Materials Chemistry and Physics 111 (2008) 309–312

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Uniformly dispersed platinum nanoparticles loading on porous carbons without using reduction agents

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ARTICLE INFO

Article history:
Received 21 September 2007
Received in revised form 17 March 2008
Accepted 10 April 2008

Keywords:
Platinum nanoparticles
Porous carbons
Reduction agents

ABSTRACT

Platinum nanoparticles loading on carbon nanotube, activated carbon, and activated carbon fiber was carried out by impregnation of hexachloro palatinate ion(IV) from hydrogen hexachloro platinate hydrate [$H_2PtCl_6{\cdot}5.7H_2O$] dissolved solution without using reduction agents, and heating the hexachloro platinate(IV) impregnated carbons up to 800 °C. When the initial platinum content was controlled to 1000 ppm in the solution, the adsorption capacities of hexachloro platinate(IV) on carbon nanotube, activated carbon and activated carbon fiber were 24%, 47%, and 76%, respectively at the equilibrium state. The adsorption isotherm type of hexachloro platinate(IV) on carbon nanotube was two-step linear and quite different from Langmuir model of activated carbon fiber due to the uniformly developed cylindrical pore structure and size distribution. The average platinum particle size on porous carbons was under 2 nm by heating the hexachloro platinate(IV) up to 400 °C in spite of non-using reduction agents, while the average size increased due to the agglomeration of some particles by heating them up to 800 °C. Therefore, uniformly distributed platinum nanoparticles loading on porous carbons can be obtained from simple impregnation of hexachloro palatinate ion(IV) from solution and heating it up to 400 °C.

1. Introduction

The direct methanol fuel cells (DMFCs) have been assumed as promising energy sources for the near future because of their high energy density, simple construction, operable at room temperature and environmentally friendly aspects [1–5]. However, DMFCs have several problems such as fuel crossover and deactivation of anode, especially, too much platinum loading in the catalyst layer [6]. To decrease the amount and increase the effect of platinum at the DMFC anode, platinum particles were usually dispersed on carbon supports such as carbon nanotube, active charcoals, carbon blacks, etc., via chemical treatments [7–9]. Recently, uniformly developed microporous carbons become attractive as using catalyst supports due to high specific surface area, high adsorption capacity, and good mechanical strength [9–11]. The electrocatalytic activity of platinum particles is mainly depended on particle size and high dispersion [12–14].

There are many methods for the loading of platinum particles on carbon to improve the electrode capacity. Most popular methods in platinum particles loading on carbon were known by adding reduction agent such as HCHO, HCOOH, $NaBH_4$, and N_2H_4 [15,16]. However, almost all of the methods have shown poor dispersion [16]. Therefore, easy and high dispersion process is now being surveyed for the effective catalyst loading on various porous carbons.

In this work, hydrogen hexachloro platinate hydrate [$H_2PtCl_6{\cdot}5.7H_2O$] was dissolved in distilled water and the adsorption capacity of hexachloro platinate(IV) [$PtCl_6^{2-}$] on porous carbons from aqueous solution was compared with each other. The $PtCl_6^{2-}$ impregnated carbons were directly heat treated in nitrogen to obtain platinum nanoparticles. The TG, X-ray diffraction (XRD) analysis, and transmission electron microscope (TEM) observation were carried out to confirm the uniformly dispersed platinum nanoparticles. The BET specific surface area was measured to study the microporosity change of porous carbons.

2. Experimental

2.1. Adsorption of $PtCl_6^{2-}$ on porous carbons

Structural properties of the porous carbons were shown in Table 1. Activated carbon fiber (ACF, Toyobo KF-1500, Japan), carbon nanotube (CNT, Iljin CNT, Korea, CM-95), and activated carbon (AC, Yulim Carbon Co., Korea) were washed in distilled water and dried over night at 383 K in a vacuum dryer. Hydrogen hexachloro platinate hydrate ($H_2PtCl_6{\cdot}5.7H_2O$, Kojima Chemicals Co.) powder was used as a platinum particle source. This platinum compound was dissolved in distilled water as much the content of platinum as 100, 200, 500, 700 and 1000 ppm. 0.1 g of porous

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doi:10.1016/j.matchemphys.2008.04.014

Table 1
Structural properties of porous carbons

Carbons	Precursor	S_{BET}[a] ($m^2\,g^{-1}$)	V_t[b] ($cc\,g^{-1}$)	R^c (Å)
ACF	Rayon	1435	0.60	16.6
AC	Coconut	1100	0.55	29.8
CNT		200	0.53	105.5

[a] BET specific surface area.
[b] Total pore volume.
[c] Average pore diameter.

carbon was added to 20 ml different platinum content solution, and agitated for 2 h, 100 rpm at room temperature. The solution was filtered with millipore filter disc, and the absorbency of filtrate was measured with UV–vis spectrophotometer (Shimadzu V-1700, Pharma Spec., Japan) at λ 325 nm. The adsorption amount of hexachloro platinate(IV) was calculated from the standard curve and compared the results before and after impregnation.

2.2. Preparation and characterization of Pt/C

Fig. 1 shows the flow diagram of platinum nanoparticles loading on porous carbons without using reduction agents. The $PtCl_6^{2-}$ (30 wt% Pt) impregnated carbons were filtered, dried, and TG analysis was carried out to study the degradation of $PtCl_6^{2-}$ as increasing the temperature in nitrogen. Then, one set of ampoules was heated up to 800 °C. When the ampoules were raised up to desired temperature, the corresponding ampoule was quenched and sealed off for further X-ray diffraction study. XRD measurements were carried out on a Regaku D/MAX2000 Ultima/PC using Cu-K_α radiation with a Ni filter. The tube voltage is maintained at 40 kV, tube current at 40 mA. The 2θ angular region between 35° and 85° was explored at a scan speed of 5° min^{-1}.

Inductively coupled plasma atomic emission spectrometer (ICP, Optima 3300DV) analysis was carried out to confirm the amount of platinum loading on carbons. The adsorption characteristics of platinum loaded porous carbons were investigated by N_2 adsorption at 77 K using Micromeritics ASAP-2010. Transmission electron microscope (JEOL, JEM-2010) observations were carried out to study the morphology, platinum nanoparticles loading and distribution on porous carbons.

3. Results and discussion

In general, hydrated halides are insoluble in water. However, platinum and palladium halides are known to be soluble in water [17]. When $H_2PtCl_6{\cdot}5.7H_2O$ was dissolved in water, it produced $PtCl_6^{2-}$ and $2H^+$ and the solution became acidic. The $PtCl_6^{2-}$ was adsorbed on porous carbons, resulting in the change of color in solution from orange-yellow to lucid.

The adsorption of $PtCl_6^{2-}$ on porous carbons from platinum solution (platinum: 500 ppm) at room temperature is shown in Fig. 2. The adsorption rate of $PtCl_6^{2-}$ and amount on ACF were very fast and large compared to other carbons due to the presence of only micropores and far larger specific surface area of the ACF.

Fig. 3 shows the adsorption capacity of $PtCl_6^{2-}$ on porous carbons from different platinum content of platinum solution at room temperature for 2 h. For 100 ppm platinum content solution, about 98% of $PtCl_6^{2-}$ was adsorbed on ACF, while 77% and 90% were adsorbed on CNT and AC, respectively. For 1000 ppm solution, 76% of $PtCl_6^{2-}$ was adsorbed on ACF, while 24% and 47% were adsorbed on CNT and AC, respectively. It is evident that the adsorption capacity of $PtCl_6^{2-}$ on ACF was prominent than other carbons as the increase of platinum content in solution.

The adsorption isotherms of $PtCl_6^{2-}$ on porous carbons are shown in Fig. 4. The adsorption amounts were quite different among the carbons and isotherm types were also different from carbons. ACF shows Langmuir type, while AC shows Freundlich and CNT shows two-step linear lines. These results implied that the pore structures developed on each carbon were different: the ACF has

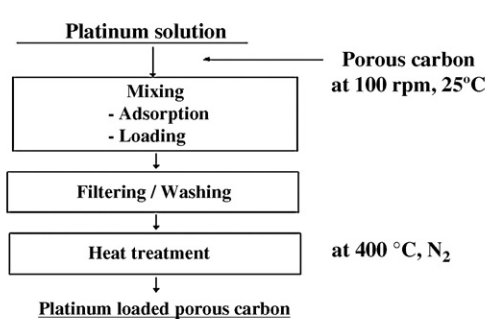

Fig. 1. Flow diagram of platinum nanoparticles loading on porous carbons.

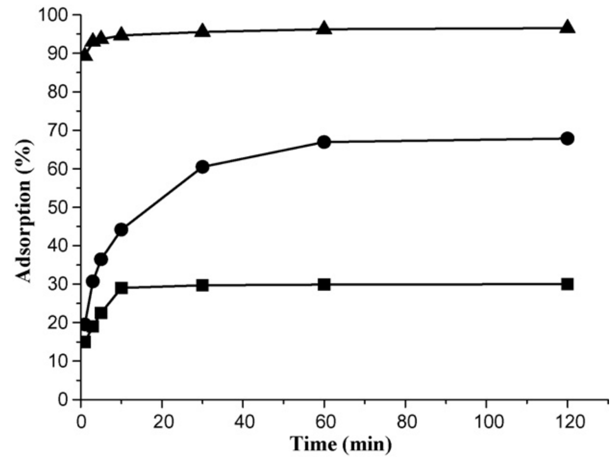

Fig. 2. Adsorption of $PtCl_6^{-2}$ on porous carbons from platinum solution (platinum: 500 ppm, (▲) ACF, (●) AC, (■) CNT).

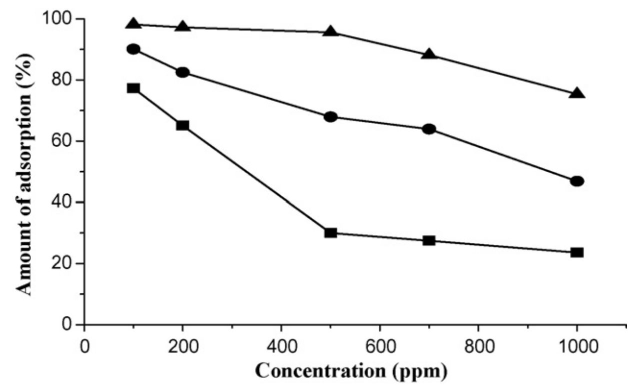

Fig. 3. Adsorption of $PtCl_6^{-2}$ on porous carbons from solution in different platinum concentration ((▲) ACF, (●) AC, (■) CNT).

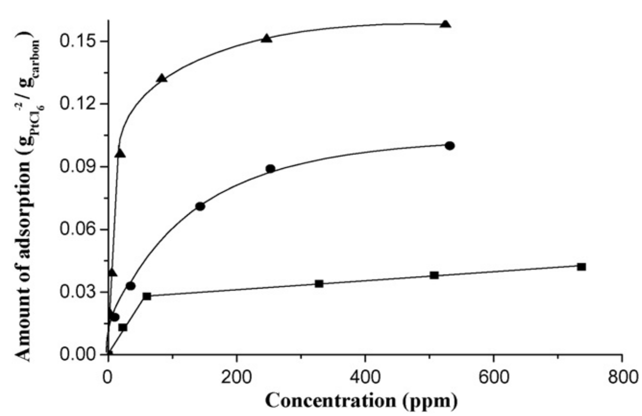

Fig. 4. Adsorption isotherms of $PtCl_6^{-2}$ on porous carbons from solution ((▲) ACF, (●) AC, (■) CNT).