$PtRu-WO_3$ Alloy Nanocomposite Electrode for Methanol Electrooxidation by Sputtering Deposition Method

스퍼터링법을 이용한 $PtRu-WO_3$ 나노복합전극 제조

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1. Introduction

The excellent catalytic activity of platinum for methanol oxidation, especially, at low temperatures (<80 °C) makes this metal catalyst ideal for use as an anode in direct methanol fuel cells (DMFCs), which are currently of great interest because of a variety of advantages that include high energy density, ease of handling a liquid, and low operating temperatures. However, it is well known that a pure platinum is readily poisoned by CO, a by-product in methanol electrooxidation, at low temperatures. Accordingly, in order to enhance its catalytic activity for methanol electrooxidation by eliminating or inhibiting the CO poisoning effect, many efforts have been reported to design and synthesize Pt-based alloy catalysts by alloying platinum with 2nd or 3rd elements on the basis of a bifunctional mechanism, electronic, or an ensemble effect. 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. 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 WO_3 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. 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 Kαsource) 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 in TFFCs were examined using conventional three electrode electrochemical system consisting of working, counter, and reference electrode at 25 °C.

3. Results and Discussion

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 PtRu alloy thin-film electrodes were characterized (Figure 1). The alloy thin-film electrodes were classified as follows: Pt-based and Ru-based alloy structure. In particular, surface enrichment of Pt in the PtRu alloy thin-film electrodes was observed by X-ray photoelectron spectroscopy. Based on structural and electrochemical understanding of the PtRu alloy thin-film electrodes, the well-controlled PtRu-WO_3 was fabricated by means of sputtering system and, as shown in Figure 2, showed higher methanol electrooxidaion current compared 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 (Figure 3). In addition, the enhanced catalytic activity in nanocomposite electrode was found to be related to proton transfer in tungsten oxide using in-situ electrochemical transmittance measurement.

4. Conclusions

In conclusion, a PtRu-WO_3 nanostructured alloy electrode comprised of PtRu alloy nanophases and amorphous, porous tungsten oxide for use in highly efficient TFFCs was fabricated using multigun sputtering system. The PtRu alloy nanometallic phase and an amorphous tungsten oxidative phase in the PtRu-WO_3 electrode were confirmed by XRD and TEM analysis. The nanostructured alloy electrode showed the best performance for use in TFFC, compared with a PtRu thin-film and a Pt one-phase electrode. The highly efficient performance of the electrode in TFFCs can be attributed to the PtRu alloy nanophases in the porous oxide.

5. References

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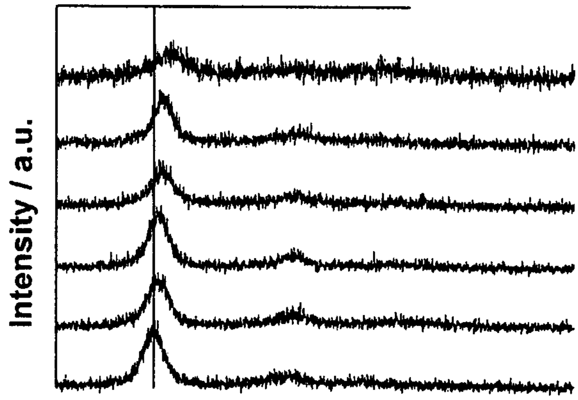

Figure 1. XRD diffraction patterns of PtRu alloy electrodes.

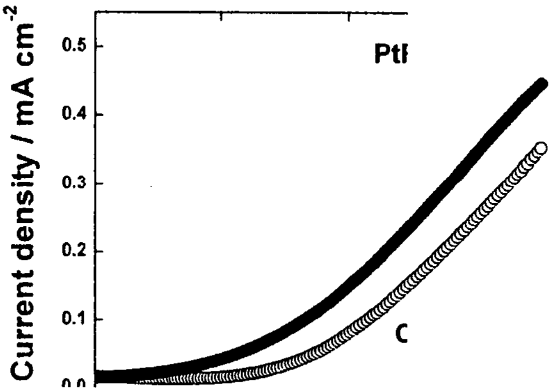

Figure 2. Current density vs. potential in the methanol oxidation region.

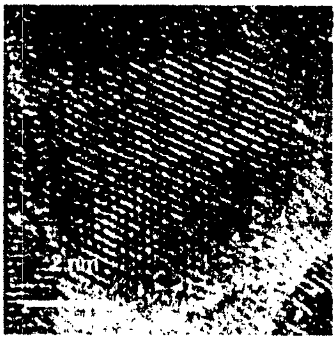

Figure 3. TEM image of PtRu nanophase in tungsten oxide matrix