

Pt-impregnation on to porous carbons without using reduction agents

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Abstract

The fuel cell capacity can be much improved by using Pt-impregnated porous carbon as a catalyst support. Therefore, the Pt-impregnation on porous carbons such as carbon nanotubes, activated carbon and activated carbon fiber was carried out by loading hexachloro platinate(IV)ion, PtCl_6^{-2} , from hydrogen hexachloro platinate hydrate dissolved solution without using reduction agents, and heating the platinate ion loaded carbons up to 400oC. When the initial Pt content was controlled to 1000 ppm in the solution, the adsorption capacities of hexachloro platinate(IV)ion on carbon nanotube, activated carbon and activated carbon fiber were 24, 47, and 76%, respectively at the equilibrium state. The adsorption amount of hexachloro platinate(IV)ion on porous carbons is depending on the specific surface area and increased as the increase of platinate ion concentration. 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 pore structure and size distribution. The TG, XRD, and TEM analysis were performed to confirmed the Pt-impregnation and distributio on porous carbon. The average Pt-particle size on porous carbons was less then two nanometer inspite of non-using reduction agents. Therefore, uniformly distributed nano sized Pt-particle impregnated carbons can be obtained from simple loading of hexachloro platinate(IV)ion and heating it up to 400oC.

Introduction

Oxidation of hydrogen is rather rapid in phosphoric acid fuel cell, however there is a disadvantage of decreasing capacity due to the over voltage in slow oxygen reduction process, which was caused by low dissolution of oxygen into phosphoric acid and slow diffusion of dissolved oxygen on to catalyst surface [1,2]. Therefore, many researches are now performing on electrochemical oxidation /reduction of hydrogen using platinum catalyst impregnated carbon electrode to increase the electrode capacity.

There are many methods for the impregnation of platinum particles on porous carbon such as activated carbons to improve the electrode capacity. Hydrogen hexachloro platinate hydrate $[\text{H}_2\text{PtCl}_6 \cdot n\text{H}_2\text{O}]$ is using as one of platinum particle sources, and the most popular method in platinum particle impregnation on carbon is adding reduction agents such as sodium dithionite $[\text{Na}_2\text{S}_2\text{O}_4]$ into the platinate hydrate solution and producing platinum colloids which is easily impregnated on porous carbon [3-5]. However, this process is very complex and costly. Also, uniformly developed porous carbons are necessary to improve effective distribution of platinum particles. Therefore, easy and low costly process is now being surveyed for the effective catalyst impregnation on various porous carbons. Recently carbon nanotubes and activated carbon fibers were developed and become attractive as using catalyst supports due to their uniformly developed micropores.

In this research, hydrogen hexachloro platinate hydrate $[\text{H}_2\text{PtCl}_6 \cdot 5.7\text{H}_2\text{O}]$ was dissolved in distilled water and the adsorption capacity of hexachloro platinate(IV), PtCl_6^{-2} , on porous carbons such as activated carbon, activated carbon fiber and carbon nanotube, from aqueous solution was investigated at various conditions without addition of reduction agents. The adsorption isotherms of hexachloro platinate(IV) was also studied. Then, this hexachloro platinate(IV) impregnated carbons were direct heat treated in nitrogen to investigate what kind of platinum compounds could be remained on porous carbons as increasing the temperature. TG, XRD analysis and TEM observations were carried out to confirm the platinum compounds and Pt particle, and BET specific surface area was measured to study the microporosity change of the porous carbons.

Experimental

Fig.1 shows flow diagrams of Pt-impregnated porous carbon preparations: (A) Choi and Shul [3], (B) Zeng et al. [4,5], and (C) our method. Hydrogen hexachloro platinate hydrate [$\text{H}_2\text{PtCl}_6 \cdot 5.7\text{H}_2\text{O}$, Kojima Chemicals Co.] power 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, 1000, 5000, 10000 and 50000 ppm. Activated carbon fiber (ACF, Toyobo KF-1500, Japan, BET surface area: $1435 \text{ m}^2/\text{g}$) was used as a catalyst support. Carbon nanotube (CNT, Iljin CNT, Korea, CM-95, BET surface area: $200 \text{ m}^2/\text{g}$) and activated carbon (AC, Yulim Carbon Co. Korea, BET surface area: $1100 \text{ m}^2/\text{g}$) were prepared to compare the adsorption capacity. A 0.1 g of porous carbons were added to 20 ml different platinum content solution, and agitated for 2 hours, at 100 rpm, 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. The hexachloro platinate(IV) impregnated carbons were dried at room temperature and TG analysis was carried out to study the degradation of hexachloro platinate(IV) as increasing the temperature in nitrogen. Then, one set of ampoules was heated up simultaneously. When the ampoules were raised up to desired temperature, the corresponding ampoule was quenched and sealed off for further XRD study. XRD analysis (D/MAX2000 Ultima/PC, Rigaku Co.) has been performed at Cu-K_α radiation. The adsorption characteristics of Pt-impregnated porous carbons were investigated by N_2 adsorption at 77K (Micromeritics, ASAP-2010). TEM observations were carried out to study the morphology and Pt particles loading on porous carbons.

Results and Discussion

In general, hydrated halides are insoluble in water. However, platinum and palladium halides are known soluble in water [6]. The hydrogen hexachloro platinate hydrate [$\text{H}_2\text{PtCl}_6 \cdot 5.7\text{H}_2\text{O}$] was dissolved in water, produced hexachloro platinate(IV), PtCl_6^{2-} and 2H^+ , and the solution became acid. The hexachloro platinate(IV) was adsorbed on porous carbons, resulting in the change of color in solution from orange-yellow to lucid.

Fig.2 shows the adsorption of hexachloro platinate(IV) on porous carbons from aqueous solution (Pt: 500 ppm) at room temperature. The adsorption rate and amount on activated carbon fiber were very fast and large compare to other carbons due to the only micropores and larger specific surface area of the activated carbon fiber.

Fig.3 shows the adsorption capacity of hexachloro platinate(IV) on porous carbons from different platinum content of aqueous solution at room temperature for 2 hours. For 100 ppm platinum content solution, about 98% of hexachloro platinate(IV) was adsorbed on activated carbon fiber, while 77% and 90% were adsorbed on carbon nanotube and activated carbon. For 1000 ppm solution, 76% of of hexachloro platinate(IV) was adsorbed on activated carbon fiber, while 24% and 47% were adsorbed on carbon nanotube and activated carbon. The adsorption capacity of hexachloro platinate(IV) on activated carbon fiber was prominent than other as the increase of platinum content in solution.

Fig.4 shows the adsorption isotherms of hexachloro platinate(IV) on porous carbons. The adsorption amount was quite different among the carbons and isotherm types were also different from carbons. Activated carbon fiber shows Langmuir type, while activated carbon shows Freundlich and carbon nanotube shows two step linear lines. These results implied that the pore structure developed on each carbons were different: the activated carbon fiber has almost all micropores, the activated carbon has some mesopores and macropores, and the carbon nanotube has only uniform mesopores. An isotherm that is convex upward is called favorable, because a relatively high solid loading can be obtained at low concentration in the fluid and it leads to narrow mass transfer zones in the bed [7]. Youssef et al [8] introduced the Langmuir equation and others on the adsorption of Cu(II) and Ni(II) to activated carbons from aqueous solution.

Fig.5 shows the TG curves of (a), as-received activated carbon fiber, (b) hydrogen hexachloro platinate hydrate powder, (c) hexachloro platinate(IV) impregnated activated carbon fiber, and (d) hexachloro platinate(IV) impregnated carbon nanotube according to the temperature in nitrogen, with which the degradation of Pt-compound can be studied. The TG curve of as-received activated carbon fiber shows

constant up to 600 °C after evaporation of water and then very slowly declined due to the emission of oxygen and hydrogen. There were several stepped decompositions of hydrogen hexachloro platinate hydrate [H₂PtCl₆·5.7H₂O] powder showing the change of composition, the curve became constant over 520 °C. The hexachloro platinate(IV) impregnated activated carbon fiber was slowly decomposed from 80 °C to 350 °C after evaporation of water and then almost constant in weight. The decomposition of hexachloro platinate(IV) impregnated carbon nanotube was similar to that of activated carbon fiber.

Fig.6 shows the XRD curves of hexachloro platinate(IV) impregnated activated carbon fiber which were heat treated up to 400 °C (c)-1 and 800 °C (c)-2, and the curve of hexachloro platinate(IV) impregnated carbon nanotube which were heat treated up to 400 °C (d)-1. There were distinguished peaks on all curves showing the loading of Pt particles on activated carbon fiber and carbon nanotube, which indicated that Pt particles can be obtained by direct heat treatment of hexachloro platinate(IV) up to 400 °C.

Table 1 shows the decomposition of hydrogen hexachloro platinate hydrate powder and hexachloro platinate(IV) ion during the heating from room temperature up to 800 °C. We can get only PtCl₂ from hydrogen hexachloro platinate hydrate powder under 550 °C. It is known that the melting point of PtCl₂ is 581 °C [9]. Therefore, Pt particles can be obtained by heating it over 581 °C. On the other hand, as already confirmed in Fig.6 (a)-1 and (a)-2, pure Pt particles can be obtained by heating hexachloro platinate(IV) around 400 °C. Therefore, Pt particle loading porous carbons can be obtained directly from heating the hexachloro platinate(IV) impregnated carbons.

Fig.7 shows the TEM observations of Pt loaded activated carbon fiber and carbon nanotube prepared at 400 °C. There are uniformly distributed Pt particles and the average particle size was about 2 nm, which means that heating up to 400 °C is enough to obtain pure nano Pt-particles on porous carbons without using reducing agents.

Table 2 shows the characteristics of Pt loaded activated carbon fiber and carbon nanotube. The BET surface area and total pore volume decreased due to the Pt particles loading. The ratio of micropore volume to total pore volume was also reduced, while average pore diameter was enlarged, especially the pore diameter of CNT was far increased. These results indicate that Pt particles mainly loaded at the entrance of smaller micropores.

Conclusions

Pt particle loading on porous carbons can be easily carried out by impregnation of hexachloro platinate(IV), PtCl₆⁻², from hydrogen hexachloro platinate hydrate [H₂PtCl₆·5.7H₂O] dissolved solution, and by direct heating the platinate ion impregnated carbons up to 400 °C. Impregnation rate and amount of Pt particles on activated carbon fibers were much faster and larger than those of carbon nanotube and activated carbon due to the far larger specific surface area and uniformly developed micropores. The adsorption isotherm types of PtCl₆⁻² were different from pore structure and pore size distribution; carbon nanotube shows linear type, while activated carbon fiber shows Langmuir type. The average Pt particle size was about 2 nm on activated carbon fiber. Pt particles were more uniformly distributed on activated carbon fibers than other porous carbons. Therefore, activated carbon fiber was very promising catalyst support for the Pt particles loading than other porous carbons.

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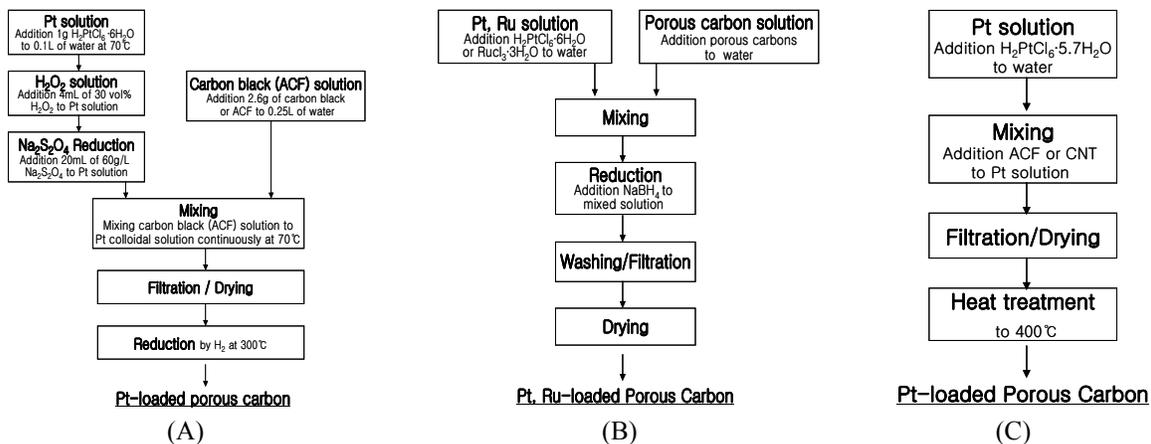


Fig. 1. Flow diagrams of Pt-loaded porous carbon preparation : (A) Choi and Shul [3], (B) Zeng et al. [4], and (C) our method

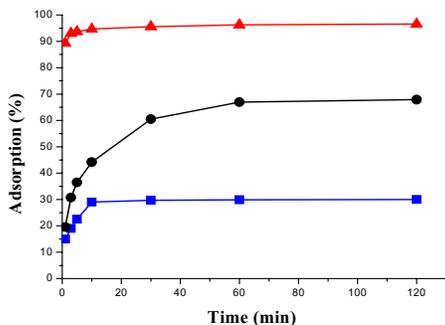


Fig. 2. Adsorption of hexachloro platinate(IV), $[PtCl_6^{2-}]$ on porous carbons from solution (Pt: 500 ppm, ▲ ACF, ● AC, ■ CNT).

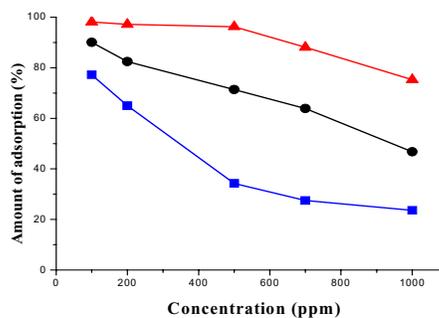


Fig. 3. Adsorption of hexachloro platinate(IV) on porous carbons from solution in different Pt concentration (▲ ACF, ● AC, ■ CNT).

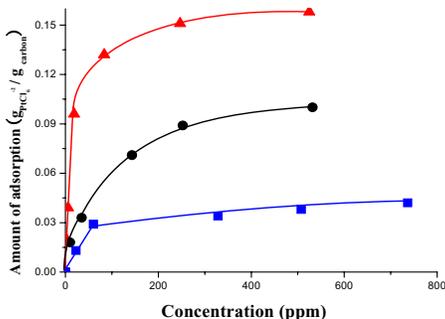


Fig. 4. Adsorption isotherms of hexachloro platinate(IV) on porous carbons from solution (▲ ACF, ● AC, ■ CNT).

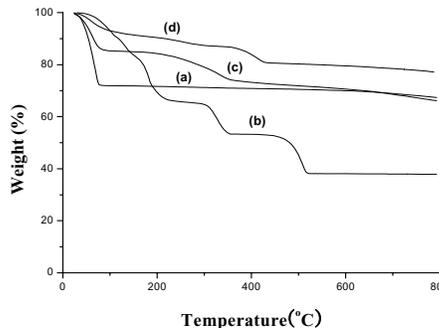


Fig. 5. TG curves of (a) as-received ACF, (b) hydrogen hexachloro platinate hydrate powder, (c) hexachloro platinate(IV) impregnated ACF, and (d) hexachloro platinate(IV) impregnated CNT (Pt: 50,000 ppm).

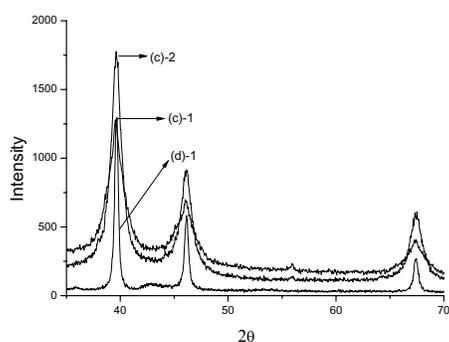


Fig. 6. XRD curves of hexachloro platinate(IV) impregnated ACF heated up to 400 °C (c)-1, 800 °C (c)-2, and (b) CNT heated up to 400 °C (d)-1.

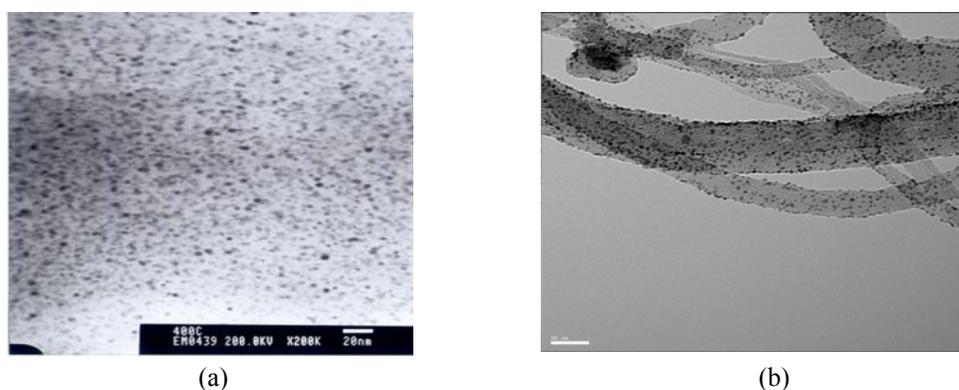


Fig.7. TEM observations of Pt-particles on (a) ACF and (b) CNT heat treated up to 400 °C of hexachloro platinate(IV) impregnated ACF and CNT.

Table 1. Decomposition of hydrogen hexachloro platinate hydrate $[H_2PtCl_6 \cdot 5.7H_2O]$ and $PtCl_6^{-2}$ as increasing the temperature

Temp.(°C)	150	250	400	550	800
$[H_2PtCl_6 \cdot 5.7H_2O]$	$H_2PtCl_6 \cdot 5.7H_2O / PtCl_2$	$PtCl_2$	$PtCl_2$	$PtCl_2$	Pt
$PtCl_6^{-2}$	--	--	Pt	Pt	Pt

Table 2. Characteristics of Pt-impregnated activated carbon fiber and carbon nanotube

	BET surface area (m ² /g)	Total pore volume (cc/g)	Micropore volume (cc/g)	Average pore diameter (Å)
As-received ACF	1435	0.60	0.57	16.6
Heat treated ACF at 400 °C	978	0.48	0.39	19.9
Heat treated ACF at 800 °C	953	0.45	0.36	19.5
As-received CNT	200	0.53	0.002	105.5
Heat treated CNT at 400 °C	122	0.46	0.001	151.0