

PT ELECTROCATALYSTS COMPOSITED ON ELECTRO-SPUN PT NANOWIRES FOR DIRECT METHANOL FUEL CELLS

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Abstract

Two types of Pt nanoparticle electrocatalysts were composited on Pt nanowires and their electrocatalytic activities for methanol electro-oxidation in direct methanol fuel cells were investigated. The high-resolution transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy results indicate that the metallic Pt nanoparticles with the polycrystalline property are uniformly composited on the electro-spun Pt nanowires. The cyclic voltammetry and chronoamperometry results demonstrate that electrodes containing 40 wt% Pt nanoparticles exhibit the best catalytic activity for methanol electro-oxidation and the highest electrochemical stability among the three samples studied for use in direct methanol fuel cells.

1. Introduction

Among the various existing fuel cells, direct methanol fuel cells (DMFCs) have recently attracted considerable interest owing to several advantages such as high energy density, low operating temperatures, and easy storage of fuels [1,2]. However, before DMFCs can be employed in industrial applications, some issues such as the low electrocatalytic activity at the anode, fuel cross-over, high price of electrocatalysts, and limited supply of electro-catalysts must be resolved. In particular, one of the key factors for the improvement of DMFC performance is the need to enhance the catalytic activity of the electrocatalysts used at the anode. To date, significant effort has been directed at improving the catalytic activity of methanol electro-oxidation. One possible approach towards this goal involves modification of existing electrocatalysts by the use of supporting materials, namely, C-based supports (CNT, Vulcan, and Graphene) and metal oxide-based supports (RuO₂ and CeO₂), and by the

use of Pt-based alloys such as PtRu and PtRh [3-5]. More recently, one-dimensional nanostructures have attracted growing interest in the field of fuel cells. For example, Kim et al. synthesized Pt nanowires for use as electrocatalysts in DMFCs by electrospinning, evaluated the effects of heat treatment, and demonstrated the methanol electro-oxidation properties [6]. Kim et al. also reported the enhancement of electrocatalytic activity for bimetallic PtRh and PtRu nanowires synthesized by electrospinning [7]. Pt nanowires electrodeposited on poly(vinylpyrrolidone) (PVP) exhibited excellent catalytic activity for methanol electro-oxidation in DMFCs as reported by Song et al. [8]. However, a number of unresolved issues related to the use of one-dimensional nanostructures in DMFCs still remain.

In this study, we have fabricated two types of Pt nanoparticle electrocatalysts composited on electro-spun Pt nanowires and demonstrated their electrochemical properties such as methanol electro-oxidation and chronoamperometry. For comparative purposes, the single Pt nanowire electrocatalysts were fabricated by an electrospinning method. Furthermore, in order to evaluate the two types of Pt nanoparticle electrocatalysts composited on electro-spun Pt nanowires, relative weights of the Pt nanoparticles to the Pt nanowires of 20 wt% and 40 wt% were selected.

2. Experiments

Pt nanoparticle electrocatalysts composited on Pt nanowires fabricated by electrospinning were prepared using an impregnation method. First, in order to fabricate the electro-spun Pt nanowires, a precursor solution of H₂PtCl₆·xH₂O (Aldrich) was dispersed in de-ionized water by mixing for 2hrs. Poly(vinylpyrrolidone) (PVP, Aldrich, M_w = 1,300,000 g/mol) was dissolved in ethanol (Aldrich)

over a period of 5hrs. The solution mixture consisting of the two precursor solutions was injected into a syringe, which was connected to a DC power supply. The feeding rate of the electro-spun Pt nanowires was maintained at 0.02 ml/h at 6.5 kV with a syringe equipped with a 25 gauge. The distance between the needle tip and the collector was fixed to ~8 cm. In order to remove the PVP polymer, the samples were calcined at 400 °C for 2h in air. The electro-spun Pt nanowires were then dispersed in 0.1 mM $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ and 0.2 mM $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ solutions, respectively, for 1 h at room temperature, in order to fabricate 20 wt% Pt nanoparticles (referred to as sample A) and 40 wt% Pt nanoparticles (referred to as sample B) on the electro-spun Pt nanowires. Subsequent addition of concentrated NaBH_4 solution as a reducing agent (100 mg/ml) resulted in the formation of Pt nanoparticles on the electro-spun Pt nanowires. After a 6h incubation period, the resultant samples were washed several times with de-ionized water and freeze-dried at -60 °C.

The morphology of the samples was characterized by scanning electron microscopy (SEM, Hitachi S-4100) and high-resolution transmission electron microscopy (HRTEM, TECHANI-F20). The crystallinity and structures of the samples were examined using X-ray diffraction (XRD, Rigaku x-ray diffractometer equipped with a Cu $K\alpha$ source). The chemical bonding states of the samples were analysed by X-ray photoelectron spectroscopy (XPS, using a VG Scientific (ESCALAB 250) spectrometer with an Al $K\alpha$ source). Electrochemical measurements of the samples were performed with conventional three electrode cells, which consist of the as-prepared samples (working electrode), Ag/AgCl (reference electrode), and Pt gauze (counter electrode). The test cells were continuously purged with nitrogen gas for 1h with stirring. Electrocatalyst inks consisting of catalysts and Nafion (8:2 weight ratio) were loaded onto the glassy carbon working electrode (0.07cm^2). The electrolytes used comprised an aqueous solution of 0.5M H_2SO_4 with 2M CH_3OH . The catalytic activities for methanol electro-oxidation of the samples were characterized by cyclic voltammetry (AUTOLAB by Eco Chemie) at a scan rate of 50 mV/s in the range of -0.2 to 1.0 V. Chronoamperometry tests were carried out at -0.5 V

versus Ag/AgCl in an aqueous solution of 0.5M H_2SO_4 with 2M CH_3OH , at room temperature.

3. Results and discussion

Fig. 1 shows the SEM images obtained from (a) the single Pt nanowire electrocatalysts, (b) 20 wt% Pt nanoparticle electrocatalysts composited on the electro-spun Pt nanowires (sample A), and (c) 40 wt% Pt nanoparticle electrocatalysts composited on the electro-spun Pt nanowires (sample B). Fig. 1(a) shows uniform Pt nanowires having a diameter of ~210-240 nm, fabricated by electrospinning (for comparative purposes). The Pt nanowires, as shown in Fig. 1(a), have a smooth surface. Figs. 1(b) and 1(c) show hetero-structured Pt nanowire electrocatalysts having diameters of ~ 226 - 279 nm, which implies the presence of small Pt nanoparticles composited on the electro-spun Pt nanowires. In particular, the small nanoparticles in Figs. 1(b) and 1(c) exhibit relatively bright regions, which could serve to promote superior electrocatalytic activity for the fuel cells. Overall, we fabricated two types of hetero-structured Pt electrocatalysts; the first comprises 20 wt% Pt nanoparticles composited on the Pt nanowires (sample A) and the other is composed of 40 wt% Pt nanoparticles composited on the Pt nanowires (sample B).

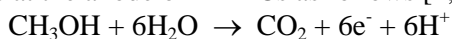
Fig. 2 shows the HRTEM images and TED (transmission electron diffraction) patterns of the samples. The single Pt nanowires fabricated by electrospinning exhibit smooth morphology in the edge regions as shown in Fig. 2(a). In the case of sample A and sample B, Pt nanoparticles on the electro-spun Pt nanowires are in the range of ~ 3-4 nm in size as shown in the insets of Fig. 2(b) and 2(c). These results indicate that sample A and sample B exhibit rough morphology on the electro-spun Pt nanowires due to loading of Pt nanoparticles. In other words, the hetero-structured Pt nanowire electrocatalysts, namely, Pt nanoparticles composited on the electro-spun Pt nanowires, exhibit better electrocatalytic activities due to the improved specific surface area when compared to the single Pt nanowire electrocatalysts. Furthermore, the TED patterns of the samples contain the diffuse ring pattern with spots around the (000) spot, indicating the polycrystalline nature of the samples.

Fig. 3 shows the XRD plots obtained for single Pt nanowires, sample A, and sample B. All of the samples exhibit diffraction peaks corresponding to

crystalline Pt at $2\theta = 39.7^\circ$, 46.2° , and 67.4° [JCPDS 04-0802, space group Fm3m[225]]. This implies that the crystalline Pt phases of the samples have an FCC structure. Furthermore, the peak intensity of the (111) plane at 39.7° is higher than the intensity of the (200) plane at 46.2° and the (220) plane at 67.2° . This implies that the samples grow mainly along the (111) plane rather than the (200) plane and the (220) plane, which would produce superior electrocatalytic activity due to improvement of the effective catalyst atoms.

To elucidate the chemical bonding states of the samples, we performed XPS examinations. Calibration on all spectral peaks was carried out using the C1s line (284.5 eV) as a reference for the charge collection. Fig. 4 shows that the Pt 4f core levels, which are composed of two pairs of doublets, exhibit Pt 4f_{7/2} and Pt 4f_{5/2} photoelectrons with peaks at ~ 71.2 eV and ~ 74.5 eV. This implies that the Pt phase exists as metallic Pt (0) states [9]. In addition, the second set of doublets observed at ~ 72.4 eV is related to Pt(II) states such as PtO and Pt(OH)₂ [10]. Furthermore, it seems that Pt-oxide states are formed from oxygen sources in the precursor solutions and by exposure of the samples to air for XPS examinations. As a result, although two different kinds of Pt-metallic atoms and oxygen atoms exist on the surface of the samples, the major contribution to methanol electro-oxidation in DMFCs comes from metallic atoms on the electrocatalysts. In other words, the zero-valent metallic states on the Pt phases primarily affect the efficiency of the electrocatalysts in DMFCs.

Fig. 5 shows the cyclic voltammograms (CVs) for methanol electro-oxidation/reduction with the single Pt nanowires, sample A, and sample B, which were characterized in the range of -0.2 to 1.0 V at a scan rate of 50 mV/s. The voltammograms of all three samples were measured in a solution mixture of 0.5M H₂SO₄ and 2M CH₃OH, in order to examine the catalytic activities for methanol electro-oxidation in DMFCs. For comparison, the single Pt nanowires were also used as electrocatalysts (anode) for DMFCs. As previously reported, methanol reacts with water to produce CO₂, 6 electrons, and 6 protons at the anode of DMFCs as follows [2, 11]:



A higher production of electrons is related to improved methanol electro-oxidation properties and

high-performance of DMFCs can be attained. As shown in Fig. 5, the cyclic voltammogram for methanol electro-oxidation consists of two peaks relative to forward peaks and backward peaks. Forward peaks are related to anodic current density and backward peaks to intermediate species such as CH₂OH, CHO, HCOOH, and CO. Therefore, the higher anodic current density corresponding to the forward peaks implies the higher methanol electro-oxidation of the electrocatalysts for DMFCs. The current densities of the single Pt nanowire electrocatalysts, sample A, and sample B are ~ 0.27 mA/cm², ~ 0.42 mA/cm², and ~ 0.56 mA/cm², respectively, at an accelerating voltage of 0.68 V. Notably, sample A and B represent higher anodic current densities, which are about 1.5 times and 2.1 times those of the single Pt nanowire electrocatalyst. This implies that sample A and B have better performance as electrocatalysts than the single Pt nanowires due to the small Pt nanoparticles (~ 3 -4nm in size) formed on the electro-spun Pt nanowires. In particular, the highest methanol electro-oxidation among the three samples was obtained with sample B. The improved methanol electro-oxidation exhibited by sample B with a higher loading of Pt nanoparticles can be attributed to the combined effects of higher specific surface area and improved electrolyte/electrode contact area. Fig. 5(b) shows the chronoamperometry profiles of the samples measured in a solution mixture of 0.5M H₂SO₄ and 2M CH₃OH at 0.5V for 500 s as a measure of electrochemical stability. All of the samples exhibit current degradation with increasing time. In particular, sample B exhibits slightly slower current degradation compared to sample A and the single Pt nanowires after 500 s. In other words, although all of the samples present similar oxidation current behaviour, resulting from the one-dimensional nanostructures, sample B shows the highest electrochemical stability among the three samples. Therefore, sample B exhibits superior methanol electro-oxidation catalytic activity and more stable electrochemical stability due to the combined effects of a higher specific surface area and improved electrolyte/electrode contact area. These results indicate that Pt nanoparticle electrocatalysts composited on Pt nanowires may lead to the fabrication of high-efficiency direct methanol fuel cells.

4. Summary

Pt nanoparticle electrocatalysts composited on electro-spun Pt nanowires were fabricated via an electrospinning method in combination with an impregnation method. The highest methanol electro-oxidation properties and best electrochemical stability were obtained at a catalyst loading of 40 wt% Pt nanoparticles, compared to single Pt nanowires and 20 wt% Pt nanoparticles, which can be attributed to the presence of the Pt nanoparticles resulting in the combined effects of higher specific surface area and improved electrolyte/electrode contact area. This implies that hetero-structured Pt nanowire electrocatalysts may be an important class of electrocatalysts for use in high-efficiency DMFCs.

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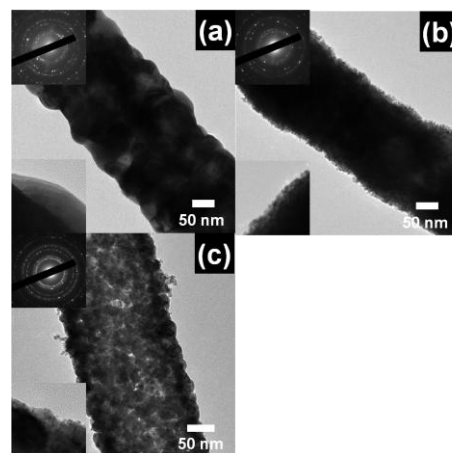


Fig.2. HRTEM images of (a) the single Pt nanowires, (b) sample A, and (c) sample B.

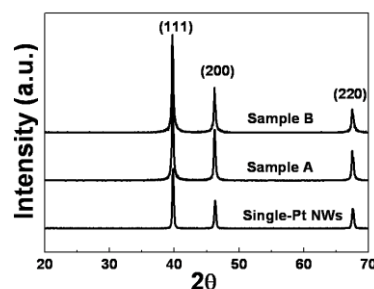


Fig.3. Powder XRD plots of (a) the single Pt nanowires, (b) sample A, and (c) sample B.

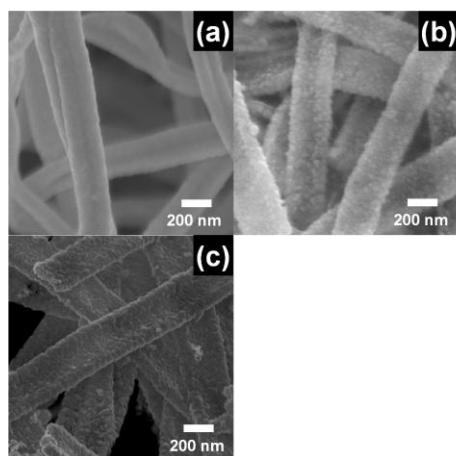


Fig.1. SEM images obtained from (a) the single Pt nanowires, (b) sample A, and (c) sample B.

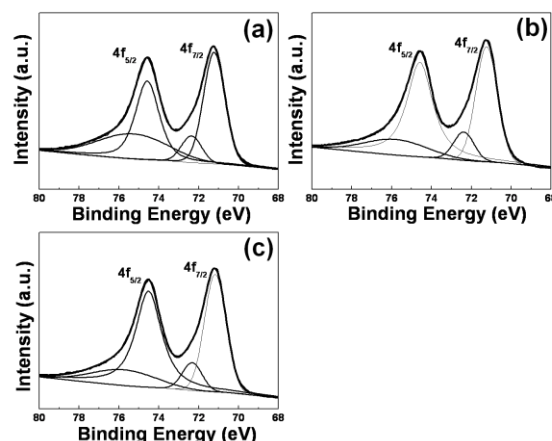


Fig.4. XPS spectra of (a) the single Pt nanowires, (b) sample A, and (c) sample B.

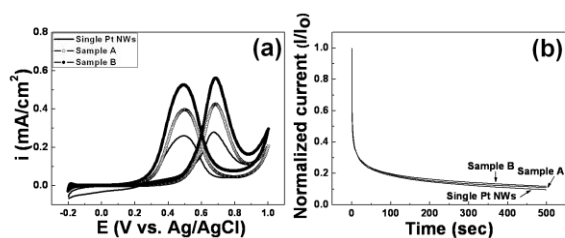


Fig.5. (a) Methanol electro-oxidation and (b) Chronoamperometry of the single Pt NWs, sample A, and sample B.

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