Nanoshell-Containing Carbon Cathode Catalyst for Proton Exchange Membrane Fuel Cell from Herbaceous Plants Lignin

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ABSTRACT

Nanoshell-containing carbon (NSCC) is one of the Pt-surrogate catalysts for proton exchange membrane fuel cell (PEMFC) invented by us to promote oxygen reduction reaction (ORR), the cathode reaction of the cell. In the present study, we selected one of renewable resources, lignin from herbaceous plants as the carbon precursor for NSCC. The lignin was admixed with cobalt phthalocyanine (CoPc), the nanoshell (NS) forming catalyst, and then carbonized at 1000°C. Transmission electron microscopy and X-ray diffraction studies confirmed the formation of NS structure. The ORR activity of the prepared NSCC increased with the amount of CoPc, and the activity of lignin-based NSCC was higher than that of phenol-formaldehyde resin-based NSCC with the same amount of CoPc added. Surface analysis by X-ray photoelectron spectroscopy revealed no metal species on the NSCC but higher N/C ratio for the lignin-based NSCC by two folds. This study shows the possibility of lignin as a precursor of NSCC cathode catalyst for PEMFC.

Keywords: Proton Exchange Membrane Fuel Cell; Oxygen Reduction Reaction; Lignin; Nanoshell-Containing Carbon

1. Introduction

The proton exchange membrane fuel cell (PEMFC) is one of the most promising technologies, however, the high cost of platinum used to catalyze the cathode oxygen reduction reaction (ORR) restricts the commercialization of PEMFCs. To solve the problem, the authors developed electrochemically active carbon materials, named nanoshell-containing carbon (NSCC). Nanoshell (NS) is a type of nanocarbon, whose structure is hollow spherical shape with a diameter of 20 - 50 nm by stacking of hexagonal carbon layers. We have prepared NSCCs using synthetic polymer based materials such as furan resin [1,2], oxine-formaldehyde resin [3], furfuryl alcohol [4-6] and phenol-formaldehyde resin [7,8]. In the reports we have mentioned that NS structure and nitrogen played important roles to improve ORR activities of carbon materials.

Another challenging topic in material and ecological science is to convert plant-based materials to highly value added materials. Lignin (LG) is one of the most abundant organic compounds on Earth exceeded only by cellulose. It is a main component of woods and herbaceous plants and has unique properties. Most of LG is consumed as fuel, however, LG is used as raw materials for several chemicals, such as vanillin, DMSO, ethanol, xylitol sugar and humic acid. As LG is a sustainable material, researches to use LG in wide area have been conducted, such as natural antioxidants [9-11], adherent [12], waste water treatment [13,14] hydrogen electrosorption [15], and bipolar plates [16]. However, there are no reports to use LG as a source in the production of NSCC or other types of catalysts for PEMFC. LG seems to have some advantages for the use of cathode catalysts in the following points:

1) Contains much aromatic hydrocarbon;
2) Contains some nitrogen [17].

Using LG as a precursor of carbon materials, LG was mixed with cobalt phthalocyanine (CoPc) and characterization of the materials were carried out. Our interests were:

1) Whether LG forms nanoshell structure or not in the presence of CoPc.
2) Whether carbon materials prepared from LG show high ORR activity or not.

2. Experimental

2.1. Sample Preparation

Two ways were used to mix carbon precursor with CoPc: mixing by ball milling in solid state and mixing in solution state for LG and phenol-formaldehyde resin, respectively.

2.1.1. Lignin-Based Samples

LG separated from herbaceous plants by alkaline delignification and commercialized under the name of Granit Lignin Powder, Protobind 2000 (Pb2000) was provided by Granit SA, Switzerland. Elemental composition of the material is presented in Table 1. As shown in Table 1, Pb2000 contained some metals, phosphorus and nitrogen. To remove the metals, 2.5 g of Pb2000 was mixed with 100 mL of 1 M hydrochloric acid and stirred at 70°C for 2 h. Then the mixture was filtered with a membrane filter with a pore size of 5 μm. The procedure was repeated three times and then the mixture was thoroughly washed with distilled water to remove acid.

CoPc was purchased from Tokyo Chemical Industry Co., Ltd. It was used without further purification.

LG and CoPc were mixed to make the Co/LG weight ratio of 0.01 - 0.14. The amount of Co added is expressed by the weight of cobalt to 100 g of the precursor (owp%, on the weight of precursor). The mixture was pulverized at 800 rpm for 3 h using a planetary ball mill (Fritsch, P-7). The pulverized sample was passed through a stainless steel sieve with a mesh size of 106 μm. Then the sample was carbonized on a quartz boat at 1000°C for 1 h under nitrogen flow of 500 mL/min at the heating rate of 10°C/min. After carbonization, the sample was pulverized again at 750 rpm for 90 min using the same ball mill and filtered with the same stainless steel sieve. Then 0.5 g of the sample was washed with 100 mL of 1 M hydrochloric acid at 70°C for 2 h and filtered with a membrane filter with a pore size of 1 μm. Acid washing was repeated three times and then the sample was thoroughly washed with distilled water until the washing water became neutral in pH. After drying the sample in a vacuum oven at 80°C, elements contained in the sample were measured by a transmission electron microscope equipped with EDS (JEOL 2010) as shown in Table 1. Most of the metal elements contained in LG raw material were removed by acid washing. Hereafter a carbon sample expressed LG(3) stands for a carbon prepared from 1 g LG and 0.03 g cobalt. Carbons thus prepared were subjected to the following characterization.

2.1.2. Phenol-Formaldehyde Resin Based Sample

One g of phenol-formaldehyde resin (Ph, PSK 2320, GUN EI Chemical Industry Co., Ltd) was dissolved in 500 mL acetone and mixed with CoPc to give the Co/Ph weight ratio of 3/100. The mixture was ultrasonicated for 30 min, acetone was removed by a rotary evaporator and the sample was dried at 70°C under reduced pressure. The obtained carbon precursor was carbonized, pulverized, filtered and washed with acid in the same way described in 2.1.1. Ph-based carbon sample is expressed in the same way with LG-based carbon samples: Ph(3).

2.2. Characterization

Transmission electron microscopic (TEM) observation was carried out for the ground sample placed on a copper grid coated with an amorphous carbon (JEOL). The TEM specimen was prepared by dropping an aliquot amount of the dispersion, which was prepared by ultrasonic dispersion of the carbon in methanol, on the copper grid. After evaporating methanol, the samples were subjected to TEM observations. The TEM equipment was JEM2010 (JEOL) operated at an acceleration voltage of 200 kV.

X-ray diffraction (XRD) profiles for the powder samples were obtained using an X-ray diffractometer (XRD-6100, SHIMADZU Corp.). The X-ray source was Cu-Kα, with operating conditions of 20 kV and 32 mA. The range of diffraction angle was 2θ = 5° - 90° and the scan speed was 1°/min.

C1s, O1s, N1s and metal elements such as Co 2p, Fe 2p, Al 2p core-level X-ray photoelectron spectra (XPS) were measured with Kratos AXIS NOVA (SHIMADZU Corp.) spectrometer by using Al-Kα X-ray (10 mA, 15 kV). The charge-up shift correction was made by setting

Table 1. Elements contained in Pb2000 before and after acid treatment.

<table>
<thead>
<tr>
<th>Element</th>
<th>Before acid treatment (mg/g)</th>
<th>After acid treatment (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>60^a</td>
<td>23^b</td>
</tr>
<tr>
<td>Ca</td>
<td>110^a</td>
<td>0.5^b</td>
</tr>
<tr>
<td>Fe</td>
<td>89^a</td>
<td>1.4^b</td>
</tr>
<tr>
<td>Mg</td>
<td>63^a</td>
<td>0.3^b</td>
</tr>
<tr>
<td>Na</td>
<td>1300^a</td>
<td>0^b</td>
</tr>
<tr>
<td>P</td>
<td>49^a</td>
<td>3^b</td>
</tr>
<tr>
<td>Ti</td>
<td>8^a</td>
<td>0.3^b</td>
</tr>
<tr>
<td>C</td>
<td>592^a</td>
<td>-^d</td>
</tr>
<tr>
<td>N</td>
<td>6^a</td>
<td>-^d</td>
</tr>
<tr>
<td>H</td>
<td>59^a</td>
<td>-^d</td>
</tr>
</tbody>
</table>

^a Analyzed using ICP by Mitsui Chemical Analysis and Consulting Service, Inc.; ^b Analyzed by TEM-EDS in our laboratory; ^c Analyzed by an organic elemental analyzer in Center for Material Research by Instrumental Analysis, Gunma University; ^d Not measured in this study.
the C1s of the carbonized sample at 284.5 eV.

Rotating disk electrode (RDE) voltammetry was employed to assess the ORR activity of the carbons. Normally, a carbon slurry was prepared in the following manner: 5 mg of the carbonized sample was mixed with 50 μL of Nafion solution (5% solution of lower aliphatic alcohols, Aldrich), 150 μL of ethanol (99.5%, Wako Pure Chemicals, Co. Ltd.) and 150 μL of ultrapure water in a plastic conical vial (1.5 mL). The working electrode was a 4 mm diameter glass-like carbon electrode (BAS Inc.). The slurry (1.78 μL) was pasted onto the whole area of the glass-like carbon electrode. The catalytic electrode was obtained after removal of the solvents by drying in the atmosphere. The electrolyte was a 0.5 M H2SO4 solution. Reversible hydrogen electrode (RHE) and glass-like carbon were used as the reference and counter electrodes, respectively. Prior to the measurements, dissolved oxygen in the acid solution was purged by bubbling nitrogen gas. Cyclic voltammetry measurements were performed by sweeping the potential between 0.0 V and 1.0 V vs. RHE at 50 mV/s for five cycles with a potentiostat (ALS 700A or ALS 2323, BAS Inc.). The reference linear sweep voltammograms (N2-LSVs) were obtained by sweeping the potential from 1.0 V to 0.0 V vs. RHE at 1 mV/s with the rotating electrode at 1500 rpm. The H2SO4 solution was then bubbled with oxygen gas to obtain O2-saturated acidic medium. The linear sweep voltammograms (O2-LSVs) were measured in this solution by sweeping the same potential range as the N2-LSVs. Finally, net voltammograms for ORR were obtained by subtracting N2-LSV from O2-LSV. The potential was represented by the RHE standard.

3. Results and Discussion

3.1. Carbon Structure

Figure 1(a) shows typical XRD profiles of the LG-based carbons. The carbon prepared in the absence of CoPc shows halo diffractions at 2θ ~ 23° and 42° indicating its amorphous nature. The addition of CoPc resulted in the developments of diffractions. The most prominent developments are observed at 2θ ~ 26°. This peak is assigned to 002 diffraction of turbostratic carbon, which is a sign of the formation of NS structure. The development of the peak saturated above 0.7 V vs. RHE indicates that the ring-like structure composed of graphitic layers. The magnified image shown in the same figure clearly indicated that the ring-like structure composed of graphitic layers. The occurrence frequency of the structure significantly increased up to 3 owp% of the amount of Co addition; the frequency seemed constant above 3 owp% of the Co addition.

Figure 1(b) shows an illustration of the deconvolution of the 002 into two components. The areal fraction of the sharp component out of the total area of this diffraction was defined as fsharp, which has been turned out to be an indicator of the development degree of NS structure [1].

3.2. Electrocatalytic Activity of the Prepared Carbons for Oxygen Reduction Reaction

Figure 4 shows the ORR voltammograms of the LG-based and Ph-based carbons. The addition of Co to the precursor clearly induced the increases in ORR activity. Here we defined i0.7, the ORR current density at 0.7 V to express the ORR quantitatively, since the current at this potential governed by charge transfer process. Figure 2 shows the relationship between the amounts of Co added and obtained values of fsharp. The value increased up to 3 owp% of the amount of Co addition then it saturated. The fsharp value of Ph(3) had a similar fsharp value to LG(3), namely 0.41 and 0.42 for Ph(3) and LG(3), respectively. TEM observation gave direct evidence of the formation of NS structure. Figure 3 shows TEM images of some representative samples. LG(0) showed uniformly amorphous appearance in agreement with the XRD analysis shown in Figure 1(a). LG(1) developed the typical signs of the formation of NS structures by showing small ring-like structures embedded in the amorphous matrix. The magnified image shown in the same figure clearly indicated that the ring-like structure composed of graphitic layers. The occurrence frequency of the structure significantly increased up to 3 owp% of the amount of Co addition; the frequency seemed constant above 3 owp% of the Co addition.

We definitely demonstrated the conversion of LG into NSCC by the carbonization in the presence of NS forming catalyst, CoPc in the present case, likewise for conventional synthetic polymers such as furan resin [1,2], oxine-formaldehyde resin [3], furfuryl alcohol [4-6], and phenol-formaldehyde resin [7,8] that we have employed previously.

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Figure 2. Dependence of $f_{\text{sharp}}$ on the amount of Co added.

Figure 3. TEM and HR-TEM images of the prepared carbons. (a-1), (a-2): LG(0); (b-1), (b-2): LG(1); (c-1), (c-2): LG(3); (d-1), (d-2): Ph(3).

Figure 4. O$_2$ reduction voltammograms of the prepared carbons. (a) LG-based samples prepared with the amount of Co up to 3 owp% and Ph-based sample; (b) LG-based samples prepared with the amount of Co above 3 owp%.

Figure 5. Dependence of $i_{0.7}$ on the amount of Co added.

development of NS structures shown in Figure 2 as we have claimed in the previous studies [1,6].

Figures 4 and 5 include the results of Ph(3), which had almost the same $f_{\text{sharp}}$ as LG(3) (Figure 2). The $i_{0.7}$ values plotted in Figure 5 demonstrates that the activity of LG(3) is seven times higher than Ph(3). States of metal and nitrogen are the possible factors to elucidate the difference in the ORR activities between LG(3) and Ph(3). XPS did not detect any Co on the surface of Ph(3) like LG(3) case, but it detected N/C atomic ratio of 0.013 for LG(3), which is two times higher than that for Ph(3) (N/C = 0.007).

Three types of nitrogen species are discussed by different researchers; i.e. pyridinic nitrogen [20], quaternary-coordinated nitrogen [21] and positively charged nitrogen [22]. In the previous paper, we have observed the enhancement of ORR activity by introducing nitrogen into carbon materials and ascribed it to the introduction of structural defects in graphitic layer [4]. We also reported a restriction of layer growth during the carbonization of a mesophase pitch by fullerene and simultaneous increase in the ORR activity [23]. Further studies will be conducted to elucidate the difference in the ORR activity...
between LG(3) and Ph(3).

4. Conclusion

The present study was conducted to ensure the possibility of LG as a raw material for preparing NSCC with ORR activity. The study revealed that a type of LG obtained from herbaceous plants was successfully converted into NSCC and showed excellent ORR activity. Furthermore, the ORR activity of the LG-based NSCC was higher than Ph-based NSCC probably due to the higher nitrogen content of the material. In this respect, the LG used here is favorable for preparing NSCC due to intrinsically higher nitrogen content than polymers from fossil resources.

5. Acknowledgements

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REFERENCES


