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**Pt nanowires prepared via a polymer template method: its promise toward high Pt-loaded electrocatalysts for methanol oxidation**

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**Introduction**

Direct methanol fuel cell (DMFC) has been recognized as a promising power source for portable applications because they use a liquid methanol fuel, which is beneficial for fuel usage, feed strategies, and simplification of the fuel cell system [1]. Platinum nanoparticles (NPs) have been generally employed as the anode electrocatalysts for DMFCs, since the nanoparticle morphology should provide high surface area through high dispersion on support materials, leading to economical and efficient use of the expensive Pt catalyst. However, presence of a number of interfaces between nanoparticles (and polymeric binders) can impede mass diffusion and charge transfer, especially resulted in a large resistance for the electron transfer. Thus, one-dimensional (1D) nanostructures, i.e. rods, tubes, and wires, of platinum would be realized as a new promising electrode catalyst for improving the performance of the DMFCs due to several beneficial features arising from their shape anisotropy on the electrochemical oxidations at electrodes: i) facile pathways for the electron transfer by reducing the number of interfaces between the nanoparticle catalysts and ii) effective surface exposure to work as active catalytic sites in the electrode-electrolyte interface.

In this work, the Pt nanowires of about 30 nm in diameter and 6  $\mu\text{m}$  long were prepared via a polymer template-synthesis method, which has advantages in that the polymer template could be easily removed and cleaned without contaminating and morphologically changing the nanowires formed. The electrochemical activities of the Pt nanowires for the hydrogen and methanol oxidation were investigated by cyclic voltammetry (CV) measurement, which were compared per unit gram of the Pt with those of the commercial 40 wt% Pt/C (Johnson Matthey Corp., denoted as Pt/C) and high surface area Pt black (Johnson Matthey Corp., denoted as Pt black) in order to investigate the potential applicability of the nanowire-structured Pt to the electrocatalyst of DMFC that requires a high content of Pt. The electrocatalytic activity was demonstrated and compared by varying the Pt content on electrode from 0.2 to *ca.* 3  $\text{mg}_{\text{Pt}} \text{cm}^{-2}$ , in which the supported nanoparticles showed the best performance over the former Pt loading, but the 1D Pt appeared to be better choice over the latter case of a high Pt content for DMFC applications.

## **Experimental**

Platinum nanowires, denoted as Pt-NWs in figures, were prepared via a template-synthesis method by electrodeposition of Pt within the pores of a track-etched polycarbonate (PCTE) membrane containing a nominal pore diameter of 10 nm (KN1CP04700, GE OSMONIC Inc.), which was modified from the method for the electroless synthesis of gold nanotubes [2]. A thin gold layer, as a working electrode for Pt electrodeposition, was first deposited by sputtering on one side of the PCTE to make the template membrane electrically conductive. The Pt deposition bath was aqueous solution of 0.01 M  $\text{H}_2\text{PtCl}_6$  (Aldrich) and 0.2 M  $\text{H}_2\text{SO}_4$  (Aldrich) with triply de-ionized Millipore water (18 M $\Omega$  cm). The pH of the solution was adjusted to 3 by manipulation of  $\text{H}_2\text{SO}_4$  solution. The Pt was deposited at a constant current density of  $-0.44$  mA for a period of 1000 s at 323 K. The Pt nanowires embedded within the pores of the template membrane were exposed by reactive ion etching (RIE) with  $\text{O}_2$  plasma to remove the PCTE layer selectively for SEM images. The Pt nanowires were successfully separated from the polymer by immersing the prepared Pt-embedded PCTE in 8 M  $\text{CH}_2\text{Cl}_2$  solution (Aldrich) to dissolve the polymer, followed by washing with ethanol solution repeatedly.

X-ray diffraction (XRD) analyses were carried out with Rigaku Rotaflex (RU-200B) X-ray diffractometer using Cu  $K\alpha$  ( $\lambda = 1.5405$  Å) source with a Ni filter to characterize structures of the Pt nanowires. Isolated Pt nanowires with/without Nafion<sup>®</sup> ionomer solution (5 wt%, Aldrich) on a glassy carbon electrode to identify actual electrode surface morphology for CV measurements, and transmission electron microscopy (TEM, JEOL JEM-2100) for the isolated Pt nanowires on the copper grid.

A catalyst ink was made of the Pt nanowires in an ethanol solution with / without Nafion<sup>®</sup> solution (5 wt%, Aldrich) which serves as an adhesive and a proton conductor (catalyst : Nafion<sup>®</sup> = 85:15 wt%), and then was casted onto the glassy carbon electrode (with area of 0.07 cm<sup>2</sup>). The amounts of Pt loading were selected and changed from 0.2 to 3 mg cm<sup>-2</sup> because they are typical Pt contents on the fuel cell electrodes from PEMFCs to DMFCs applications, respectively. It was observed that the Pt nanowires were stably stuck on the glassy carbon electrode and no visible dissolution from the electrode appeared even without Nafion<sup>®</sup> ionomer during fabrication of the working electrode and electrochemical tests. After drying in an oven at 343 K to prepare the catalyst thin-film impregnated on the glassy carbon as the working electrode, the mass of the resulting catalyst was measured by microbalance (CP2P, Sartorius) in the error range of  $\pm 0.001$  mg. Electrochemical measurements were performed over a three-electrode cell at 298 K by using cyclic voltammetry (CV) method with EG&G model 273A potentiostat/galvanostat (AUTOLAB, Eco Chemie.). A Pt wire and Ag/AgCl (in 3.0 M KCl) were used as a counter and a reference electrode, respectively. The CVs were recorded in the potential range of  $-0.2$  and  $1.0$  V (vs. Ag/AgCl) at a scan rate of  $50$  mV s<sup>-1</sup> in a  $\text{N}_2$ -purged 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte in the absence and presence of 2.0 M  $\text{CH}_3\text{OH}$  at 298 K for the hydrogen and methanol electrooxidation, respectively.

## **Results and discussion**

X-ray diffraction (XRD) patterns in Figure 1 were obtained over the PCTE, the Pt nanowires embedded in and separated from the PCTE, the glassy carbon, and the commercial Pt black and Pt/C catalysts. The first intense peak around  $17^\circ$  corresponds to the PCTE membrane, thereby proving that the diffraction patterns found in the Pt nanowires-filled PCTE (Figure 1d) represent the face-centered cubic Pt. No significant changes appear in the PCTE template after electrodeposition of Pt metal. It can be seen from Figure 1c that the isolated Pt nanowires exhibited characteristic fcc-Pt diffraction

peaks, i.e. (111), (200), (220), and (311) planes at the corresponding diffraction angles [3], indicating highly polycrystalline. There were no noticeable peaks for Pt oxides in our XRD measurements. The diffraction peak of the Pt nanowires are slightly shifted to higher  $2\theta$  value compared with the commercial Pt black and Pt/C catalysts, which may be attributed to the anisotropic structure of the nanowire.

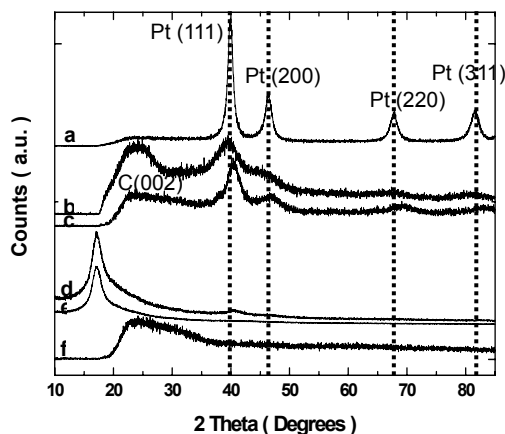


Fig. 1. XRD patterns of (a) Pt black, (b) Pt/C, (c) Pt nanowires separated from the PCTE, (d) Pt nanowires embedded in the PCTE, (e) PCTE, and (f) glassy substrate.

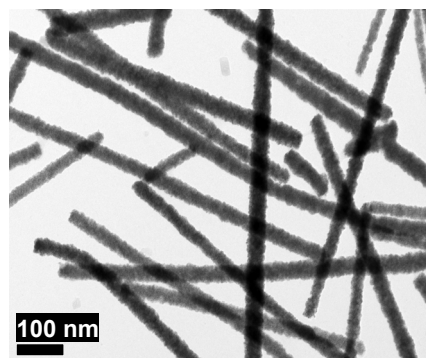


Fig. 2. TEM image of the Pt nanowires prepared from the polycarbonate template membrane

Figure 2 shows representative TEM images of the isolated Pt nanowires, revealing a uniform diameter of about 30 nm. The length of the Pt nanowires varies from about 0.5  $\mu\text{m}$  to 6  $\mu\text{m}$  because some of them might be broken during the ultrasonication for TEM sample preparation. The images in Figure 2 reveal that the Pt nanowires in this work possess some extent of surface roughness, which may provide higher specific surface areas than the calculated one with assumption of smooth and nonporous cylindrical geometry

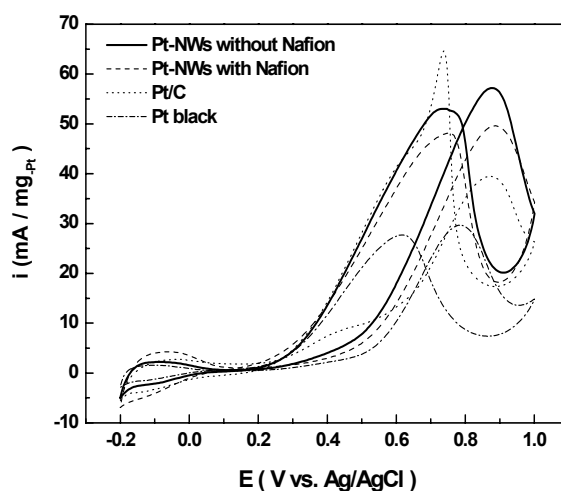


Fig. 3. Cyclic voltammograms of the Pt nanowires, Pt/C and Pt black catalysts in 2 M  $\text{CH}_3\text{OH}$  + 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte solution at a scan rate of 50  $\text{mV s}^{-1}$ .

Figure 3 shows typical cyclic voltammograms of the Pt-based catalysts over the methanol electrooxidation. The amounts of Pt loadings mounted on the working electrode were  $2.90 \pm 0.025 \text{ mg cm}^{-2}$  for the Pt nanowires,  $3.03 \pm 0.037 \text{ mg cm}^{-2}$  for the Pt/C, and  $3.13 \pm 0.043 \text{ mg cm}^{-2}$  for the Pt black; these high metal loadings of ca.  $3 \text{ mg cm}^{-2}$  were employed throughout this work in order to compare the electrocatalytic activity toward methanol electrooxidation since the electrocatalysts of the DMFC are generally fabricated with such high metal content (ca.  $2.0 - 5.0 \text{ mg cm}^{-2}$ ) to produce moderate electricity at low temperatures. However, because the thickness of the catalyst layer would be one of the influential factors for the electrocatalytic activity, the thinner layer with larger amount of Pt catalyst would be required for the effective DMFC catalysts as the Pt nanowires with high content is demonstrated in this work.

Figure 3 shows representative CVs of the Pt-based catalysts in  $0.5 \text{ M H}_2\text{SO}_4 + 2 \text{ M CH}_3\text{OH}$  solution. The shapes of all curves are typical for the electrooxidation reactions of simple organic alcohols, showing two anodic current peaks in positive and negative sweeps. The forward peak current for the positive sweep, produced from anodic processes during the methanol electrooxidation, of the Pt nanowire catalysts with ( $49.6 \text{ mA mg}_{\text{-Pt}}^{-1}$ ) and without ( $57.2 \text{ mA mg}_{\text{-Pt}}^{-1}$ ) Nafion<sup>®</sup> ionomer showed significantly higher catalytic mass activities than the nanoparticle catalysts of Pt/C ( $39.4 \text{ mA mg}_{\text{-Pt}}^{-1}$ ) and the Pt black ( $29.7 \text{ mA mg}_{\text{-Pt}}^{-1}$ ). It should be noted that the similar amounts of Pt in weight were mounted on the all Pt electrode preparation in this work to compare the electrocatalytic performances with the high Pt content of ca.  $3 \text{ mg cm}^{-2}$  for the DMFC electrode. This may be attributed to the inherent physicochemical and electrical properties of the Pt nanowires: i) the Pt electrodes fashioned of nanowires can provide facile pathways for the electron transfer by reducing the number of interfaces between the electrocatalysts, (i.e. larger electronic conductivity) whereas the nanoparticles such as the Pt black and the Pt/C are likely to impose more impedance for electrons to transfer particle to particle, ii) the anisotropic morphology of the Pt nanowires with a high aspect ratio (ca. 200 or larger in this work) would allow an efficient use of Pt while a considerable fraction of Pt particles seems to be entirely embedded in the Pt nanoparticle catalyst systems after impregnation with ionomer and fabrication of the electrode.

## Conclusions

In this work, structurally well-defined Pt nanowires with diameter of 30 nm and length of ca.  $6 \mu\text{m}$  were prepared via a polymer template-synthesis method by electrodeposition of Pt within the pores of a track-etched polycarbonate membrane. The Pt nanowires showed the higher catalytic mass activities for the hydrogen and methanol electrooxidation than the Pt nanoparticle catalysts over the electrode systems that require high Pt content for the low temperature alcohol fuel cells, which suggests that nanostructured catalysts fashioned with 1 dimensional nanowires or nanotubes may be promising electrocatalysts for the DMFC electrode that requires a high Pt content by taking advantages of its improved physicochemical and electrical properties.

## Reference

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