INFLUENCE OF UREA TREATMENT OF MESOPOROUS CARBONS ON ELECTROCHEMICAL ACTIVITY OF PT-RU CATALYSTS FOR FUEL CELLS

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Abstract

In this work, the mesoporous carbons (MCs) were urea treated to for high nitrogen-containing groups with different amounts of urea and used as carbon supports of Pt-Ru nanoparticle for fuel cells. The surface and structural properties of the carbon supports and Pt-Ru catalysts were characterized by X-ray diffraction (XRD), surface area analyzer, X-ray photoelectron spectroscopy (XPS), elemental analyzer (EA), and inductive coupled plasma-mass spectrometer (ICP-MS). The electrochemical activity of Pt-Ru catalysts was investigated by cyclic voltammetry measurement. As the result, the nitrogen functional groups of carbon supports were increased with an increase in the amount of urea up to 4 g, while the average of Pt-Ru nanoparticle size was decreased owing to the improvement of dispersibility of the Pt-Ru catalysts. The electrochemical activity of the Pt-Ru catalysts was improved by the larger available active surface area due to the increase of nitrogen functional groups. Therefore, it was found that surface treatment using urea could influence the surface characteristic of carbon supports, resulting in enhanced electrochemical activity of the Pt-Ru catalysts of fuel cells.

Introduction

Many types of fuel cells are attracting much attention for their potential as clean mobile power sources in the near future.[1] Typically, platinum (Pt) or platinum alloy-based nanoparticles, which are impregnated on carbon supports, are the best electrocatalysts for anodic and cathodic reaction of fuel cells.[2] These catalysts materials are very noble, and thus there is a need to minimize the catalyst loading, without sacrificing electrochemical activity.[3] Raw carbon supports have a tendency to aggregate together spontaneously on account of their very fine structure and high surface energy.[4] Therefore, surface treatment is an essential process for carbon materials. Increasing the quantities of carbon surface functional groups using surface treatments, without decreasing its surface area, would increase the dispersion of the catalysts function.[5,6] Urea treatment can improve the performance of the carbon catalysts. The presence of nitrogen-containing surface functional groups influences on the surface behaviors of carbons to a considerable extent.[7]

In this work, the effects of the urea treatment for MCs (U-MCs) on the modification of surface nitrogen functional groups and the deposition of Pt-Ru catalysts were investigated.

Experimental

The synthesis of MCs was performed using SBA-15 as the template and sucrose as the carbon source.[8] The starting composition of SBA-15 was 10 g of P123 : 0.01 mol TEOS : 0.60 mol HCl : 20 mol H_2O. The product was filtered, washed three times with 50% ethanol-water solution and calcined at 823 K. MCs were prepared by impregnating the pores of the silica template with a solution of sucrose followed by heat treatments as described in literature.[9] The surface of MCs was modified by urea treatments in liquid phase to optimize their ability to disperse active Pt-Ru nanoparticles. MCs were treated with different urea amounts i.e., 0, 1, 3, 4, and 5 g at 333 K, stirred for 24 h. The mixture was placed in a drying oven at 373 K for overnight. And then, the mixture was completed by pyrolysis at 1173 K for 2 h under nitrogen atmosphere. The urea

treated MCs (U-MCs) were filtered, washed until the water reached pH neutrality and dried at 383 K overnight. The U-MCs, according to the different urea amounts used, were named as U0-MCs, U1-MCs, U3-MCs, U4-MCs, and U5-MCs. Carbon-supported Pt-Ru nanoparticles were prepared by chemical reduction method. H_2PtCl_6 and $RuCl_3$ from metal precursors were added to the above suspension under mechanical stirred conditions. Next, the reducing agents HCHO and NaOH were added dropwise to the Pt-Ru slurry and stirring for 6 h at 353 K. Argon gas was passed all process to present by products. The Pt-Ru catalysts were then dried in a vacuum oven at 343 K for 12 h.[10]

Results and Discussion

Fig. 1 shows the low-angle XRD patterns of MCs after urea treatment. The U0-MCs show three well-resolved peaks, referred as (1 0 0), (1 1 0) and (2 0 0) reflections, associated with *p6mm* hexagonal symmetry. Surface treated samples show similar low-angle XRD patterns indicating that *p6mm* structure is maintained after urea treatment. However, the U5-MCs shows the smallest peak intensity suggesting a decrease of the structural order.[11]

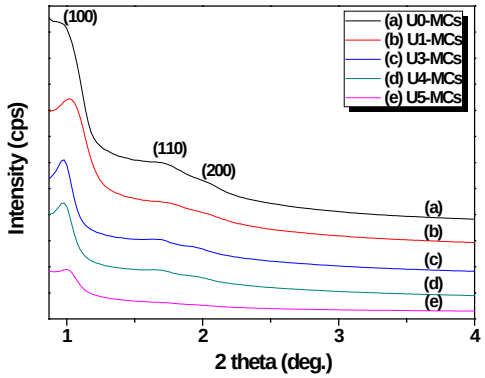

Fig. 1. Low-angle XRD patterns of the carbon supports.

Fig. 2 shows the N_2/77 K isotherms and corresponding pore size distributions of the urea treated carbon supports. As shown in Fig. 2(a), all samples exhibit Type IV isotherms with hysteresis loops caused by capillary condensation in mesopores, which means that all samples have mesoporous structures. The shapes of the adsorption-desorption isotherms decreased with an increase in the amounts of urea to the carbon supports. In addition, the mesopore sizes determined from the maximum in pore size distribution curves decreased with an increase in the amounts of urea to the carbon supports. As shown in Fig. 2(b), the pore sizes decreased with an increase in the amounts of urea up to 4 g to the carbon supports. The BET specific surface area and pore volumes of the carbon supports are listed in Table 1.[12,]

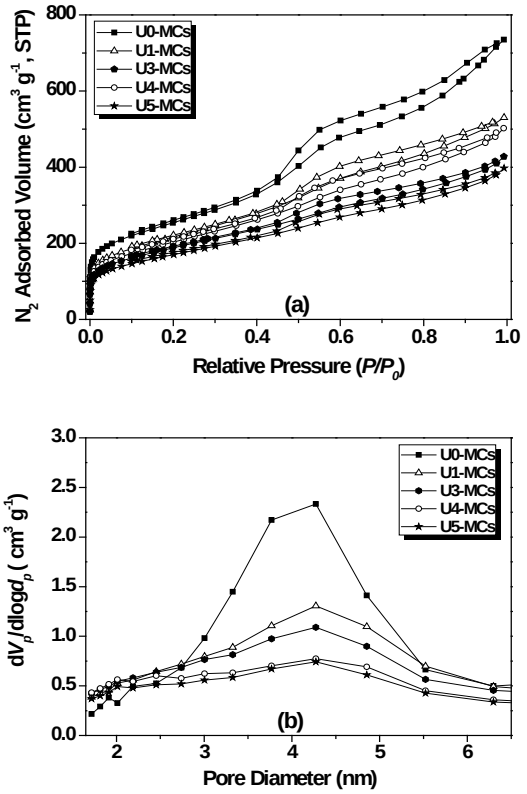

Fig. 2. Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) curves of carbon supports.

Table 1. Textural properties of the prepared carbon supports

Sample	S_{BET}[a] (m^2/g)	V_{Total}[b] (cm^3/g)	V_{Meso}[c] (cm^3/g)	D_P[d] (nm)
U0-MCs	890	1.13	1.04	5.08
U1-MCs	760	0.82	0.72	4.31
U3-MCs	720	0.77	0.69	4.28
U4-MCs	660	0.66	0.56	3.98
U5-MCs	600	0.61	0.52	4.06

[a]S_{BET}: Specific surface area calculated using BET equation at a relative pressure range of 0.2-0.35.
[b]V_{Total}: Total pore volume is estimated at a relative pressure P/P_0 = 0.990.
[c]V_{Meso}: Mesopore volume determined from the subtraction of micropore volume from total pore volume.
[d]D_P: Average pore diameter.

Fig. 3 shows the XPS survey scan spectra of the urea treated MCs. The C_{1s}, O_{1s}, and N_{1s} peaks of urea treated MCs are found at the binding energy of about 285, 532, and 404 eV, respectively. The oxygen and nitrogen groups were observed for the MCs by urea treatment, and the introduction of the oxygen and nitrogen functional groups increased with increasing urea content, as was confirmed. It was found that C_{1s} peak diminished with an increase in the amount of urea, while the O_{1s} and N_{1s} peak increased with an increase in the amount of urea up to 4 g.[13] However, the U5-MCs leads to the decrease of the O_{1s} and N_{1s} than U4-MCs. It is primarily attributed to the change of functional groups of the U5-MCs.

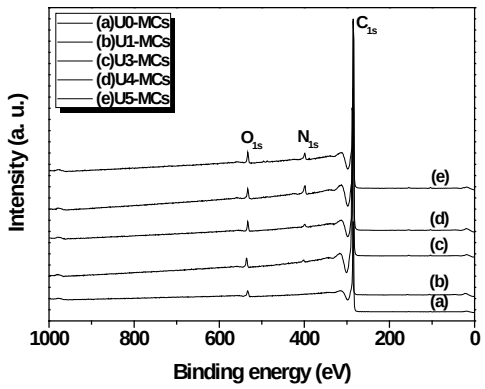

Fig. 3. XPS survey scan spectra of the urea treated carbon supports.

Table 2 shows the EA results of the urea treated MCs surfaces. The content of nitrogen is increased by the urea treatment. This is obviously referred to the increase of nitrogen-containing functional group on the MCs surfaces. The result can be explained that the urea treatment produces nitrogen-containing functional groups on the MCs surfaces.[14]

Table 2. EA results of urea treated carbon supports

Samples	Elemental analysis		
	C_{1s}	O_{1s}	N_{1s}
U0-MCs	98.2	1.4	1.1
U1-MCs	92.9	1.6	2.9
U3-MCs	88.5	1.8	5.5
U4-MCs	83.5	2.1	7.4
U5-MCs	86.3	2.2	6.8

Fig. 4 shows the high-angle XRD patterns of the Pt-Ru/U-MCs catalysts. The peaks at 2θ=40°, 47°, 68°, and 82° were associated with the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) types of Pt, respectively. The characteristic peaks for the Ru, however, are not clearly shown in the high-angle XRD patterns. This is possibly because the Ru nanoparticle phases are not fully developed and their nanoparticle sizes are relatively small for the Pt catalysts. From the high-angle XRD results, the mean sizes of the Pt nanoparticle were calculated using the Scherrer equation (1).[15]

$$L = \frac{0.9\lambda}{\beta_{2\theta}\cos\theta_{\max}} \qquad (1)$$

where λ is the X-ray wavelength (1.54056 Å for the Cu Kα radiation), $B_{2\theta}$ is the width of the diffraction peak at half-height, and θ_{max} is the angle at the peak maximum position. The crystalline size of Pt-Ru catalysts was presented in Table 3. The nanoparticle size of Pt-Ru catalysts decreased from 3.9 to 3.2 nm with an increase in the amounts of urea from 0 to 4 g, which is related to affecting the surface by urea treatment. It can be considered that surface treated MCs have a secured deposition area for Pt-Ru nanoparticles, due to the removal of weak or unstable boundary layers on the surfaces of carbon supports. Therefore, Pt-Ru nanoparticles are well dispersed and become smaller. As a result, Pt-Ru nanoparticles size is related to the modified surface characteristics of surface treated carbon supports. Furthermore, the contents of Pt-Ru in Pt-Ru/U-MCs catalysts are presented in Table 3. Pt-Ru/U4-MCs catalyst showed the highest value (Pt : 16.4 wt.%

and Ru : 7.4 wt.%), whereas the Pt-Ru/U0-MCs catalyst showed the lowest value (Pt : 10.2 wt.% Ru : 4.2 wt.%), clearly indicating that in the case of surface treated MCs, Pt and Ru loading levels were enhanced with increasing the amounts of urea up to 4 g. It can be seen that the urea treatment of the MCs surfaces lead to the increase of nitrogen-containing functional groups, resulting in improving the loading contents.

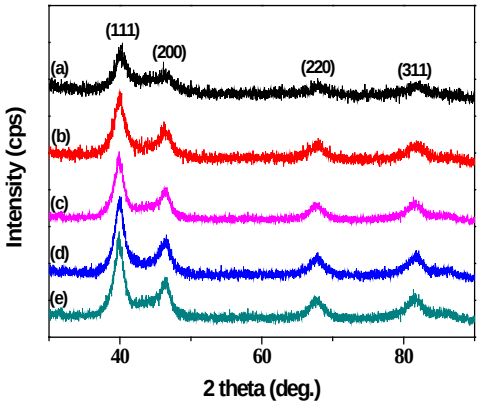

Fig. 4. High-angle XRD curves of Pt-Ru catalysts: (a) Pt-Ru/U0-MCs, (b) Pt-Ru/U1-MCs, (c) Pt-Ru/U3-MCs, (d) Pt-Ru/U4-MCs, and (e) Pt-Ru/U5-MCs.

Table 3. Nanoparticle mean size and loading contents of Pt-Ru catalysts

Samples	Pt (wt.%)[a]	Ru (wt.%)[a]	Loading levels(%)[a]	Crystalline size (nm)[b]
Pt-Ru/U0-MCs	10.2	4.2	43	3.9 ± 0.2
Pt-Ru/U1-MCs	12.6	5.4	52	3.7 ± 0.1
Pt-Ru/U3-MCs	14.2	6.2	58	3.5 ± 0.2
Pt-Ru/U4-MCs	16.4	7.4	67	3.2 ± 0.2
Pt-Ru/U5-MCs	15.3	6.6	62	3.4 ± 0.1

[a] Measured from ICP-MS results.
[b] Measured from XRD results.

Fig. 5 Shows the TEM images of Pt-Ru/U-MCs catalysts. The TEM images provided the morphologies of the catalysts. In addition, TEM images indicate that the dispersion of the Pt-Ru nanoparticles on the carbon supports are properly uniform, an especially important characteristic for an electrocatalyst. In particular, Pt-Ru/U4-MCs catalyst has uniformly deposited Pt-Ru as well as the highest loading levels and the smallest size. However, for Pt-Ru/U3-MCs and Pt-Ru/U5-MCs, the Pt-Ru is more aggregated and less dispersed than the Pt-Ru/U4-MCs catalyst.[16] It can be seen that the urea treatment of the MCs surfaces lead to the increase of nitrogen-containing functional groups, resulting in improving the dispersion of Pt-Ru nanoparticle.

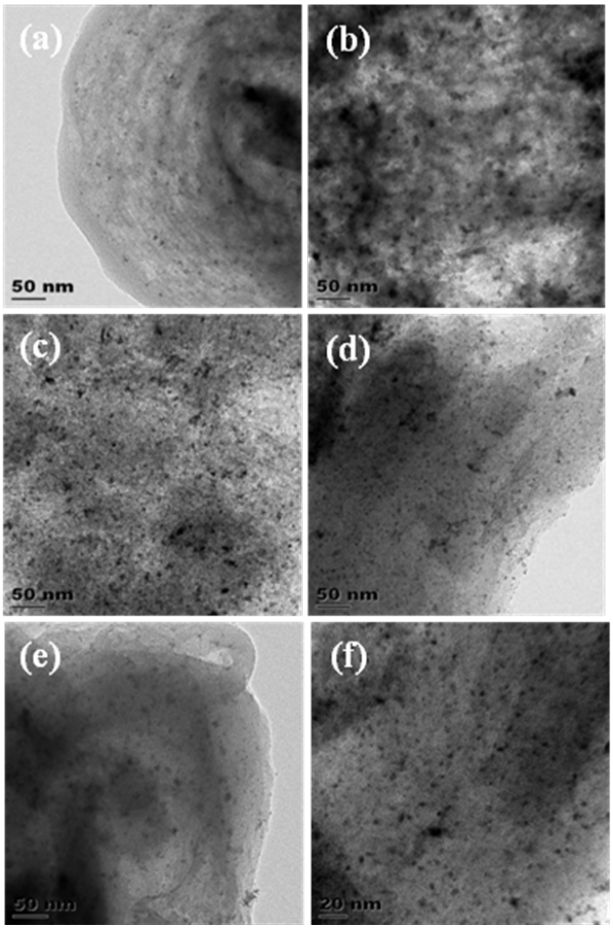

Fig. 5. TEM images of Pt-Ru catalysts: (a) Pt-Ru/U0-MCs, (b) Pt-Ru/U1-MCs, (c) Pt-Ru/U3-MCs, (d) Pt-Ru/U4-MCs, (e) Pt-Ru/U5-MCs, and (f) Pt-Ru/U4-MCs.

Fig. 6 shows the cyclic voltammetry of the prepared catalysts in 0.5 M H_2SO_4 solution. It was found that the electrochemical activities of the Pt-Ru catalysts were enhanced with increasing the ratios of urea up

to 4. This is evidence that the urea treated MCs has the higher electrochemical activity than the Pt-Ru/U0-MCs. However, further surface treatment over 4 g amounts of urea leads to a greater decrease in the electrochemical activity than Pt-Ru/U4-MCs. Pt-Ru/U4-MCs shows the best electrochemical activity among the catalysts due to its largest peak. It was probably related with the small nanoparticle size and high loading contents in Table 3.[17,18] It is probably related to the fact that the urea treatment of MCs surfaces lead to the increase of nitrogen-containing functional groups.

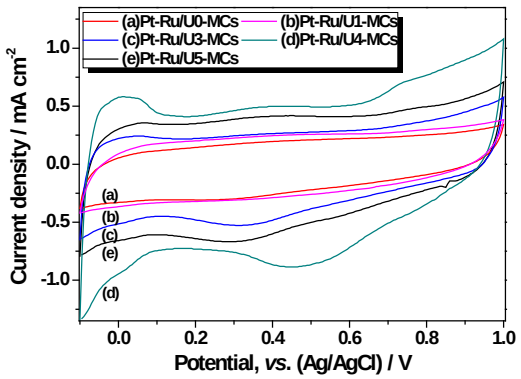

Fig. 6. Cyclic votammetry of Pt-Ru catalysts in 0.5 M H_2SO_4 with 20 mV/s scan rate.

Fig. 7 shows the cyclic voltammetry Pt-Ru catalysts in 1.0 M CH_3OH + 0.5 M H_2SO_4. The votammograms exhibit the highest current for methanol electrooxidation on the Pt-Ru/U4-MCs. The peak potentials and rising potentials for methanol electrooxidation on the five catalysts with urea treated carbon support are almost the same, namely 650 mV (positive scans) and 450 mV (negative scans), respectively. The electrochemical activity increased with increasing urea amounts, reaching the maximum at 4 g, owing to the smaller nanoparticle size of 3.2 nm. It is though that smaller nanoparticles and high loading levels lead to larger available active surface of the Pt-Ru catalysts, resulting in better electrocatalytic properties for methanol oxidation.[19,20]

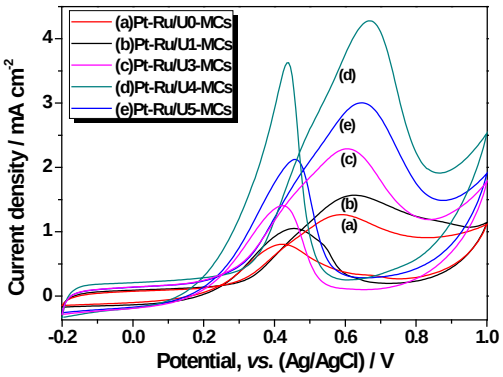

Fig. 7. Cyclic votammetry of Pt-Ru catalysts at 20 mV/s scan rate in 1.0 M CH_3OH + 0.5 M H_2SO_4 solution.

Conclusions

In this work, the effect of urea treatment of carbon supports on the electrochemical behaviors of Pt-Ru/U-MCs catalysts is investigated. The results show that the urea treatment modified MCs surfaces, indicating the introduction of the nitrogen groups, which led to the optimal conditions for Pt-Ru dispersion. The electrochemical activity is enhanced with an increase in the amounts of urea up to 4g. However, further treatment over 4 g amounts of urea leads to a decrease of the electrochemical activity. This is mainly attributed to the change of functional groups and decomposed structure of the MCs, owing to excessive surface treatment. Consequently, it was found that the optimal surface treatment amount of urea was 4 g for the highest electrochemical activity of Pt-Ru catalysts.

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