전극 재료용 나노 촉매 개발에 의한 DMFC 성능 향상 연구

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Improving the Performance of Direct Methanol Fuel Cell Using Nano-structured Electrocatalysts

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서론

Replication has been the mainstay for the molding that is required to synthesize a novel material on various length and shape using a removable template. Especially, considering that the various ordered molecular sieves have been emerged and are expected to come out, it is possible to synthesize new types of nanostructured metals and those materials are potentially useful in future catalysis, quantum-electronic devices and electrochemical sensing. Recently, metal replica prepared using highly ordered silica have been reported. However, these were single metal structures synthesized with Pt, Au or Ag precursor and the detail application has not been suggested yet, except for imaging the channels in mesoporous molecular sieves. We here report the synthesis of PtRu nanowire network made from SBA-15 template and show that these novel materials can be used as a good electrocatalyst for enhancing the performance of direct-methanol fuel cell (DMFC).

실험

PtRu nanowire network was synthesized using SBA-15 silica as a template. SBA-15 was obtained using the triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, BASF) as the surfactant and tetraethyl orthosilicate (98%, Aldrich) as the silica source under acidic conditions following a modification of the procedure described in the literatures[1]. In order to prepare the PtRu nanowire network, calcined SBA-15 materials were immersed in aqueous solution (Pt : Ru = 3 : 1, atomic ratio) of Pt and Ru precursors. The solvent was evaporated in a rotary evaporator. This procedure for incorporating metal precursor inside SBA-15 was repeated, so that the Pt content corresponded 70 wt % of SiO_2 weight. Pt and Ru species in SBA-15 was reduced by hydrogen flow while the temperature was increased from room temperature to 583 K, maintained at 583 K for 2 h and evacuated at 583 K for 30 min. The silica framework of this sample was dissolved completely with 10% hydrofluoric acid. PtRu black powder thus obtained was filtered, washed and dried in a vacuum oven at room temperature.

결과 및 고찰

As the X-ray diffraction pattern in Fig. 1(a) shows, the silica template gives an XRD pattern of highly ordered SBA-15 sample, which is characteristic of a hexagonal structure.

And XRD pattern shown in Fig. 1(b) indicates that the mesoscopic ordering of SBA-15 was maintained after the H_2 reduction of $(NH_3)_4Pt(NO_3)_2$ and $(NH_3)_6RuCl_3$ of SBA-15 structure with the observation of low angle peaks that can be indexed as (100), (110) and (200) reflections. There are no significant changes to the silica templates after metal loading, except for the decrease in peak intensity. However, XRD pattern of template-free PtRu nanowire network in Fig. 1(c) only shows the (100) reflection. Because the metals did not fill the entire pore volume of SBA-15 and the synthesized PtRu nanowire is not long, (110) and (200) reflection may not be found. The way to control the length of this replica will be discussed in *TEM study*.

Pt nanowire network was also synthesized with the same procedure and high angle diffraction peaks of Pt and PtRu nanowire networks were observed after the removal of silica template [Fig. 1, inset (a) and (b)]. Small sharp lines except for each fcc peak are from the Si standard. The pattern of PtRu nanowire network shows a single fcc phase and detectable small amount of any other crystalline phases, such as hexagonal close-packed (hcp) Ru. This observation can be supported by a comparison of the lattice parameters of the prepared nanowire networks. The lattice parameter for the Pt and PtRu nanowire networks is 3.9204 Å and 3.3166 Å, respectively. These are nearly in good agreement with the available literature values[2]. However, considering that PtRu nanowire network was synthesized using aqueous solution (Pt : Ru = 3 : 1, atomic ratio) of $(NH_3)_4Pt(NO_3)_2$ and $(NH_3)_6RuCl_3$, the atomic fraction of Ru alloyed with Pt is 39 % and the remaining Ru atoms are present as hcp phase[2].

For confirming the oxidation state of the Pt and Ru of the nanowire network, X-ray photoelectron spectroscopy was used. The main Pt $4f_{7/2}$ peak occurred at a binding energy of 71.3 eV, which was 0.5 eV higher than that of metallic Pt (70.8 eV). McBreen and Mukerjee observed the electrons of Pt d band by x-ray absorption spectroscopy and reported that Pt alloying with Ru increased the number of Pt d band vacancies[3]. Since the Ru 3d line could be affected by the overlapping with C 1s signal from adventitious carbon at 284.6 eV, the Ru $3p_{3/2}$ line was analysed and the main Ru $3p_{3/2}$ peak was observed at a binding energy of 461.9 eV which is very close to the value reported for pure metallic ruthenium, i.e. 461.8 eV.

Transmission electron microscopy (TEM) was used to image the nanowire network. As the TEM images of the template-free PtRu samples synthesized using mesoporous SBA-15 in Fig. 2(a), the nanowires with the length from 50 nm to 150 nm are not scattered and shown in bundle. Considering the samples for TEM images were prepared after sonicating a small amount of the material in ethanol and there were no residual silica template, which were confirmed by EDX and XPS data, it can be known that three-dimensional PtRu nanowires with uniform diameter were prepared using SBA-15 template. The length of nanowires which are interconnected each other can be controlled with the amount of metal-loading and the temperature-increasing rate during the thermal reduction procedure. And the step to maintain the temperature at 373 K during the reduction procedure is also important for preparing the interconnected nanowires, because the H_2O in SBA-15 template is helpful for the movement of metal precursors in the channel structures. Fig. 2(b) shows an HRTEM image of template-free PtRu nanowire network. It can be known that there are bridges between the nanowires which have 7~8 nm diameter. And it is also observed that the direction of lattice fringe of nanowires and bridge is same (indicated by arrow in Fig. 2(b)). It means that the bridge and the adjacent nanowires have the same PtRu alloy phase.

Until now, metal replicas synthesized using SBA-15 have been generally studied for imaging the detail channel structures of the template. However, if ordered bimetal or alloy structure can be synthesized, these materials will also be able to have some potential as a good catalyst. We here report an enhanced performance of DMFC which the PtRu nanowire network discussed above was used as an electrocatalyst of anode for methanol electrooxidation. Many results have been reported for improving the activity of methanol electrooxidation. But they have been generally focused on the composition or the kind of metals, and there are few reports to enhance the DMFC peformance controlling the morphology of electrocatalysts. PtRu nanowire network gives the higher DMFC performance than commercial PtRu black catalyst. Considering the BET surface areas of PtRu nanowire network and commercial PtRu black are 31 and 78 m2/g, respectively, it is not easy to understand why PtRu nanowire network shows the higher performance even though the intrinsic surface area of the electrocatalyst does not seem to be a dominant factor in determining relative DMFC performance. We, however, speculate because the relative anode performance depends strongly on surface diffusion and the spillover of proton and oxygen-containing surface species, electrical conductivity of the catalyst layer and mass transport of methanol/water and CO_2 as a reaction product, PtRu nanowire network having ordered structure should be advantageous to the effective catalyst layer in DMFC. Further study on these possibilities will be reported in future.

In summary, we demonstrated for the first time that the nanowire network composed of more than a metal acts as a novel material for catalyzing a reaction that the morphology of catalyst can be an important factor for improving activity. Considering that the various ordered molecular sieves are expected to come out and a superior electrode material is critical to commercializing DMFC that will be an alternative power source of portable electronic devices, with further development this approach could become a strong candidate for an alternative to synthesizing electrocatalysts in fuel cell.

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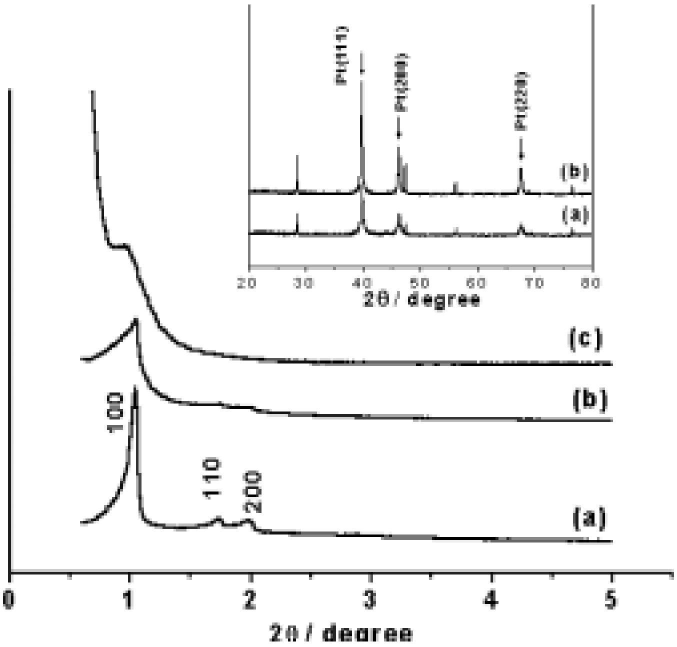

Fig. 1. X-ray diffraction patterns of (a) SBA-15 silica, (b) PtRu/SBA-15 composite and (c) template-free PtRu nanowire network obtained after removing silica from PtRu/SBA-15. Inset: XRD patterns of (a) PtRu and (b) Pt nanowire network at high angle after removing silica from PtRu/SBA-15 and Pt/SBA-15 composite. Small sharp lines except for fcc peaks are from the Si standard.

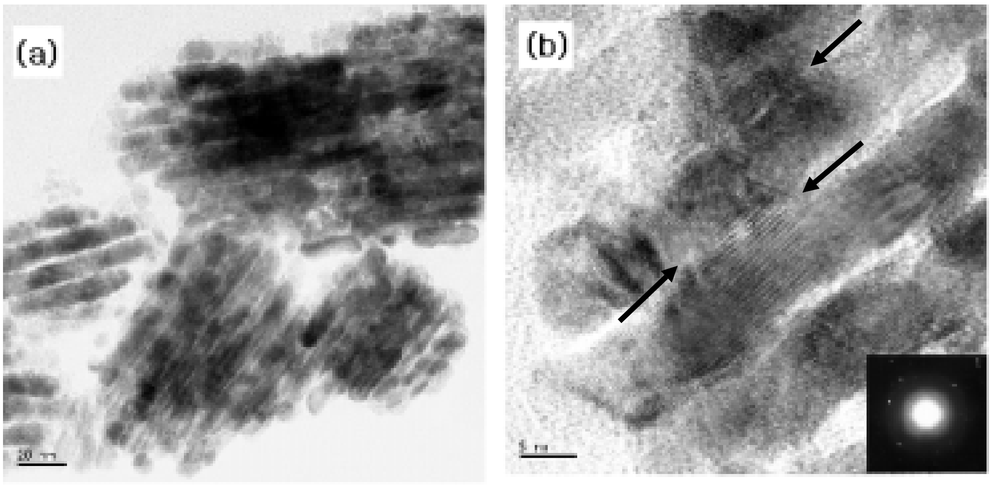

Fig. 2. Bright-field (a) TEM and (b) HRTEM images of PtRu nanowire network obtained by removal of silica template with 10% HF solution. A selected area electron diffraction pattern recorded on PtRu nanowire network is shown in the inset of (b).