

코스퍼터링법에 의한 박막형 전극 구조 개발

Development of Thin-Film Electrode Structure by Co-Sputtering Method

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1. Introduction

Recently, small-scale electronic devices ranging from small digital devices to MEMS have been the subject of considerable interest, since they are amenable for use in a variety of applications. Such devices will be fabricated on a small scale, that is, they must have a small mass and volume, which are not favorable for supplying electric power. 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. The electrodes for fuel cells generally consist of more than two phases such as nanosize noble metals (Pt) and porous materials (usually carbon powder and porous oxide), as an assistant or support for the metals¹. In this paper, a Pt-WO_x two-phase electrode using a co-sputtering system with two targets of Pt and WO₃ is reported and compared with the Pt one-phase electrode.

2. Experimental

Pt-WO_x two-phase films were grown using an RF magnetron co-sputtering system. Indium tin oxides (ITO, Samsung Corning Co, Ltd) coated transparent glasses were used as the substrate. Cu grids were also used as substrates for analysis by transmission electron microscopy (TEM). The Pt-WO_x two-phase film was sputter-deposited using the Pt and WO₃ target and was compared with Pt one-phase film that had been sputter-deposited. X-ray diffraction (XRD, Rigaku X-ray diffractometer equipped with a Cu K_α source) analysis of as-prepared electrodes was used for the analysis of crystallinity. In order to understand the utility of the co-sputtering method in the fabrication of TFFCs and to evaluate performance of formed electrodes, the I-V and I-time

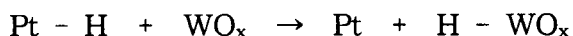
characteristic curves of the formed electrodes for the electrooxidation of methanol as a fuel in the TFFCs were examined using a conventional electrochemical measurement² with so-sputtered TFFCs electrodes as working electrodes in a solution of 2 M CH₃OH and 0.5 M H₂SO₄.

3. Results and Discussion

Figure 1 shows TEM image of Pt-WO_x two-phase electrode fabricated by the co-sputtering system. The Pt-WO_x two-phase electrode formed using both the Pt and WO_x targets consists of a nanosized Pt crystalline phase of 4 - 5 nm (dark points in the TEM image,) and an amorphous, porous tungsten oxidative phase (relatively bright region), indicating the formation of nano-metallic Pt phase with an excellent crystallinity, and not a Pt oxide phase, despite the oxide deposition by co-sputtering method. That is, the crystalline planes of Pt nano-metallic phase representing a lattice spacing of a polycrystalline structure (0.228 nm) is also observed in high-resolution TEM image (the inset of Figure 1) in contrast to the amorphous phase of oxide. Moreover, the existence of a Pt nano-phase dispersed with the oxide phase is characteristic of the Pt-WO_x two-phase electrode. The presence of a polycrystalline Pt nano-metallic phase and amorphous tungsten oxidative phase are confirmed by X-ray diffraction patterns. That is, Pt-WO_x two-phase electrode contains the structural properties of both the polycrystalline metal and amorphous oxide, consisting of two phases in one electrode layer. The possible origins of the Pt nano-metallic phase with an amorphous WO_x may be as follows: the prevention of migration of deposited Pt ad-atoms by the amorphous WO_x matrix and excellent unreactivity of Pt during co-sputtering at RT. Accordingly, the size of the nano-phases in the oxide matrix may be controlled by several experimental parameters such as the power of each target and the working pressure, studies of which are currently underway.

In general, the electrodes in conventional fuel cells require high-surface-area nano-metallic phases and matrix materials for supporting the nano-phases in order to produce an excellent power density (or current density) as the power source. Accordingly, the cell performance of the devices is mainly dependent on

the active surface area of the nano-metallic phases and the extent of interaction between metallic phases and support materials in one electrode layer. That is, the active surface area of electrodes in a device will increase the current density produced during any electrochemical process. The activity of the metallic phase can be improved and stabilized by support materials. The novel electrode structure consisting of a distinct mixture of nano-metallic phase and amorphous oxide matrix, as already seen in Figure 1, will lead to excellent performance of TFFCs, compared with a more dense thin film layer composed of one phase. Figure 2 (a) shows the current density for the electrodes versus the accelerating potentials for Pt-WO_x two-phase and Pt one-phase electrodes. The improved current density can be attributed to an enhanced activity of the nano-metallic phase. The characteristic curve of current *vs.* time at the methanol oxidation potential, representing the stability of the performance, is also shown in the Figure 2 (b). The superiority of the novel electrode to a conventional thin film electrode in the TFFCs may be responsible for the improved activity of the Pt metallic phase mixed with the porous oxide and synergy effects, such as the spill-over effect³ of porous tungsten oxides. The spill-over effect in the Pt-WO_x has been known as the following process:



In particular, transfer of proton, produced on platinum during electrooxidation process of methanol as fuel, into tungsten oxide would make platinum as clean active reaction sites and thus enhance electrooxidation current density.

4. Conclusions

In conclusion, an electrode structure comprised of two phases of Pt and WO_x was fabricated using a co-sputtering system. The co-existence of a polycrystalline Pt nanometallic phase and an amorphous, porous tungsten oxidative phase in the electrode layer was confirmed by TEM and XRD analysis. Due to the fact that the Pt metallic phase is mixed with the porous oxide and synergy effects such as the spillover effect caused by porous

tungsten oxides, the co-sputtered two-phase electrode showed excellent performance for use in TFFC, compared with the Pt one-phase electrode. Therefore, it would be expected that the co-sputtering method can be used to produce a mixed electrode composed of nano-crystalline noble metals and amorphous, porous oxides, such as Pt-WO_x, for use in TFFCs.

5. References

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Figure 1. Transmission electron micrograph of Pt-WO_x two-phase electrode deposited using the co-sputtering system consisting of nano-crystalline Pt and amorphous WO_x in a matrix.

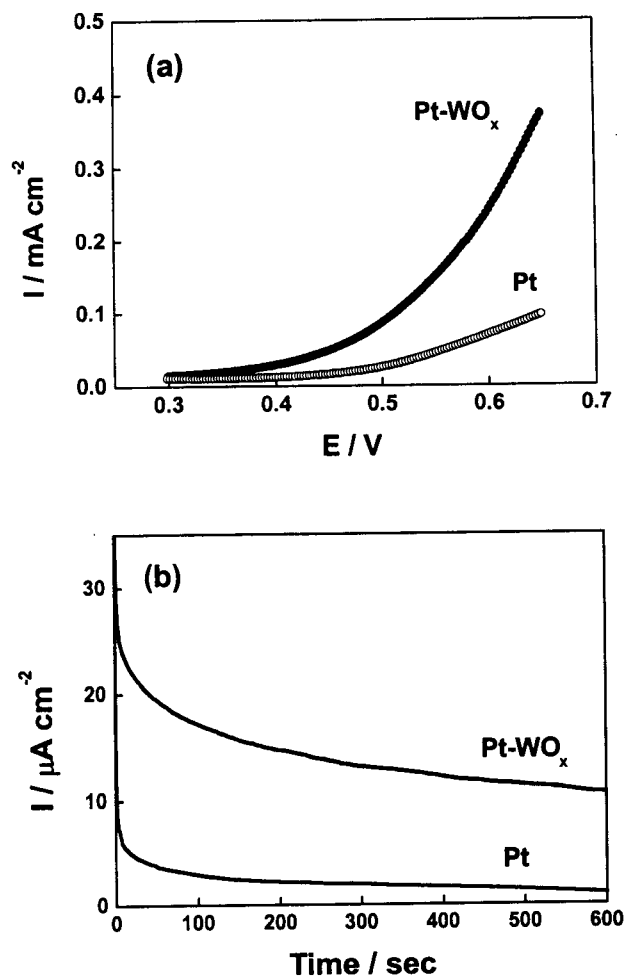


Figure 2. (a) Current density vs. accelerating potentials and (b) current density vs. time at the oxidation potential for the Pt-WO_x two-phase and the Pt one-phase electrode.