SiO_2/CARBON NANO FIBER USING CATALYTIC DECOMPOSITION FOR THE CATALYST-SUPPORTS OF DMFC

Kidon Nam[1,2], Seongyop Lim[1], Sang-Kyung Kim[1], Doohwan Jung[1,2,♠]

[1]Fuel Cell Research Center, Korea Institute of Energy Research, 102 Gajeong-ro Yuseong-gu, Daejeon 305-343, Korea
[2]Advanced Energy Technology, University of Science & Technology, 113, Gwahangno, Yuseong-gu, Daejeon 305-333, Korea

Introduction

Many scientists have been focused on the characteristics of SiO_2 (silica) and carbon nanofibers, and a large number of methods for its synthesis were announced. These materials are used as field electron emission sources, composite materials, scanning probe microscopy tips, carrier material for various catalysts, electrode materials, etc**.**

The chemical compound silicon dioxide, known as silica, is an oxide of silicon with a chemical formula of SiO_2 and has been known for its hardness. In addition, SiO_2 is manufactured and used variously according to usage. SiO_2 as hydrophilic materials for function layer are easily produced by the sol-gel method at low temperatures.

Carbon nanofibers are produced from the catalytic decomposition of hydrocarbon gases or carbon monoxide over selected metal particles. Carbon nanofibers are cylindric nanostructures with graphene layers arranged as stacked cones, cups or plates. Carbon nanofibers (CNFs) with graphene layers wrapped into perfect cylinders are called carbon nanotubes. Unlike SiO_2, CNFs have a hydrophobic property.

In the present work, preparation of silica particles by hydrolysis of tetraethoxysilane (TEOS) in sol-gel method and CNFs by catalytic decomposition of ethylene are reported as catalyst-support for DMFC. This paper deals with mechanism of CNT growth over SiO_2-supported catalyst, the effects of temperature, ethylene as carbon source. Also, in the single cell test for DMFC, roles of SiO_2 and CNFs as the function layer were found out.

Experimental

1. Preparation of catalyst; NiFe- SiO_2

SiO_2 spheres were synthesized by sol–gel methods. To load the metals on the surface of SiO_2, a mixture of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) and iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) were dissolved in the solution during the sol-gel method. In our experiment, the molar ratio of (Ni : Fe : SiO_2 = 1.6 : 0.4 : 100) was used to fabricate NiFe–SiO_2 catalyst. After a mixing round at 90 ^oC for 24 h, the catalyst was dried and heated at 773K for 2 h in a quartz tube.

2. Preparation of SiO_2-CNF

The catalyst was placed into a quartz tube. The furnace was first heated to range in temperature from 400 ^oC to 600 ^oC at a speed of 10 ^oC/min in N_2 atmosphere, and then a mixture of C_2H_4 (160 cc/min) and H_2 (40 cc/min) was introduced into the quartz tube maintained at the same temperature for the production of CNFs. Then the quartz tube was cooled to room temperature in N_2 atmosphere. Cooled SiO_2-CNFs samples were obtained.

3. Preparation of Pt–Ru/(SiO_2*-CNF) catalysts*

The Pt–Ru catalyst supported on SiO_2-CNFs for the DMFC is prepared by impregnation method. $H_2PtCl_6 \cdot 6H2O$ (Aldrich) and $RuCl_3 \cdot 3H_2O$ (Aldrich) were used as the precursors of the catalysts. The SiO_2-CNFs were mixed with $H_2PtCl_6 \cdot 6H_2O$ (Aldrich) and $RuCl_3 \cdot 3H_2O$ (Aldrich) in deionized water. The mixed solution was stirred for 12 h and the SiO_2-CNFs were impregnated with PtRu(or Pt) metals using a 0.5 M $NaBH_4$ solution as a reduction agent for 1 h. After the impregnation, the solutions with PtRu(or Pt) metals were filtered and dried at 80 ◦C for 24 h. The particle size and characteristics of the PtRu(or Pt) catalyst supported on the SiO_2-CNFs were measured using SEM, TEM, XRD, BET technique, CV, and Single cell test.

Results and Discussion

Transmission electron microscope (TEM) images of 450 nm SiO_2 with CNFs are given in Fig. 1. Growth of CNFs do not attain evenly at 400 ^oC and begin in earnest at 500~600 ^oC. Length and diameter of CNFs tend to be increased by temperature. Each of CNFs are showed the herringbone type CNFs, which is well-attached to SiO_2.

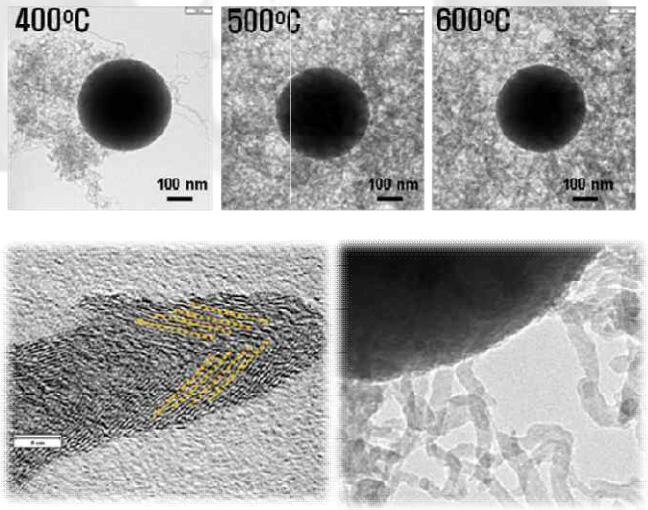

Fig. 1. TEM image of SiO_2-CNFs.

To serve an anode or cathode electrode catalyst for a DMFC, PtRu or Pt metals are loaded on the SiO_2-CNFs. The preparation process of the PtRu(or Pt)/ SiO_2-CNFs catalyst is shown in Fig. 2.

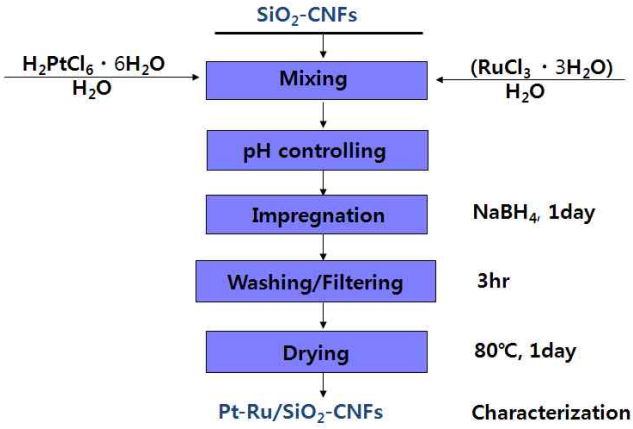

Fig. 2. Preparation of PtRu(or Ru) catalyst supported on SiO_2-CNFs.

Cyclic voltammograms of the Pt–Ru catalysts supported on SiO_2-CNFs are shown in Fig. 3. All of the PtRu/SiO_2-CNFs showed greater levels of hydrogen activity compared with the commercial J. In particular, the activity of 60wt% PtRu/(SiO_2-CNF500) catalyst shows greater hydrogen activity at (-0.2~0.1) V than other catalysts and the commercial J catalyst (60 wt.% PtRu/Vulcan XC 72R). The electro chemical surface areas of PtRu/SiO_2, PtRu/SiO_2-CNF400, PtRu/SiO_2-CNF500 and PtRu/SiO_2-CNF600 are about 86, 84, 96 and 85 m^2/g, respectively.

Cyclic voltammograms of the Pt catalysts supported on SiO_2-CNFs are shown in Fig. 4. These catalysts as cathode electrode are possible because activities of Pt/SiO_2-CNFs are similar with commercial J catalyst (70wt% Pt/AC)

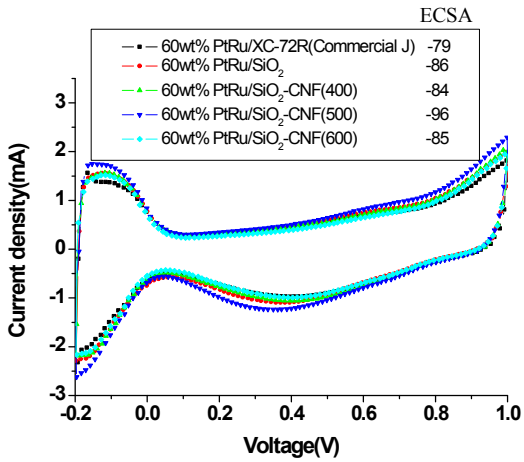

Fig. 3. CV graph of 60wt% PtRu/(SiO_2-CNFs).

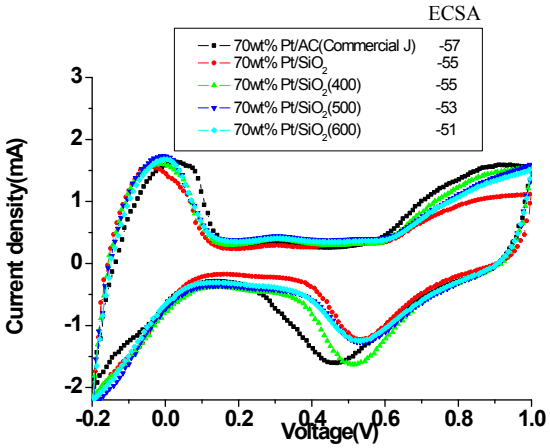

Fig. 4. CV graph of 70wt% Pt/(SiO_2-CNFs).

Conclusions

We can get the SiO_2-CNFs as function layer for the catalyst supports of DMFC. There are some advantages for advanced researches;

-Application of hydrophilic-hydrophobic regions
-Humidity control in PEFC (DMFC)
-Methanol feeding control in DMFC
-Electrode structure control

Acknowledgments.
This work has been done in the frame of Fuel Cell Core Technology Development Project supported by Ministry of Knowledge Economy (MKE), Korea.

References

[1] C. Park and R. T. K. Baker, J. CATALYSIS 1998; 179: 361–374.
[2] Seongyop Lim, Seong-Ho Yoon, Yozo Korai, Isao Mochida, Carbon 2004; 42: 1765-1781.
[3] Yasuzumi Yamada, Yu-ki Hosono, Nobuyuki Murakoshi, Na-oki Higashi, Hiro-aki Ichi-oka, Takanori Miyake, Na-oki Ikenaga, Toshimitu Suzuki. Diamond & Related Materials 2006; 15: 1080–1084.
[4] Kidon Nam, Doohwan Jung, Sang-Kyung Kim, Donghyun Peck, Seungkon Ryu. J. Power Sources 2007; 173: 149–155.