Effect of surface modification of mesoporous carbon supports on the electrochemical activity of fuel cells

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Mesoporous carbon (MC) was prepared from mesoporous silica (SBA-15) via a conventional templating method for use as a Pt–Ru catalyst support in fuel cells. The effect of surface modifications of the carbon support at different pH on the electrochemical activities of the Pt–Ru/MC catalysts was investigated. The Pt–Ru nanoparticle size and loading were dependent on the surface characteristics of the MC. Base-modified MC-supported Pt–Ru showed the smallest average nanoparticle size (3.3 nm) and the highest loading (77%) among the chemically modified MC-supported Pt–Ru catalysts. The electrochemical activity of the catalysts was enhanced when the MC supports were treated with basic or neutral agents rather than by acid modification.

1. Introduction

Fuel cells have attracted considerable attention as clean power sources for portable electronic devices and electric vehicles, and as on-site power generation systems, owing to their low emissions and high energy conversion efficiencies [1,2]. Generally, platinum (Pt) or platinum alloy-based nanoparticles, which are impregnated on carbon supports, are the best electrocatalysts for the anodic and cathodic reactions of fuel cells [3,4].

In fuel cell systems, attention has been focused on the development of the support material, which is one of the key factors in increasing the utilization of Pt or Pt alloy metal catalysts. The most common low Pt or Pt alloys are supported by high specific surface area carbon and are used in both the anode and the cathode. To achieve high catalytic performance with low Pt loading, considerable effort must be placed on Pt utilization and improvement of its electrochemical activity [3,5–7]. The electrochemical activity depends not only on the unique nature of the Pt or Pt alloy catalysts, such as their size, size distribution, shape, and oxidation state, but also on the morphological structures of the carbon support and metallic nanoparticles, such as the carbon specific surface area, carbon aggregation, metal dispersion, and metal–carbon interactions [8–10]. Thus, it is important to the optimization of carbon supports in direct methanol fuel cell (DMFC) system.

Recently, there is Pt supported on commercial carbons including Vulcan SC-72, Black Pearls BP 2000, Ketjen Black, etc., which used for methanol oxidation reaction in direct methanol fuel cells [11]. And, some nanostructured carbon supports including carbon nanotubes [12,13], carbon nanofibers [14,15], carbon nanocages [16], and graphene-derived carbons [17], etc. are reported as a catalyst to improve CO tolerance in research fields. It is known that the electronic perturbations exerted by graphitic supports on Pt nanoparticles have improved CO tolerance. Also, mesoporous carbon (MC) used as catalyst support is another new area in DMFC catalysis [11,18].

Generally, the electrochemical reactions in the DMFC catalysis occur on the surface of the metal nanoparticle involving electron and proton transport, in which required an efficient three-phase reaction zone at nanoscale. Furthermore, the effective transport passage for liquid-phase reactants (CH3OH, H2O) and the gas-phase product (CO2) is important to active the DMFC catalyst. Thus, MC with a pore size range of 2–50 nm is believed to be a more promising catalyst support than micro- and macroporous carbons in terms of the dispersion and utilization of the metal catalysts [11]. Too many small micropores (<2 nm) in carbon supports deteriorate catalyst activity and durability, resulting from that the mass transport of reactants and product is unsuitable in these micropores. Meanwhile, the pore size of carbon supports is too large (>50 nm), the surface area will become small, and the electrical resistance will increase.

On the other hand, virgin MC has a tendency to aggregate spontaneously because of its very fine structure and high surface energy. Therefore, surface modification is an essential process for carbon materials. Increasing the quantity of carbon surface functional groups by surface modification without decreasing its surface area would increase the dispersion of metal nanoparticles [19–21]. The nanoparticulate fraction would be more active than
larger particles because their surface area would be maximized. Ideal catalysts are based on well-dispersed nanoparticles on carbon supports [22–24]. To the best of the authors’ knowledge, the effect of the surface modification of mesoporous carbon supports is not completely understood [25,26].

In this study, the size and loading of metal nanoparticles were examined by modifying the MC support for a Pt–Ru catalyst. The effects of chemical modification of the MC support on the preparation and electrochemical activities of the MC-supported Pt–Ru catalysts were investigated.

2. Experimental

2.1. Synthesis of mesoporous silica (SBA-15) and mesoporous carbon (MC)

The MC was synthesized using SBA-15 as the template and sucrose as the carbon source. SBA-15 was prepared using a reported method with P123 (PEO20PPO70PEO20, Tri-block copolymer, Sigma–Aldrich Co.) and TEOS (Tetraethyl orthosilicate, Sigma–Aldrich Co.) as the silica source [27]. The starting composition of SBA-15 was 10 g P123:0.01 mol TEOS:0.60 mol HCl:20 mol H2O. The mixture was stirred for 1 day at room temperature. The mixture was then placed in an oven for 24 h at 378 K. The product was filtered, washed three times with 50% ethanol–water solution, and calcined at 823 K.

The MC was prepared by impregnating the pores of the silica template with a sucrose solution followed by heat treatment, as described elsewhere [28]. SBA-15 (5 g) was added to a solution containing H2O (25 g), H2SO4 (0.7 g), and sucrose (6.25 g). The mixture was placed in a drying oven at 373 K for 6 h and then at 433 K for a further 6 h. After additional H2O (16 g), H2SO4 (0.45 g), and sucrose (4 g), the sample was treated again at 373 and 433 K. Carbonization was completed by pyrolysis at 1173 K under a nitrogen atmosphere. Finally, the sample was washed with 3 wt.% HF solution and ethanol with continuous stirring for 2 h to remove the silica template from the silica–carbon composite.

2.2. Surface modification of MC

The MC surface was modified by acid/base treatments to optimize its ability to disperse the active Pt–Ru nanoparticles. MC samples were treated at different pH, i.e. virgin MC (V-MC), neutral (0.2 N C6H5O), base (0.2 N KOH)-treated MC (N-MC), base (0.2 N KOH)-treated MC (B-MC), and acid (0.2 N H3PO4)-treated MC (A-MC), at 333 K and with constant stirring for 24 h. The chemically modified MC samples (M-MC) were filtered, washed until the water reached pH neutrality, and dried overnight at 383 K [29].

2.3. Preparation of carbon-supported Pt–Ru nanoparticles

The M-MC was dispersed in distilled water using an ultrasonicator. All the samples contained 20% catalyst by weight. Pt–Ru catalysts (0.25 g) with an atomic ratio of 1:1 were obtained by the chemical reduction of the metal precursors, H2PtCl6 and RuCl3, in the above suspension with constant mechanical stirring. Both HCHO and NaOH, as reducing agents, were then added slowly to the above solution and stirred for 5 h at 353 K. A constant flow of argon gas was used during the process to remove organic by-products. The Pt–Ru/M-MC catalysts were dried in a vacuum oven at 343 K for 12 h [30].

2.4. Characterization of the carbon supports and Pt–Ru catalysts

The carbon supports and Pt–Ru catalysts were characterized by X-ray diffraction (XRD, Rigaku, Model D/MAX 2200V/PC) using Cu Kα radiation with 40 kV and 20 mA. The carbon supports were analyzed by X-ray photoelectron spectroscopy (XPS, VG ESCALAB MKII), using a Mg Kα X-ray source at a base pressure of 10−8–10−9 Torr. The N2 adsorption–desorption isotherms were measured at 77 K using a Belsorp MAX. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of approximately 0.99. The pore size distribution (PSD) curves were analyzed using the Barrett–Joyner–Halenda (BJH) method. The position of the maximum of the PSD curves was considered the mean pore diameter (Dp). The mean pore diameter was calculated using

\[
D_p = \frac{4V_{\text{total}} \times 1000}{S_{\text{BET}}}
\]

where Vtotal is the total pore volume and S_{BET} is the specific surface area.

The Pt–Ru loading was determined by inductively coupled plasma–mass spectrometry (ICP-MS, ELAN 6100). Transmission electron microscopy (TEM, A JEM 2100F) was used to observe the dispersion characteristics of the Pt–Ru catalysts at 200 kV. Also, the average particle size and particle size distribution were obtained from a few randomly chosen areas in the TEM image containing approximately 200 nanoparticles each.

2.5. Electrochemical activity of the Pt–Ru catalysts

Cyclic voltammetry (CV, PGSTAT 30, Eco Chemie, Netherlands) of the Pt–Ru/M-MC catalysts was performed using a three-electrode cell system, with Ag/AgCl as the reference electrode, Pt wire as the counter electrode, and a carbon paste electrode covered with a layer of Pt–Ru/M-MC catalyst as the working electrode. The electrolytes were 0.5 M H2SO4 and 1.0 M CH3OH + 0.5 M H2SO4.

3. Results and discussion

3.1. Structural characterization of carbon supports

Fig. 1 shows the low angle XRD patterns of the MC before and after surface modification. Fig. 1e shows the low angle XRD patterns of the calcined SBA-15, which exhibited three characteristic...
peaks, (100), (110), and (200), associated with p6mm hexagonal symmetry. In addition, the V-MC showed three peaks at small angles, indicating that the sample had an ordered mesoporous structure. The surface-modified samples showed similar low angle XRD patterns, indicating that the p6mm structure had been maintained after chemical modification. The A-MC sample had the smallest peak intensity suggesting a decrease in structural order. Therefore, A-MC exhibited the most decomposed MC structure, leading to a decrease in structural order [31].

Fig. 2 shows the N₂ adsorption–desorption isotherms and corresponding pore size distributions of the surface-modified carbon supports. The curves for the carbon supports showed type IV isotherms, according to the IUPAC classification, as well as a hysteresis loop due to capillary condensation in the mesopores at relative pressures >0.4, which indicated that all the carbon supports had a mesoporous structure [32].

As shown in Fig. 2a, the V-MC, which was prepared without surface modification, showed the highest adsorption–desorption capacity for N₂, indicating the highest mesoporosity. On the other hand, A-MC, which had been prepared using 0.2 N H₃PO₄ for surface modification, showed the lowest adsorption–desorption capacity for N₂. The level of N₂ adsorption to the carbon supports decreased with the decreasing pH in the surface treatment. In addition, the mesopore sizes, determined from the maximum pore size distribution curves of the carbon supports, decreased with the decreasing pH in the surface treatment of the carbon supports, as shown in Fig. 2b. In addition, the specific surface area and total pore volume of the carbon supports decreased with decreasing pH in the surface treatment, as listed in Table 1.

The specific surface area of A-MC showed prominent changes compared to V-MC. This suggests that a strong acid–base reaction occurred between the originally basic carbon surface and the acidic chemical solution. This can result in micropore and mesopore degradation or blockage. Acidic modification is believed to cause an increase in V-MC aggregation, resulting in an increase in crystallite size and concentration of crystalline boundaries as the hexagonal mesopore structure of V-MC. After chemical modification, B-MC and N-MC showed slightly higher specific surface areas than A-MC. Table 1 also shows that the mean pore diameter of the carbon supports decreased with decreasing pH [33,34].

Fig. 3 shows an XPS survey of the carbon supports. All the supports showed carbon and oxygen peaks at binding energies of 284.5 (C₁s) and 530.2 eV (O₁s), respectively, indicating that the carbon supports consisted solely of carbon and oxygen. A-MC exhibited an enhanced peak intensity at 530.2 eV due to the development of oxidized groups from the acid modification of the carbon surface. The intensity of the 530.2 eV peak in B-MC increased due to oxidation of the carbon surface by oxygen in the basic solution. On the other hand, the peak intensity of the characteristic 530.2 eV peak was lower in N-MC. Overall, the oxygen-functional groups on the carbon surface were effectively changed by acidic or basic chemical modification [35,36].

### Table 1: Textural properties of the prepared carbon supports.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_{BET}^a (m²/g)</th>
<th>V_{total}^b (cm³/g)</th>
<th>V_{meso}^c (cm³/g)</th>
<th>D_{p}^d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-MC</td>
<td>1039</td>
<td>1.31</td>
<td>1.25</td>
<td>5.04</td>
</tr>
<tr>
<td>B-MC</td>
<td>998</td>
<td>1.25</td>
<td>1.17</td>
<td>5.01</td>
</tr>
<tr>
<td>N-MC</td>
<td>970</td>
<td>1.21</td>
<td>1.13</td>
<td>4.99</td>
</tr>
<tr>
<td>A-MC</td>
<td>843</td>
<td>1.05</td>
<td>0.92</td>
<td>4.98</td>
</tr>
</tbody>
</table>

| a | S_{BET}: Specific surface area calculated using the BET equation at a relative pressure range of 0.2–0.35. |
| b | V_{total}: Total pore volume was estimated at the relative pressure P/P₀ = 0.990. |
| c | V_{meso}: Mesopore volume determined by subtracting the micropore volume from the total pore volume. |
| d | D_p: Average pore diameter. |

3.2. Structural characterizations of the Pt–Ru catalysts

Fig. 4 shows the high angle XRD patterns of the Pt–Ru/M-MC catalysts. All the catalysts showed the typical characteristics of a
crystalline Pt face-centered-cubic (fcc) structure. The XRD peaks were indexed to the (111), (200), (220), and (300) planes at 40°, 46°, 67°, and 83° 2θ, respectively. The high angle XRD patterns confirmed that the Pt nanoparticles had been impregnated into the carbon supports. On the other hand, the characteristic peaks for Ru were not observed clearly in the high angle XRD patterns. This was probably because the Ru nanoparticle phases were not fully developed, and their particle sizes were relatively small in the Pt–Ru/M-MC catalysts. In addition, the XRD patterns of the Pt–Ru/M-MC catalysts showed a single diffraction peak (39.9° 2θ), corresponding to pure Pt with a slight shift toward higher values. The angle shifts of the Pt peaks revealed a binary formation between the Pt and the Ru due to a combination of the base metals in the fcc structure of Pt. In comparison, the Pt–Ru/A-MC catalyst showed a small peak for metal deposition, which indicates that the metal was not deposited effectively on the carbon surface compared to B-MC and N-MC. This was attributed to an incomplete Pt–Ru reduction reaction due to the highly acidic characteristics of the MC surface.

The mean Pt nanoparticle sizes were calculated from the high angle XRD data using the Scherrer equation (2) [38,39].

\[
L_c = \frac{K \lambda}{\beta \cos \theta}
\]  (2)

where \(K\) is the Scherrer constant (0.89), \(\lambda\) is the wavelength of X-ray radiation (0.154 for Cu Kα), \(\beta\) is the half-height width of the (2 2 0) peak, and \(\theta\) is the angle in radians of the peak maximum.

Table 2 lists the crystallite size of the Pt–Ru/M-MC catalysts. In the case of the Pt–Ru/B-MC catalyst, the broadness of the peak increased, indicating a decrease in Pt nanoparticle size. In the case of the Pt–Ru/V-MC catalyst, the mean Pt size was 4.1 nm, which is typical for Pt nanoparticles (3–5 nm). The nanoparticle size of the Pt–Ru catalysts decreased from 4.1 to 3.3 nm with increasing pH, which was attributed to chemical modification of the surface. With the Pt–Ru/B-MC catalyst, the mean nanoparticle size decreased to 3.3 nm. Basic conditions were favored for the preparation of the Pt nanoparticle-incorporated carbon supports because the Pt precursor needed to be reduced with a reducing agent [40,41]. In addition, the base-modified MC surface provided a secure deposition area for Pt–Ru nanoparticles due to the removal of weak or unstable boundary layers from the surfaces of the carbon supports. Therefore, Pt–Ru nanoparticles on B-MC were well dispersed and smaller than those on V-MC, and the Pt–Ru nanoparticle size was related to the modified surface characteristics of the carbon supports. Table 2 lists the Pt–Ru content in the Pt–Ru catalysts as determined by ICP-MS. The Pt–Ru/B-MC catalyst showed the highest values, 15.8 wt.% (Pt) and 6.7 wt.% (Ru), whereas the Pt–Ru/V-MC catalyst exhibited the lowest values, 9.4 wt.% (Pt) and 4.3 wt.% (Ru). These results suggested that the Pt and Ru loading on the surface-modified MC increased with increasing pH.

Fig. 5 shows TEM images of the Pt–Ru/M-MC catalysts. The TEM images provided not only the Pt–Ru nanoparticle sizes but also the morphologies of the catalysts. The dispersion of the Pt–Ru nanoparticles on the carbon supports was uniform, which is particularly important for electrocatalysts [42,43]. With increasing pH, Pt–Ru nanoparticles were deposited on the carbon supports. In particular, the Pt–Ru/V-MC catalyst showed uniformly deposited Pt–Ru as well as the highest loading and smallest particle size. On the other hand, for the Pt–Ru/A-MC and Pt–Ru/N-MC catalysts, the Pt–Ru deposits were more aggregated and less dispersed than the Pt–Ru/B-MC catalyst.

### 3.3. Electrochemical activities of the Pt–Ru catalysts

Fig. 6 shows the CV curves of the Pt–Ru/M-MC catalysts in 0.5 M H2SO4. In the absence of methanol, the typical surface processes for polycrystalline Pt, such as the adsorption/desorption of hydrogen, and to a lesser extent, oxide formation and reduction, can be observed by CV of the electrode prepared with the Pt/C composite. The CV traces were stable even after scanning several cycles. The electrochemical activities of the Pt–Ru/M-MC catalysts increased with increasing pH, suggesting that the chemically modified carbon supports had higher activity than V-MC.

Normally, it is well known that the oxygen-functional groups on the carbon catalyst support have positive effects on the kinetics or stability of the methanol oxidation reaction as well as the well-described effect of facilitating high dispersion of the catalytic nanoparticles [44,45]. In addition, the presence of oxygen-functional groups increases the hydrophilicity of carbon, which increases the dispersion of the Pt nanoparticles increase, resulting in the more specific surface to mediate methanol oxidation reaction. The metal–carbon interaction is improved by the oxygen-functional groups, because the stability of carbon catalyst supports is increased by hinderance of the sintering of the metallic nanoparticles [46]. The oxygen-functional groups on carbon catalyst supports can also promote electro-oxidation by providing –OH groups in fuel cell system [47].

In particular, the Pt–Ru/B-MC catalyst had the highest electrochemical activity among the catalysts examined, because the loading and dispersion of the Pt–Ru nanoparticles on the carbon surfaces were improved.
supports increased with decreasing nanoparticle size, leading to an improvement in the electrochemical activity of the Pt–Ru/M-MC catalysts. Therefore, for the Pt–Ru/A-MC and Pt–Ru/N-MC catalysts, the Pt–Ru nanoparticle sizes increased, and the loading decreased compared to the Pt–Ru/B-MC catalyst, as shown in Table 2. This was attributed to the changes in the surface functional groups and the lower specific surface areas of the V-MC and N-MC catalysts due to the high level of aggregation [48,49].

The electrochemical surface area (ECSA) of Pt was calculated from the hydrogen desorption peak areas in the CV curves using the following equation [50]:

$$\text{ECSA} = \frac{Q}{0.22 \text{ mC/cm}^2}$$

where $Q$ is the electric charge for hydrogen desorption and $0.22 \text{ mC/cm}^2$ is the hydrogen adsorption constant for polycrystalline Pt.

The ECSA of these catalysts was calculated, as shown in Table 3. The chemical surface areas (CSA) of the Pt–Ru catalysts were also calculated using the following equation [50]:

$$\text{CSA} = \frac{6 \times 10^6}{\rho \times d}$$

where $d$ is the mean Pt particle diameter in Å (from TEM results) and $\rho$ is the density of Pt metal (21.4 g/cm$^3$). The utilization efficiency was calculated using the following equation [50]:

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$Q$ (mC)</th>
<th>ECSA (m$^2$/g)</th>
<th>CSA (m$^2$/g)</th>
<th>Pt utilization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt–Ru/V-MC</td>
<td>0.09</td>
<td>16.1</td>
<td>55.1</td>
<td>29.2</td>
</tr>
<tr>
<td>Pt–Ru/B-MC</td>
<td>0.34</td>
<td>60.7</td>
<td>73.5</td>
<td>82.6</td>
</tr>
<tr>
<td>Pt–Ru/N-MC</td>
<td>0.29</td>
<td>51.8</td>
<td>72.2</td>
<td>71.7</td>
</tr>
<tr>
<td>Pt–Ru/A-MC</td>
<td>0.26</td>
<td>46.5</td>
<td>71.4</td>
<td>65.1</td>
</tr>
</tbody>
</table>

Fig. 5. TEM images and particle size distributions of the Pt–Ru catalysts: (a) Pt–Ru/V-MC, (b) Pt–Ru/B-MC, (c) Pt–Ru/N-MC, and (d) Pt–Ru/A-MC.

Fig. 6. Cyclic voltammograms of the Pt–Ru catalysts in 0.5 M H$_2$SO$_4$ at a 20 mV/s scan rate.
Pt utilization efficiency = $\frac{ECSA}{CSA}$

Generally, catalysts with smaller particle sizes have higher ECSA values than those with larger particle sizes and distributions. Fig. 7 shows the CV data for the Pt–Ru/M-MC catalysts in 0.5 M H$_2$SO$_4$ containing 1.0 M CH$_3$OH. All the catalysts deposited on the chemically modified MCs exhibited, for the forward scan, a rather definite oxidation peak at approximately 700–810 mV vs. Ag/AgCl. The Pt–Ru/B-MC and Pt–Ru/N-MC catalysts showed a higher current density for the anodic peak at 0.83 and 0.76 mA, respectively, as well as a more definite peak shape compared to the Pt–Ru/V-MC catalyst. This indicated that the electrochemical activity was enhanced when the MC was modified by basic or neutral agents. On the other hand, the Pt–Ru/A-MC catalyst showed a lower current density, meaning that the electrochemical activity had decayed. The electrochemical activity increased with increasing pH due to the smaller nanoparticle size, leading to an improvement in Pt–Ru nanoparticle dispersibility. The Pt–Ru/B-MC catalyst showed the highest current density of the anodic peak, indicating the highest electrochemical activity among the Pt–Ru/M-MC catalysts examined. This was evidence that the Pt–Ru/B-MC catalyst would have high activity toward methanol oxidation. The smaller nanoparticles and high loading led to a larger available active surface for the Pt–Ru/M-MC catalysts, resulting in electrochemical activity for methanol oxidation. Therefore, the superior electrocatalytic performance of the Pt–Ru/M-MC catalyst can be improved significantly by chemical modification of the carbon supports, due to the high specific surface area and high concentration of surface functional groups on the carbon supports [20,43,48–51]. Overall, the electrochemical activity was best on the base-modified MC-supported Pt–Ru nanoparticles.

4. Conclusion

In this work, Pt–Ru catalyst support was prepared by a conventional templating method. And the chemical modification was performed at different pH, to investigate the electrochemical activities of the mesoporous carbon (MC)-supported Pt–Ru catalysts for fuel cells. From the results, the electrochemical activities of Pt–Ru/M-MC catalysts enhanced with increasing pH. In particular, the basic treatment of MC (Pt–Ru/M-B) was revealed as the optimum to prepare the best electrochemical performance, resulting from higher loading and dispersion as well as smaller size of Pt–Ru nanoparticles. Therefore, for the exploration for a new generation of DMFC application in the near future, some directions on the evolution of the innovative and excellent carbon catalyst supports are suggested: (i) some new carbon materials including nano- and meso-structure have been demonstrated to be feasible, (ii) the effective surface modification of carbon supports, (iii) advanced loading methods for metallic nanoparticles, which could bring about a breakthrough in fuel cell system.

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