

Short communication

Synthesis of porous carbons having surface functional groups and their application to direct-methanol fuel cells

Jeong-Bae Lee^{a,b}, Yong-Ki Park^a, O-Bong Yang^b, Yongku Kang^a, Ki-Won Jun^a, Yun-Jo Lee^a, Hee Young Kim^a, Kew-Ho Lee^a, Won Choon Choi^{a,*}

^a Advanced Chemical Technology Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong, Daejeon, Republic of Korea

^b Division of Chemical Engineering and Technology, Chonbuk National University, Jeonju, Jeonbuk 561-756, Republic of Korea

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Abstract

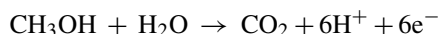
Pitch-based porous carbons having $-\text{SO}_3\text{H}$ groups on their surfaces were synthesized by carbonization of mesophase pitch and then sulfonation of the resulting compounds. As-synthesized carbons were characterized by BET surface area analysis, pore volume analysis and XRD. The concentration of $-\text{SO}_3\text{H}$ groups present on the carbons was measured by neutralization titration. PtRu nano-clusters were supported on the pitch-based porous carbons, and these electrocatalysts were used as anodic materials in a DMFC. Membrane-electrode assemblies prepared using these electrode materials showed an improved power density compared with a commercial 60% PtRu/Vulcan XC-72. This performance is ascribed to the higher ionic conductivity of the anode layer and the well exposed catalytic active sites.

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1. Introduction

Direct-methanol fuel cells (DMFC) operating below 100 °C are emerging as an attractive option for electrochemical power [1] because of their many advantages including high-energy density, the ease of handling a liquid and the low operating temperature. On the anode side of a DMFC, aqueous methanol is electro-oxidized to produce CO_2 and electrical current:



The oxidation of methanol is catalyzed by carbon-supported PtRu particles and an increased performance of the membrane/electrode assembly (MEA) can be obtained by preparing them as a thin layer on carbon. In order to use the carbon as a support material for the electrocatalyst, many characteristics such as surface area, pore size distribution, morphology and surface properties need to be considered. Firstly, Pt clusters, supported on porous carbon having a high surface area, are crucial for

preparing an electrode for use in fuel cell systems, because of the higher activity resulting from higher Pt dispersion. However, as the high porosity of carbon results in a thick electrode with increased resistance of the MEA, the surface area and pore size distribution of a carbon-supported electrocatalyst should be optimized. Secondly, the electrocatalyst is coated onto a gas diffusion layer using Nafion or Teflon as a binder. Therefore, the binder can plug the micro or meso-pores of the carbon-supported electrocatalyst and reduce the efficiency of noble metals such as platinum. Thirdly, the surface properties of the carbon should be considered in the design of carbon-supported electrocatalysts for high performance. In particular, the hydrophilic and hydrophobic nature, proton spillover, electric conductivity and adsorption/absorption of CH_3OH and H_2O are very important surface properties.

Much attention has been focused on the synthesis of ordered graphitic carbons using arc discharge [2,3], chemical vapor deposition [4] and template synthesis techniques [5] for fuel cell applications. It was reported that the catalyst support of a DMFC electrode, using hollow graphitic carbon synthesized by a solid-phase synthetic procedure, had a high crystallinity, resulting in the high electrical conductivity [6]. Bimodal porous

* Corresponding author. Tel.: +82 42 860 7626; fax: +82 42 860 7590.
E-mail address: mrchoi@kriect.re.kr (W.C. Choi).

carbon having uniform macro-pores was also used as an excellent support for the electrode catalyst because of the facile diffusion of fuels and products through these pores [7]. Based on these results, it is suggested that a high graphitic property and well-designed pore structure are most desirable. Further physiochemical properties of these carbons should be improved for enhanced utilization of the precious metal catalyst.

Current densities in fuel cells do not scale with their intrinsic surface areas and metal loadings. This problem is compounded by the use of polymeric binders for making the carbon-supported PtRu powders into the desired electrode geometry [8]. This hindrance mainly results from the ineffective mass transfer and diffusion in a thick electrode layer that has numerous interfaces between fine nano-particles and polymeric binders. Taking these drawbacks into consideration, if the weight ratio of the polymeric binder to catalyst is minimized, the catalyst utilization and specific power density can be increased dramatically. However, since an important role of a polymeric binder such as Nafion is as a proton conductor in the electrocatalyst layers of DMFC, the reduction of ionic conductivity should also be considered when reducing the Nafion loading. In this study, we synthesized pitch-based porous carbon having surface SO_3H groups, which can act as proton carriers, and demonstrated that it can successfully be used as a catalyst support for DMFC electrodes.

2. Experimental

Pitch-based porous carbon (PPC) was prepared by using a synthetic Mitsubishi mesophase pitch AR (H/C ratio 0.58–0.64 and softening point 275°C). The pelletized mesophase pitch was dispersed in benzene (pitch:benzene = 1:5.7, w/w) for 10 h, mixed with calcined silica (200–425 mesh, 150 \AA) (pitch:silica = 1:0.94, w/w) in a round bottomed flask, and then stirred at about 80°C to evaporate the benzene. The resulting mixture was carbonized at 700, 800 and 900°C for 3 h under a nitrogen atmosphere and the silica was removed with 25% HF solution. The obtained carbon slurry was filtered, washed thoroughly with DI water, and then dried at 100°C . For sulfonation of the as-synthesized PPC, it was heated in concentrated sulfuric acid at 250°C for 15 h. The material was then washed repeatedly using boiling DI water until the filtrate was free from sulfate. The obtained carbons are denoted as PPC-700S, -800S and -900S with the numerals representing the carbonization temperature. Neutralization titration was performed to measure the amount of SO_3H attached to the carbons [9].

In order to prepare a thin layer of catalyst for measuring proton conductivity, an ink-like catalyst slurry containing Nafion ionomer was coated onto a polyimide film and then it was hot-pressed at 120°C and 2400 psi. This catalyst layer over a polyimide film was suspended in DI water for 12 h. The proton conductivity was measured by means of ac impedance spectroscopy over a frequency range of 100 Hz–100 kHz using a system based on a Gain-Phase Analyser 4194 (Hewlett-Packard). The catalyst thin layer was placed in the middle of a specially designed cell (see Fig. 1) and the pro-

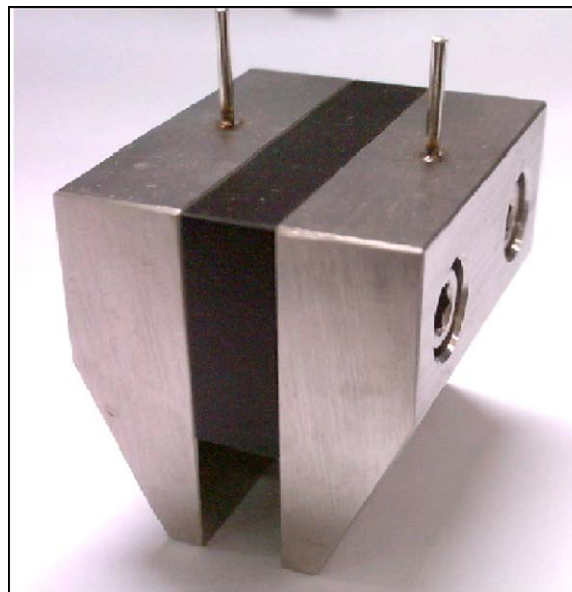


Fig. 1. The two-electrode cell for measuring the proton conductivity.

ton conductivity (σ) of the sample in the transverse direction was calculated from the impedance data using the following equation:

$$\sigma = \frac{L}{RS}$$

where L , R and S denote the distance between electrodes, the resistance of the membrane and the cross-section of the membrane, respectively.

Carbon-supported PtRu catalysts were synthesized at room temperature by using NaBH_4 as a reducing agent. Equimolar quantities of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ were dissolved in DI water and then the carbon powder was added to this solution. The NaBH_4 solution ($\text{NaBH}_4/\text{metal}$ molar ratio = 10) was quickly poured into this mixture and vigorously stirred for 3 h. The resulting slurry was filtered, washed thoroughly with DI water and then dried in a vacuum oven. The metal loading on carbon was determined to be 60 wt%.

DMFC current–voltage curves were obtained using the synthesized carbon-supported PtRu as an anode catalyst and Pt black (Johnson Matthey, Hispec 1000) as a cathode catalyst. To make the membrane–electrode assembly (MEA), catalyst inks containing the appropriate weight percent of Nafion ionomer solution were sprayed directly on pre-treated Nafion 115 electrolyte membrane and then dried in a vacuum oven. Before sandwiching the MEA between anode and cathode, the graphite blocks with 4 cm^2 cross-sectional area were pressed at 120°C and 1500 psi for 3 min. All anode and cathode precious metal loadings were about 3 and 5 mg cm^{-2} , respectively. Methanol (1 M , $2\text{ cm}^3\text{ min}^{-1}$, 0 psig) and un-heated oxygen (500 ml min^{-1} , 0 psig) were delivered to the anode and cathode compartments, respectively.

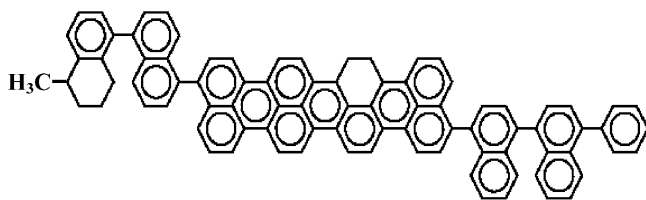


Fig. 2. The structure of mesophase pitch.

3. Results and discussion

3.1. Analysis of pitch-based porous carbon

Sucrose, phenolic resin, furfuryl alcohol and resorcinol are generally used as carbon precursors in the synthesis of mesoporous carbons using removable template [10–13]. Even though the resulting carbons exhibit graphitic properties, the amorphous domain is much larger than the graphitic one, which results from the low carbonization temperature (700–1000 °C). However, if the mesophase pitch that already contains graphitic building blocks (see Fig. 2) is used as a carbon source, it may be possible to synthesize a graphite-like carbon even at a low carbonization temperature, because the poly aromatic carbons are enlarged during the pyrolysis process. As shown in Fig. 3, the XRD patterns of the prepared PPCs demonstrate that these carbon materials are well-graphitized with (002) *d*-spacing [14].

The acid (–SO₃H group) densities of the synthesized carbons and a commercial Vulcan XC carbon are summarized in Table 1. The results show negligible amount of –SO₃H groups on PPC-900, which is the pitch-based carbon before the sulfonation procedure, and on Vulcan XC-72, but 3.03–4.8 mmol g^{–1} on the PPC-700S, -800S and -900S. The BET surface area and pore volumes of these samples (see Table 1) indicate that PPC-700S, -800S and -900S are graphitic porous carbons having an effective density of the acid groups. During the preparation of carbon, if the rate of dehydroxylation is faster than that of carbonization then it will result in porous materials [15,16]. A suitable choice

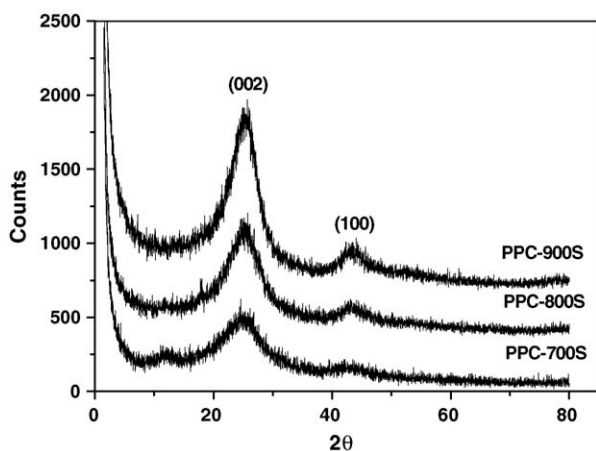


Fig. 3. XRD diffractograms of PPCs calcined at various temperatures (700, 800, 900 °C).

Table 1

Acid (–SO₃H group) densities, BET surface area and micropore volumes of the synthesized pitch-based porous carbons and Vulcan XC-72

	BET surface area (m ² g ^{–1})	Micropore volume (cm ³ g ^{–1})	Acid density (mmol g ^{–1})
PPC-700S	233.6424	0.0319	4.80
PPC-800S	210.6750	0.0136	3.13
PPC-900S	191.7668	0.0321	3.03
PPC-900 ^a	–	–	0
Vulcan XC-72	234.9517	0.0300	0

^a Pitch-based carbon before sulfonation procedure.

of the carbon source and the conditions of carbonization are important in preparing porous carbons.

3.2. Ionic conductivity of carbon and Nafion composite layer

Inclusion of a Nafion binder with comparatively high ionic conductivity can improve the electrode performance significantly. However, as the presence of this material leads to an extended distribution of complex phase boundaries in the electrode layer, the optimum composition of binder and catalyst powder is important [17,18]. The Ionic conductivities of the various thin carbon (Vulcan XC-72)–Nafion composite layers are shown in Fig. 4. As expected, the ionic conductivities depend significantly on the weight percentage of the samples, and therefore it is necessary to minimize ohmic losses and mass transport overpotentials in the electrode. Very low Nafion results in poor contact of the electrolyte with the catalyst, and hence shows poor electrode performance. However, too high a concentration of the Nafion ionomer causes reduction in electrode performance due to blocking of the catalyst sites and the electrode pores, as well as reduction of gas permeability and an increased mass transfer overpotential [19].

The ionic conductivities of the catalyst (PtRu/PPC-700S, -800S and -900S) layers with 10 and 33% Nafion contents are shown in Fig. 5. It can be seen that the ionic conductivity increases as the Nafion percentage increases from 10 to 33%

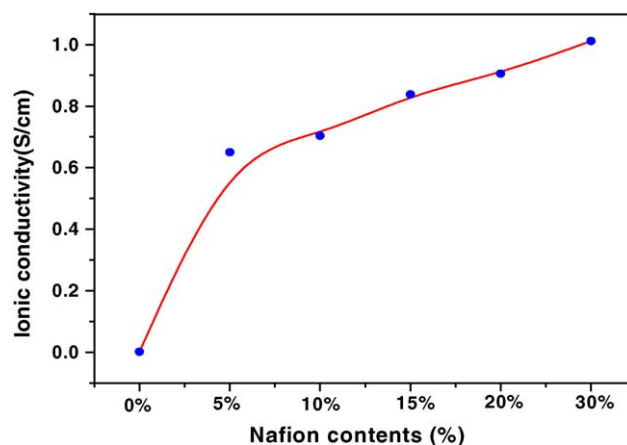


Fig. 4. The ionic conductivity of Vulcan XC-72 sprayed on the polyimide film compared with Nafion content.

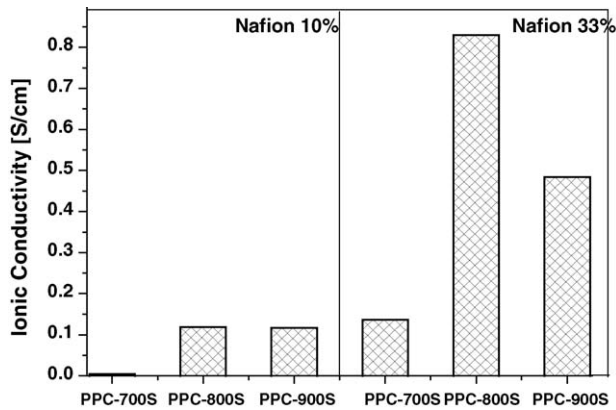


Fig. 5. The ionic conductivity of various carbons (PPC-700S, -800S, -900S) sprayed on the polyimide film at the 10 and 33% Nafion content.

and the highest value is obtained when 33% Nafion is present in the PtRu/PPC-800S catalyst layer. Considering that the acid density of the as-synthesized PPC-700S is higher than others, it is interesting to note the highest ionic conductivity for PtRu/PPC-800S. It should be mentioned here that the ion-path length, which results from micropores of carbon support, is one of the main factors in decreasing the ionic conductivity in the electrode layer. Development of the pore structure of carbon is sensitive to the synthesizing conditions. PPC-800S carbon had a smaller micropore volume ($0.0136 \text{ cm}^3 \text{ g}^{-1}$) than PPC-700S and -900S (see Table 1).

3.3. Membrane–electrode assembly performance in DMFC

In order to evaluate the MEA performance in which PtRu/PPCs are used as the anode catalysts, MEA was prepared by using commercial 60% PtRu/Vulcan XC-72 (E-Tek, atomic ratio of Pt/Ru = 1). The variation of current density and maximum power density with Nafion binder content in the anode and the cell temperature are shown in Fig. 6. The power density increases as the Nafion binder content is raised from 10 to 33% at the cell temperature of 30 °C. The lower power density

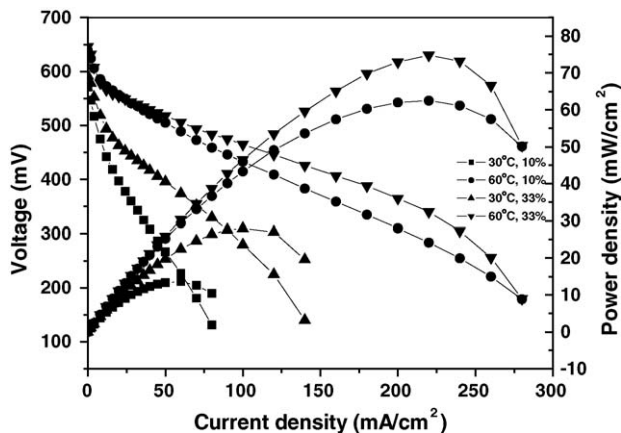
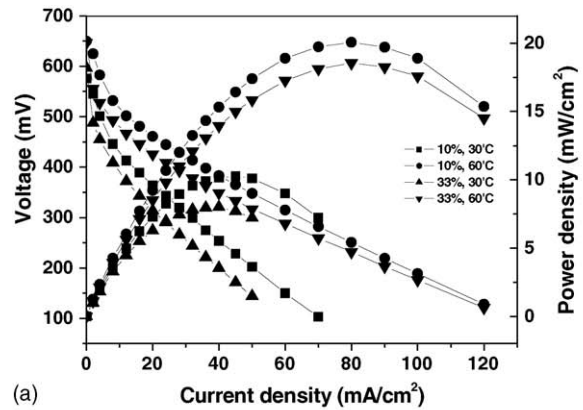
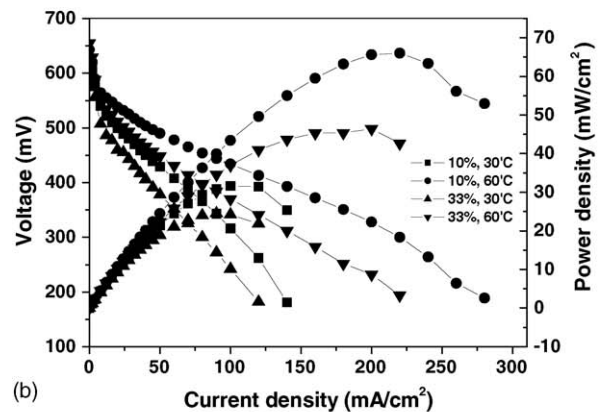


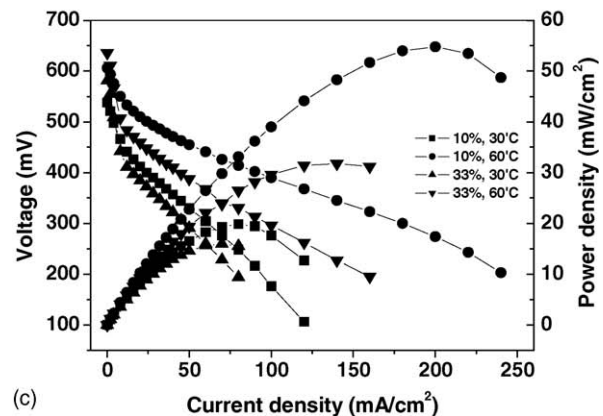
Fig. 6. The comparison of the current density and power density curves for a direct-methanol fuel cell using a commercial 60% PtRu/Vulcan XC-72. The Nafion contents are 10% (■, ●) and 33% (▲, ▼) at 30, 60 °C, respectively.



(a)



(b)



(c)

Fig. 7. The comparison of the current density and power density curves for a direct-methanol fuel cell using a (a) 60% PtRu/PPC-700S, (b) 60% PtRu/PPC-800S, (c) 60% PtRu/PPC-900S with Nafion115. The Nafion contents are 10% (■, ●) and 33% (▲, ▼) at 30, 60 °C, respectively.

at a low Nafion content (10%) may result from proton transfer discontinuity in the anode layer [20]. A similar tendency is also observed at the cell temperature of 60 °C.

Fig. 7 shows the typical variation of the current and power density of MEAs with PtRu/PPC-700S, -800S and -900S electrocatalysts as the anodic materials. Notably, the power density of each MEA fabricated with an anode layer having Nafion binder concentration of 10% is higher than that fabricated with anode layer having Nafion binder concentration of 33%. Compared with the trend of MEA prepared using commercial 60% PtRu/Vulcan XC-72 (Fig. 6), it is an opposite result. As

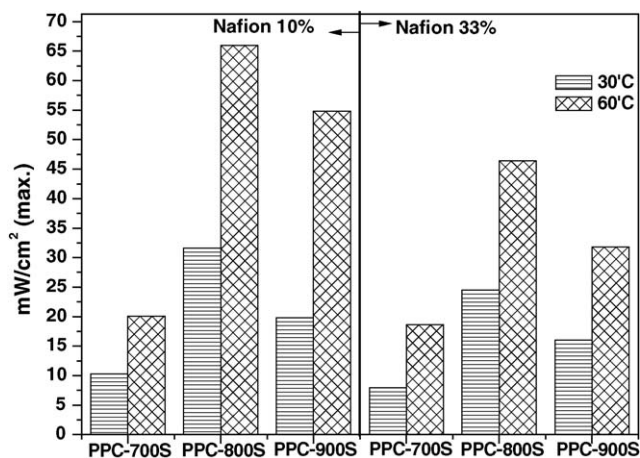


Fig. 8. The maximum power density values obtained for 60% PtRu/PPCs with 10 and 33% nafion content at 30 and 60 °C.

mentioned in the previous section, PPC-700S, -800S and -900S are having $-\text{SO}_3\text{H}$ functional groups which can act as proton conductors. It means that the optimum Nafion content of the anode layer in which PtRu/PPCs are used can be reduced, compared to Vulcan XC-72 carbon having no surface functional groups. At a given precious metal loading, increasing the weight percent of ionomer can increase the anode catalyst layer thickness and hence result in increased internal resistance of the MEA. Further, the decrease in performance at the higher Nafion content may be due to blocking of the catalyst active sites, reducing gas permeability and increasing mass transfer polarization.

The variation of maximum power density with PtRu/PPC-700S, -800S and -900S at the anode is shown in Fig. 8. PtRu/PPC-800S catalyst shows higher power density than those of PtRu/PPC-700S and -900S. Considering the ionic conductivity of PPC-800S with those of PPC-700S and -900S (Fig. 5), the higher power density of PtRu/PPC-800S may result from the higher ionic conductivity of the anode layer.

4. Conclusion

PtRu nano-particles supported on pitch-based porous carbons having surface $-\text{SO}_3\text{H}$ groups were examined for potential DMFC anode catalyst materials. Analysis of the material showed that PPCs were well-graphitized with (0 0 2) *d*-spacing with acid densities of 3.03–4.8 mmol g^{-1} of SO_3H , and a BET surface area of 191–233 $\text{m}^2 \text{g}^{-1}$. Since the acid groups on the carbon support carry protons, the required Nafion binder concentration

in the electrode layer of the MEA can be reduced. From a comparison of the MEA performance with different anode catalysts (PtRu/PPC-700S, -800S and -900S) and Nafion binder concentrations (10 and 33%), the DMFC with the 60% PtRu/PPC-800S and a Nafion binder concentration of 10% produced the highest power density of 66 mW cm^{-2} at 0.3 V and 60 °C. Even though this power density output was not significantly improved compared to the performance of an MEA in which a commercial anode catalyst was used, the results support that the approach of synthesising PPCs with $-\text{SO}_3\text{H}$ functional group which is a very efficient way of increasing precious catalyst utilization and gas permeability, and decreasing the mass transfer polarization.

Acknowledgment

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