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Preparation of mesoporous carbon templated by silica particles for use as a catalyst support in polymer electrolyte membrane fuel cells

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Abstract

Mesoporous carbons were prepared using commercial silica particles and a formaldehyde–resorcinol resin as a template and carbon precursor, respectively. By changing the molar ratio of template to carbon precursor, mesoporous carbons with different mesoporosities (MC-*X*, *X* represents the molar ratio of template to carbon precursor) were produced. The resulting MCs had a high-surface area and large pore volume. In particular, the highest mesoporosity was observed for MC-3. Pt catalysts-supported on MC-*X* were prepared using formaldehyde as a reducing agent for use as a cathode catalyst in a polymer electrolyte fuel cell (PEMFC). The size of Pt crystallite was dependent on the properties of corresponding carbon support. As a whole, a carbon support with a high-surface area and high-mesoporosity served the best in terms of a high-dispersion of Pt nanoparticles. In a unit cell test of the PEMFC, a Pt catalyst with a high-mesoporosity and fine dispersion of metal showed an enhanced performance. The findings indicate that the surface area combined with the mesoporosity had a positive influence on the metal dispersion and the distribution of ionomer, leading to the enhanced cell performance.

Keywords: Mesoporous; Carbon; Mesoporosity; Oxygen reduction; Fuel cell

1. Introduction

A growing interest has developed for the use of polymer electrolyte membrane fuel cells (PEMFC) as an alternative power source for portable devices and electric vehicles [1]. For practical applications of PEMFC, it is necessary to design a high-performance membrane electrode assembly (MEA). It is generally accepted that the performance of an MEA is closely related to the properties of the catalysts used in its preparation. On the other hand, the catalytic performance of a fuel cell catalyst is influenced by the physico-chemical state of the metal component (usually Pt) [2] as well as the textural properties of the carbon support [3,4]. Therefore, the design of a carbon support with a favorable structure constitutes an important first step in improving cell performance [4].

In this study, mesoporous carbon (MC) supports were prepared using silica particles and a formaldehyde–resorcinol resin as a template and a carbon precursor, respectively. MCs with different mesoporosities were prepared by controlling the molar ratio of template (silica particle)/carbon precursor. The prepared supports and supported Pt catalysts were systematically characterized. In particular, the effect of mesoporosity on catalytic performance was intensively investigated.

2. Experimental

2.1. Preparation of mesoporous carbons and supported Pt catalysts

Mesoporous carbons (MCs) were prepared using a formaldehyde (Aldrich Co.)–resorcinol (Fluka) resin and Ludox HS-40 (Aldrich Co.) as a carbon precursor and a removable template. Resorcinol was first dissolved completely in a formaldehyde solution, followed by the addition of Ludox HS-40. Sodium carbonate (Na_2CO_3, Aldrich Co.) to catalyze the polymerization

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of formaldehyde and resorcinol was then added to the above mixture. The final composition of the mixture was sodium carbonate (0.01):resorcinol (1.0):formaldehyde (2.0):silica template (3–12). After initiating the polymerization, the mixture was aged at 80 °C for 12 h and followed carbonization at 850 °C for 5 h in a follow of nitrogen. The silica template was removed by treatment with a dilute HF solution, to give mesoporous carbons (MC-*X*, *X* represents the molar ratio of silica to carbon precursor).

MC-supported Pt catalysts were prepared by reduction using formaldehyde as reducing agent as reported in the literature [5]. In a typical procedure, known amount of hexachloroplatinic acid was dissolved into deionized water and carbon supports were dispersed under vigorous stirring. The pH of the mixture was adjusted to be 12 using 0.5 M NaOH dropwise. Formaldehyde was added to the solution and the above solution was heated up to 90 °C and kept at this temperature to reduce Pt ion for 5 h. $NaNO_3$ as sedimentation promoter was added into the solution slowly for the sedimentation of Pt on carbon support. The above mixtures were filtered, washed with copious amount of water and dried at 100 °C for 24 h. Pt loadings were adjusted to 20 wt.% in final catalysts.

2.2. Half cell and single cell tests

Cyclic voltammograms were obtained using a conventional three-electrode system with saturated calomel electrode and a platinum gauge as the reference and counter electrode, respectively. The working electrode was prepared by coating a small amount of catalyst ink on disk-type graphite. The electrochemically active surface areas for the prepared Pt catalysts were calculated from the charge for hydrogen adsorption in cyclic voltammograms [6].

The membrane electrode assemblies (MEAs) were fabricated using a previously described method [7]. Both sides of the electrode consisted of a commercial gas diffusion layer (E-TEK) and carbon-supported catalyst layer. The anode contained a commercially available 20 wt.% Pt/C catalyst with a loading of 0.4 mg Pt/cm^2 and the cathode contained the prepared Pt/MCs with a metal loading 0.5 mg Pt/cm^2, which was kept identical for all the MEAs. A Nafion-115, which was pre-treated by boiling in 3 wt.% H_2O_2 for 3 h and then in a 0.5 M H_2SO_4 solution, was used as the solid electrolyte. The anode–membrane–cathode was then assembled by hot-pressing at 120 °C for 3 min. The geometric area of the electrode was 5 cm^2 and the cell was operated at 75 °C. Hydrogen (anode) and oxygen (cathode) was fed at a rate of 350 and 400 ml/min, respectively.

3. Results and discussion

Fig. 1 shows the N_2 sorption isotherms (a) and corresponding pore size distributions (PSD) (b) of the prepared carbon supports. A carbon material designated as C-0, which was prepared without a silica template, exhibited a very low-sorption capacity for nitrogen, indicating the non-porous nature of this carbon material. On the other hand, when silica particles were used as a removable template, the resulting MCs show a sharp capillary condensation at a high-relative pressure, indicating the presence of relatively large pores. It should be noted that the shape of the isotherm changes gradually with the molar ratio of the silica template to the carbon precursor.

During polymerization of resorcinol and formaldehyde, silica sol would be aggregated to form a silica template larger than silica sol (Ludox HS-40), which results in increasing the pore size of final MC carbons. The degree of aggregation of silica sol has known to be dependent on several factors such as the pH of precursor solution, the ratio of silica sol to carbon precursor and surface properties of silica sol [8–10]. In this research, the aggregation of silica sol, corresponding to the pore size of MC carbons, would be highly related to the ratio of silica sol to carbon precursor because the other two factors were kept constant. According to the literature [9,10], the aggregation of silica sol is favorable with the increase in the ratio of silica sol to carbon precursor, resulting in the formation of larger pores in silica-templated carbon and this is well consistent with our results in that the pore size of MC carbon was increased with increasing the molar ratio of silica sol to carbon precursor. On the other hand, it has been known that the textural properties of templated carbon was also affected by the molar ratio of template to carbon precursor [10] and the optimum point to obtain a carbon with the highest pore volume and surface area would be related to the synthetic condition (the pH of precursor solution, temperature) and the type of carbon precursor and

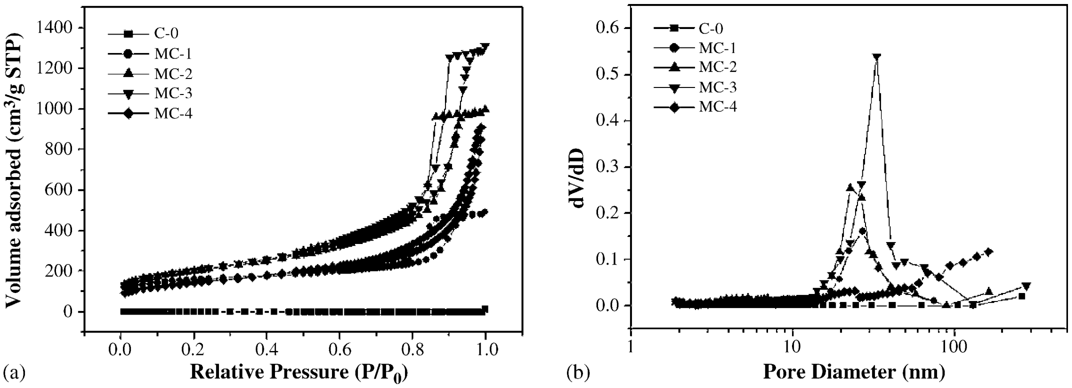

Fig. 1. (a) N_2 isotherms and (b) corresponding pore size distributions of carbon supports.

Table 1
Textural properties of the prepared carbons and Pt catalysts

	BET surface area, S_{total} (m^2/g)	Pore volume, V_{total} (cm^3/g)	Mesopore surface area, s_{meso} (m^2/g)	Micropore surface area, s_{micro} (m^2/g)	$S_{\text{meso}}/S_{\text{total}}$
C-0	34	0.00874	–	–	–
MC-1	506	0.672	234	272	0.46
MC-2	710	1.513	642	68	0.90
MC-3	724	2.016	683	41	0.94
MC-4	503	1.396	395	108	0.785
Pt/C-0	16	0.0064	–	–	–
Pt/MC-1	338	0.61	214	124	0.68
Pt/MC-2	652	1.413	601	51	0.92
PtMC-3	672	1.702	632	40	0.94
Pt/MC-4	452	1.215	359	93	0.794

template [11]. In our case, the surface area and pore volume of MC carbon were gradually increased with increasing silica sol contents in the starting reaction mixture (up to MC-3) and excessive addition of silica sol (at MC-4) resulted in decreasing the surface area and pore volume. At lower contents of silica sol, it appeared that the number of silica template, generated from the aggregation of silica sol, was relatively insufficient to get a carbon with higher surface area and pore volume [12]. On the contrary, an intensive aggregation of silica sol would be occurred at higher contents of silica sol, to lower templating effect of silica sol and consequently, to decrease the surface area and pore volume of resulting MC carbon [10].

Interestingly, prepared MC carbons (MC-1–MC-3) exhibited type IV isotherm which is typical in mesoporous materials. However, the MC-4 showed somewhat different shape of isotherm (almost close to type II isotherm) from those of MC-1–MC-3. As described previously, due to the intensive aggregation of silica sol, the MC-4 exhibited the largest pore size with broad pore size distribution from 50 nm to above 100 nm. It should be noted that the type II isotherms was typically observed in non-porous or macroporous material [13]. Therefore, it is reasonable to conclude that the isotherm of the MC-4 carbon is an intermediate form between types II and IV. The N_2 isotherm of the supported Pt catalyst (not shown here) exhibited the same trends as the corresponding carbon support indicating that the basic pore structures of the supports are not changed after the metal was loaded. The textural properties of the prepared carbons and the corresponding Pt catalysts are listed in Table 1. As a whole, all of the MCs had a high-surface area and a large pore volume. Supported Pt catalysts exhibited lower a surface area and pore volume than the corresponding carbon supports. It is interesting to compare the $S_{\text{meso}}/S_{\text{total}}$ of carbon support, which can be considered to be an index of mesoporosity. The lowest value of $S_{\text{BJH}}/S_{\text{BET}}$ was observed for C-0. As the molar ratio of template to carbon precursor increased to three (MC-3), the $S_{\text{meso}}/S_{\text{total}}$ began to increase and was then lowered for the case of MC-4. It is likely that this tendency is closely related to the templating effect of silica particles.

Fig. 2 shows X-ray diffraction patterns of the prepared Pt/MC-*X* catalysts. The broader peak at 25 °C is related to the carbon support. All of the catalysts prepared gave rise to peaks, consistent with face centered cubic phase of Pt crystallites. The average crystallite size was calculated from the Scherrer equation based on Pt (2 2 0). Compared to Pt/MCs, the Pt/C-0 catalyst was comprised of larger Pt crystallites, indicating that the mesoporosity of the carbon support is a positive factor in the dispersion of metal. The differences in Pt particle size are insignificant among Pt/MCs catalysts, irrespective of the mesoporosity of the carbon support.

Morphology and particle size of the prepared catalysts were observed by transmission electron microscopy (TEM, JEOL, JEM-3010). Fig. 3 shows representative TEM images of the supported Pt catalysts (Pt/MC-3). Similar TEM images were obtained in the other Pt/MCs catalysts. High-porosity with spherical pores (about 20 nm) and finely dispersed Pt particles on the MC-3 carbon can be observed at low-magnification (Fig. 3(a)). In the HR-TEM image of the Pt/MC-3 catalyst (Fig. 3(b)), the size of the Pt crystallites were confirmed to have values similar to those calculated from the Scherrer equation using XRD results.

Fig. 4 shows a representative cyclic voltammogram (CV) of the Pt catalyst (Pt/MC-3), which was used to estimate the active

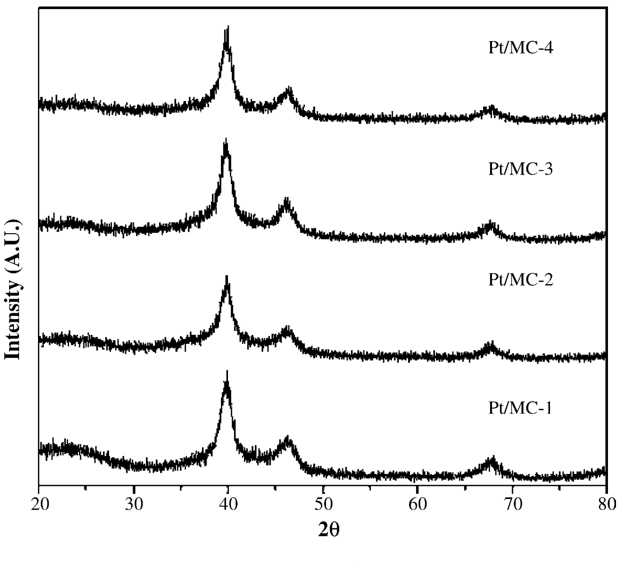

Fig. 2. XRD patterns of the Pt/MCs.

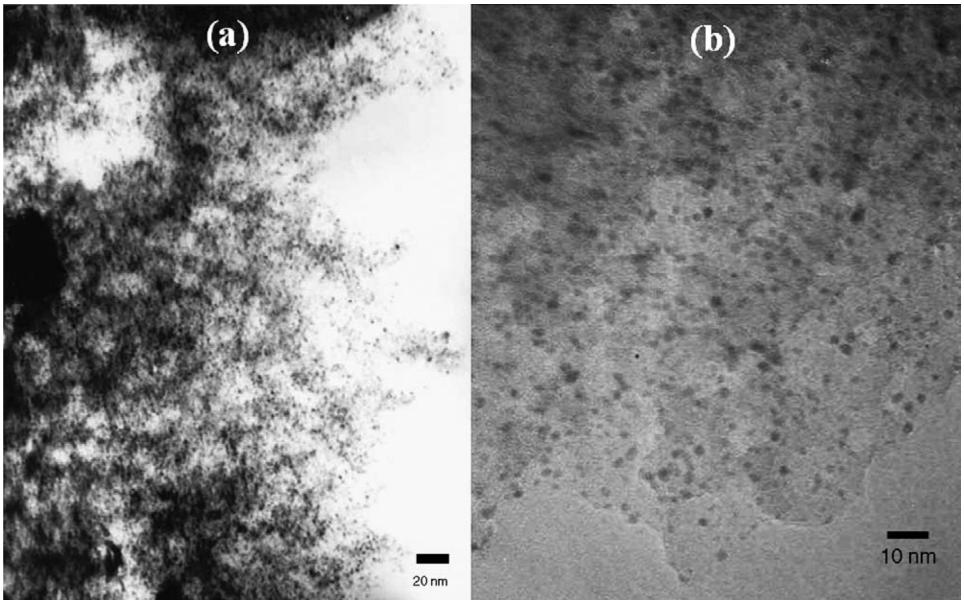

Fig. 3. (a) TEM and (b) HR-TEM image of Pt/MC-3.

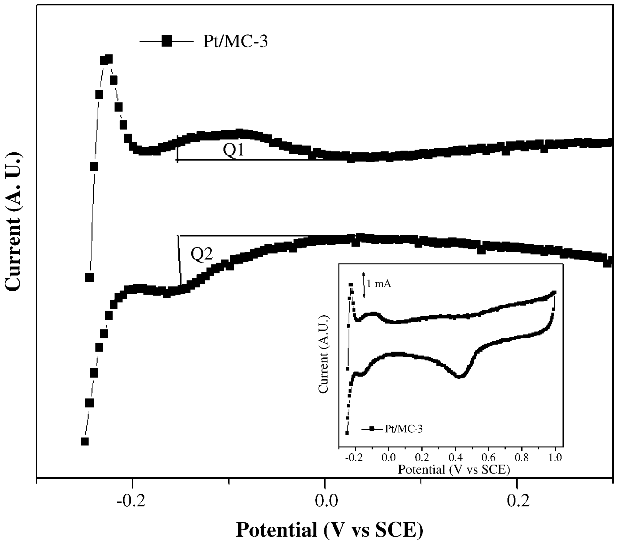

Fig. 4. Cyclic voltammogram and coulombic charge for hydrogen adsorption/desorption of supported Pt catalyst (Pt/MC-3).

surface area using the coulombic charge for hydrogen desorption. The CV shows typical electro-adsorption and desorption of H_2 on the Pt site, a Pt pre-oxidation and a Pt reduction peak. The electrochemically active surface areas (EAS) of the prepared Pt catalysts (Table 2) were calculated from the mean value of coulombic charge between charges exchanged during the electro-adsorption (Q1) and desorption (Q2) of H_2, the values of which were corrected for eliminating the double layer charging current. The Pt/C-0 was found to have the lowest EAS and double layer charging current of the Pt catalysts tested in this work. On the other hand, Pt catalysts-supported on MCs showed a relatively large double layer charging current, demonstrating high-surface area of Pt/MCs. As a whole, the EAS values for the Pt/MCs are as follows: Pt/MC-3 $\geq$ Pt/MC-2 > Pt/MC-4 $\geq$ Pt/MC-1. From this result and the crystallite size calculated by the Scherrer equation, it can be concluded that the carbon support with a high-surface area with a high-mesoporosity can be favorable for metal dispersion.

Table 2
Mean particle size calculated from the Pt (2 2 0) using the Scherrer equation and the electrochemically active surface area (EAS)

	Particle size (Å)	EAS (m^2/g)
Pt/C-0	–	<3
Pt/MC-1	39.8	45
Pt/MC-2	36.4	53
Pt/MC-3	35.9	56
Pt/MC-4	38.5	47

The unit cell performances of polymer electrolyte fuel cell at 75 °C are shown in Fig. 5. Since, the one type of catalyst with the same loading was coated on the anode side, these variations in cell performance can be totally attributed to the performance

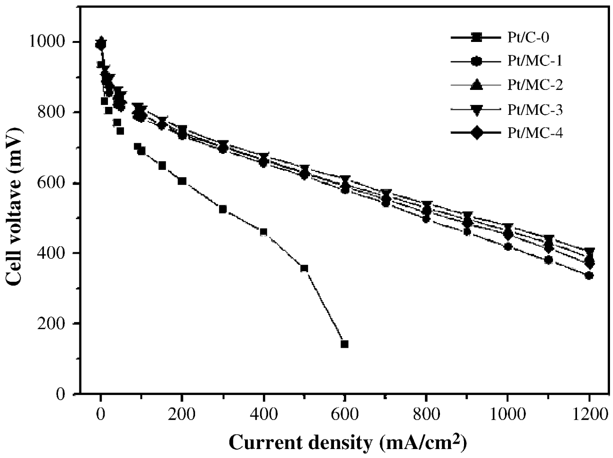

Fig. 5. Cell performances of the prepared Pt catalysts.

of the cathode catalysts, which is indicative of catalytic performance for the reduction of oxygen. As previously observed, the different dispersions of active metal particles could be assigned to variations in the catalytic performance for the reduction of oxygen [14–17]. In addition to the metal dispersion, the mesoporosity of the supported Pt catalysts might play an important role in the unit cell performance. It is well known that electro-chemical catalysis in a fuel cell takes place in the interface of the fuel, the catalyst surface and the electrolyte, i.e. a triple-phase boundary [18]. It is likely that a support with a high-surface area and mesoporosity would be favorable for both a high-metal dispersion and the easy diffusion of ionomer. With these analyses, it can be concluded that the high-performance of Pt/MC-3 can be attributed to the favorable pore structure, resulting in a higher metal dispersion and the facile formation of a triple-phase interface.

4. Conclusions

Mesoporous carbon supports were fabricated by a silica templating method. By controlling the molar ratio of silica template to carbon precursor, it was possible to produce carbon supports with different mesoporosities. The textural properties of the carbon support, such as surface area and mesoporosity, affected the metal dispersion of the final-supported Pt catalyst. In a unit cell test of the PEMFC, the Pt catalyst with a high-metal dispersion and mesoporosity exhibited an enhanced cell performance. Thus, a carbon support with high-surface area and a high-mesoporosity would be favorable for the dispersion of Pt and the diffusion of ionomer, leading to a high-catalytic performance of the resulting Pt catalyst.

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