and their growth into clusters. Then the nuclei grow to bigger particles with time. The situation is different comparing with conventional dry methods, microwave heating reduces active components on site and dries the sample in minutes scale. In the case of Pt/C catalyst, Pt formed on carbon sites without mass transfer, and once the formation of nuclei had occurred the reaction ceased immediately since the heating time is very limited, resulting in smaller clusters. The most important step is that the platinum salt should be uniformly fixed on the surface of carbon before the reduction on site.

In conclusion, the method described here provides the possibility of rapid and one-step preparation of high loading nanomaterials supported on a special matrix. The present work showed a typical application of this method. Principally, this method can be universally used to prepare nano-scaled materials.

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