소형 직접 메탄올 연료전지를 위한 나노 합금 전극

Nanostructured Alloy Electrode for use in Small-Sized Direct Methanol Fuel Cells

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Abstract

PtRu alloy and PtRu-WO_3 nanocomposite thin-film electrodes for methanol electrooxidation were fabricated by means of a sputtering method. The structural and electrochemical properties of well-defined PtRu alloy thin-film electrodes were characterized using X-ray diffraction, Rutherford backscattering spectroscopy, X-ray photoelectron spectroscopy, and electrochemical measurements. The alloy thin-film electrodes were classified as follows: Pt-based and Ru-based alloy structure. Based on structural and electrochemical understanding of the PtRu alloy thin-film electrodes, the well-controlled physical and (electro)chemical properties of PtRu-WO_3 showed superior specific current to that of a nanosized PtRu alloy catalyst. The homogeneous dispersion of alloy catalyst and well-formed nanophase structure would lead to an excellent catalytic electrode reaction for high-performance fuel cells. In addition, the enhanced catalytic activity in nanocomposite electrode was found to be closely related to proton transfer in tungsten oxide using in-situ electrochemical transmittance measurement.

1. Introduction

The catalytic, physical, (electro)chemical, electronic and optical properties of nanostructure materials are extremely different from those of bulk materials. Because the size and structure of nanoparticles have a significant effect on catalytic reactions, well-controlled nanostructures are essential for achieving efficient catalysts and in the preparation of catalysts for use in fuel cells. In particular, direct methanol fuel cells (DMFCs) have attracted considerable interest because of a variety of merits such as low operating temperatures, ease of handling a liquid fuel, the high energy density of methanol, and applications to micro-sized fuel cells[1-4]. The excellent catalytic activity of platinum for methanol oxidation, especially, at low temperatures makes this metal electrocatalyst ideal for use as an anode in DMFCs. However, since pure platinum is readily poisoned by intermediates produced during methanol electrooxidation, at low temperatures, Pt-based alloy or nanocomposite catalysts by alloying or mixing platinum with 2^{nd} or 3^{rd}

elements need to be designed and synthesized[5,6]. In general, the CO poisoned platinum can be regenerated via the reaction of surface CO with oxygen species associated with an element such as ruthenium to yield CO_2. Accordingly, PtRu alloy structure is extremely essential for enhanced methanol electooxidation. In addition, many efforts have been reported to modulate composition and structure of PtRu alloy nanoparticles and investigate methanol electrooxidation in nanoparticles.

Recently, small-scale electronic devices ranging from small digital devices to micro-electromechanical systems (MEMS) have attracted considerable interest. Such devices can be fabricated on a small scale, that is, they must have a small mass and volume. Accordingly, the power source for these applications should be small-sized for on-chip or integration as well as have sufficiently available capability to operate the intended devices. More recently, the miniaturization of DMFCs, which uses methanol directly as a fuel source, has been the subject of intense study. The excellent catalytic activity of electrodes for small sized fuel cells is strongly dependent on the thin-film electrode structure such as a nanocomposite consisting of alloy nanophases in a porous material. We recently reported on a nanocomposite structure consisting of Pt nanophase and oxide matrix that provides enhanced catalytic activity. However, the use of conventional physical deposition methods for preparing two-phase electrodes containing nanometallic phases as catalysts and porous oxide to achieve effective catalysis and high-performance electrodes in fuel cell is difficult. Accordingly, a sputtering system comprised of a multigun *i.e.* individual guns for metal and oxide targets for alloy formation and nanocomposite structure would be ideal.

2. Experimental

The PtRu-WO_3 nanostructured alloy electrode was grown using an RF magnetron sputtering system. Indium tin oxides (ITO, Samsung Corning Co, Ltd) coated on transparent glasses were used as the substrate. Cu grids were also used as substrates for analysis by transmission electron microscopy (TEM). Pt, Ru and WO3 were used as the target materials. The base pressure was less than $5x10^{-6}$ torr and the working pressure was $5x10^{-3}$ torr for all films examined. Sputtering was performed under an atmosphere of inert Ar gas at 40 SCCM at room temperature (RT). The PtRu-WO_3 electrode was deposited for 2 min at RF powers of 20, 100 and 60 W on the Pt, Ru and WO_3 target, respectively. The Pt one-phase and PtRu thin-film electrode was deposited at an RF power of 20 W for Pt target, 20 and 100 W for Pt and Ru target, respectively, for 2 min. X-ray diffraction (XRD, Rigaku X-ray diffractometer equipped with a Cu K_α source) analyses of as-prepared electrodes was used to analyze the degree of crystallinity. In order to evaluate the performance of the electrodes, the I-V and I-t characteristic curves for the electrooxidation of methanol fuel in TFFCs were examined using conventional three electrode electrochemical system consisting of working, counter, and reference electrode at 25 °C. The deposited thin-film electrodes, Pt gauze, and Ag/AgCl were used as working, counter, and reference electrode,

respectively. All potentials were reported vs. normal hydrogen electrode (NHE) in this paper. The solution of 2.0 M CH_3OH in 0.05 M H_2SO_4 for methanol electrooxidation was stirred constantly and purged with nitrogen gas. All chemicals used were of analytical grade.

3. Results and Discussion

Alloy formation between Pt and Ru was confirmed by X-ray diffraction patterns, as shown in Fig. 1. The PtRu-WO_3 nanostructured and PtRu thin-film electrodes have a higher angle shift due to substitution of Pt with smaller-sized Ru atoms showing Pt-based face-centered-cubic structure without XRD peaks of any other elements. The angle of the (111) peak of the nanostructured alloy and thin-film electrodes is 40.5 and 40.4, respectively, compared with pure Pt (2θ=39.8). It has been reported that Pt can be alloyed with up to 60 at% of Ru to form a Pt-based crystalline structure.8 It has been well known that the PtRu alloy electrode is extremely superior to a pure Pt one-phase electrode in fuel cells, especially, direct methanol fuel cells that use methanol as a fuel. Accordingly, the alloy states may provide a highly efficient electrode for methanol electrooxidation in TFFCs [7,8]. However, in particular, the characteristic of an electrode for achieving excellent performance in TFFCs should contain not only an alloy such as PtRu but nanophases in the oxide as well. The multigun sputtering system was used to assist in the design and fabrication of the nanostrucutred alloy electrode as shown in Fig. 2. Figure 2(a) shows TEM images of a PtRu-WO_3 electrode fabricated using the multiguns sputtering system. The PtRu-WO_3 electrode formed using Pt, Ru and WO_3 targets consists of PtRu alloy nanophases of ~ 5 nm (dark region) and an amorphous, porous tungsten oxidative phase (relatively bright region). The ring pattern shown in the inset of Fig. 2(a) indicates the formation of PtRu alloy nanophases. Crystalline plane of the nanophases can be observed in high-resolution TEM image as shown in Fig. 2(b) suggesting that the crystallinity of PtRu alloy in the oxide is excellent. Compared to the (111) plane of 0.228 nm in the pure Pt, the distance of the (111) plane in the alloy nanostructured electrode is reduced to 0.224 nm, indicative of good alloy formation between Pt and Ru elements using the multigun sputtering system. Both composition of tungsten oxide in the PtRu-WO_3, determined by Rutherford backscattering spectroscopy and X-ray photoelectron spectroscopy, was 15 ~ 20 at %.

Figure 3(a) shows a plot of the current density for methanol electrooxidation with respect to the accelerating potentials for PtRu-WO_3, PtRu and Pt electrodes. The PtRu alloy electrode shows superior catalytic activity to that of pure Pt, that is, a higher current density, due to the alloy effect. However, more importantly, PtRu-WO_3 nanostructured alloy electrode shows the highest electrooxidation current density among the electrodes. The characteristic curve of current density as a function of time at the methanol oxidation potential of 0.6 V, as shown in Fig. 3(b), indicates the steady-state catalytic activity of methanol electrooxidation in TFFCs. The order of steady-state catalytic activity was found to be PtRu-WO_3 > PtRu > Pt. It is well known that the performance of electrodes in conventional fuel cells is strongly dependent on the active surface area of the nanometallic phases and the extent of alloy formation between Pt and 2^{nd} metals.

Accordingly, highly efficient performance for TFFCs can be realized by achieving an increased active surface area by nanophases and an improved catalytic activity of the alloy structure in nanostructured electrodes.

4. Conclusions

Alloy formation and the electrochemical properties of PtRu alloy thin-film electrodes could be modulated by appropriate control of the power of the sputtering guns. The PtRu-WO_3 nanocomposite thin-film electrode comprised of PtRu alloy nanophases with particularly selected composition and tungsten oxide showed excellent catalytic activity for methanol oxidation. The well-dispersed alloy catalyst and well-formed nanophase structure in the nanocomposite electrode would lead to a superior catalytic reaction at the electrode in a fuel cell. Furthermore, another important aspect of enhancement for methanol oxidation in the nanocomposite electrode was found to be the role of tungsten oxide, which is proven from an electrochromic phenomenon [8], in addition to the alloying and dispersion of the catalysts.

5. References

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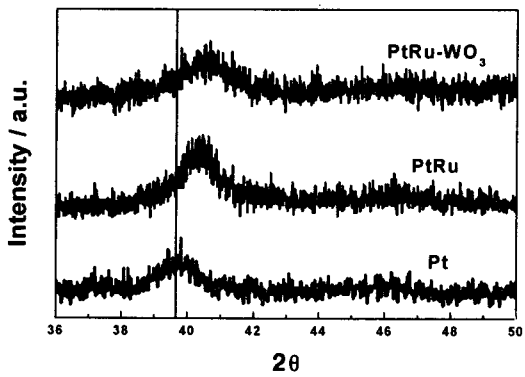

그림 **1.** X-ray diffraction patterns of Pt, PtRu, and PtRu-WO_3 deposited using sputtering or a multigun sputtering system. (The vertical solid line indicates original peak position of pure Pt in XRD pattern.)

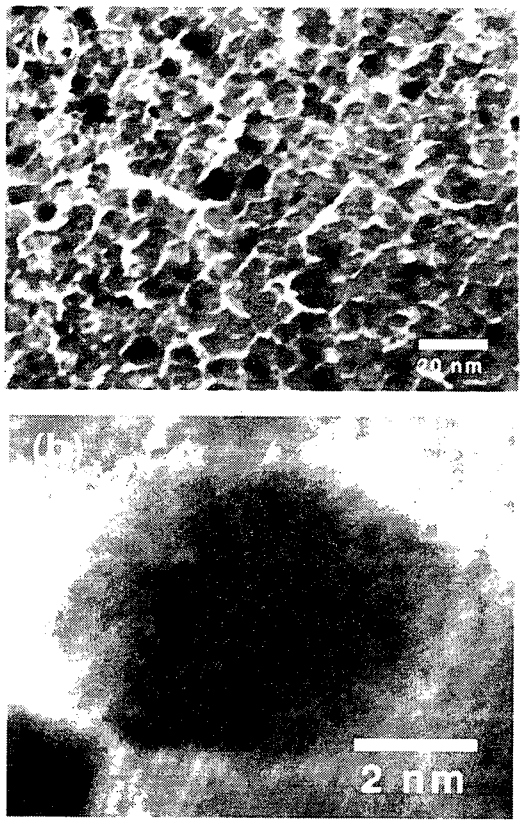

그림 **2.** (a) Transmission electron micrograph (TEM) image of a PtRu-WO_3 electrode deposited using the multigun sputtering system (The inset represents the ring pattern of the electrode by transmission electron diffraction (TED)) and (b) a high-resolution TEM (HRTEM) image consisting of nanocrystalline PtRu and amorphous WO_3 in a matrix.

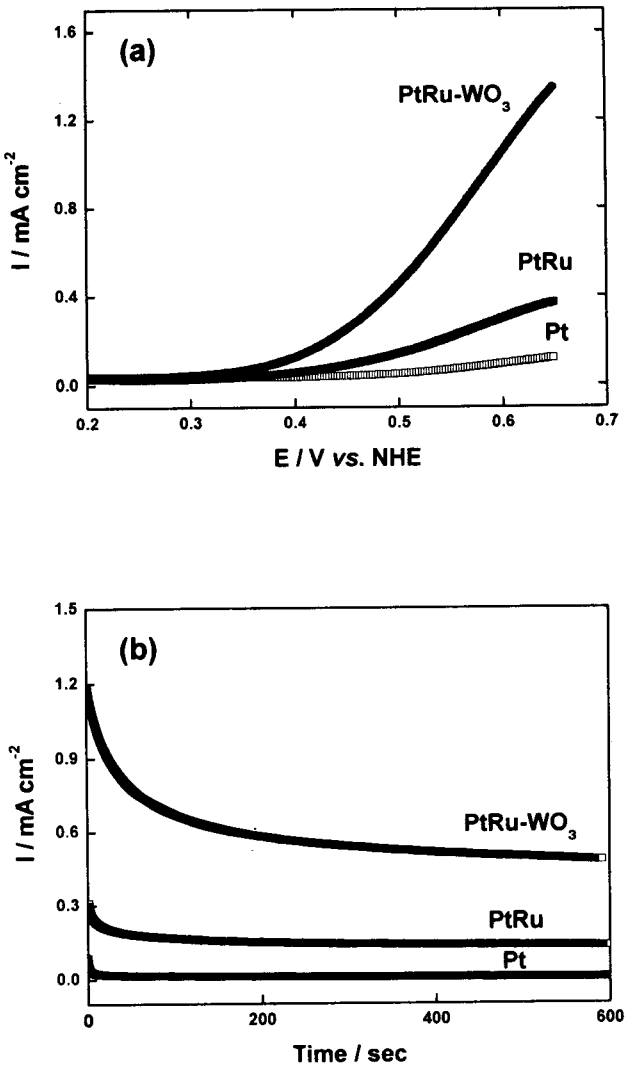

그림 **3.** (a) Current density *vs.* accelerating potentials for the PtRu-WO_3 nanostructured electrode, PtRu, and Pt thin-film electrode and (b) plot of current density *vs.* time at the oxidation potential of 0.6 V.