Pt-O 환원 반응을 이용한 연료 전지용 나노 다공성 Pt 촉매 합성

Synthesis of Nano-porous Pt by Thermal Reduction of Pt-O as Fuel Cell Cataysts

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1. Introduction

Ceramic fuel cells (CFCs) including solid oxide fuel cells (SOFCs) have attracted recent attentions because of their huge potentials for high conversion efficiency when combined with thermal energy utilization and fuel flexibility. Another advantage of CFCs is no need for liquid management as ceramic electrolytes that conduct ions through crystal defects in solid states and by-product water is generated in gas phase. High operation temperature of CFCs around 700~1000ºC, however, has limited practical usage. There are several efforts to reduce running temperature below 400ºC by employing thin electrolyte membranes or by replacing conventional zirconia-based electrolytes with other doped oxides which exhibits higher ionic conductivity [1-5]. At those intermediate temperature regimes, platinum (Pt) or Pt alloys are still the best-performing materials as catalysts.

To maximize surface kinetics during operation, it has been required to increase concentration of triple phase boundaries (TPBs) where fuels, ions, and electrons are in physical contact and charge transfer reactions dominantly take place. In this respect, a nano-porous structure is desirable for Pt catalysts on CFCs. In this work, we propose a novel method for fabrication of nano-porous Pt by sputtering in oxidizing environments forming Pt-O followed by thermal reduction as catalytic electrodes for solid SOFCs.

2. Experimental Details

Pt layers were prepared using DC sputtering on both cathode and anode for 80sec of sputtering time in order to grow about 80nm-thick layers. Pressure of the sputtering chamber was adjusted to 1, 5, and 10Pa in pure oxygen environments. The Pt layers were annealed at 600ºC in a reducing environment at a high-vacuum level (~10^{-6}Torr) for 2hours. To analyze oxidation and reduction states, x-ray photoelectron spectroscopy (XPS) was used in a SSI S-Probe monochromatized XPS spectrometer with Al (Kα) radiation (1486 eV). Commercial 100μm-thick 8% yttria stabilized zirconia wafers (CERAFLEX 8Y) were used as substrates. For performance evaluation, current-voltage (I-V) relations and maximum power densities were compared. For the I-V data collection, a Gamry FAS2 Femtostat system was used. Pure hydrogen was fed as fuel with the flow rate of 15sccm.

3. Results and Discussions

Using the XPS, we have confirmed that sputtering of Pt in oxygen environments produces mixture of Pt-O and metallic Pt while the reduced Pt layers mostly consist of pure metal. In the SEM images, we have observed that thermal reduction of the oxidized Pt introduces nano-scale pores (Fig. 1). It is interesting that sputtering with 1Pa of oxygen has formed completely dense layers. We suspect that the pores in the 1Pa layer are generated by desorption of trapped oxygen molecules or oxide ions. The 5Pa and 10Pa layers have preserved porous structures before and after the thermal annealing with slight increase of pore size presumably due to agglomeration of nano-particles. The I-V results have indicated that higher pressure improves the power output by about 10~12% as introduces finer pores with greater TPB density (Fig. 2).

4. Conclusions

As an effort to fabricate high performance catalytic electrodes for low temperature SOFCs, we successfully synthesized nano-porous Pt by sputtering with oxidation followed by thermal reduction. We speculate that the pores are produced by adsorption of trapped oxygen or thermal nucleation. We have also confirmed that pressure elevation during sputtering has enhanced fuel cell performance with finer pores and larger TPB density.

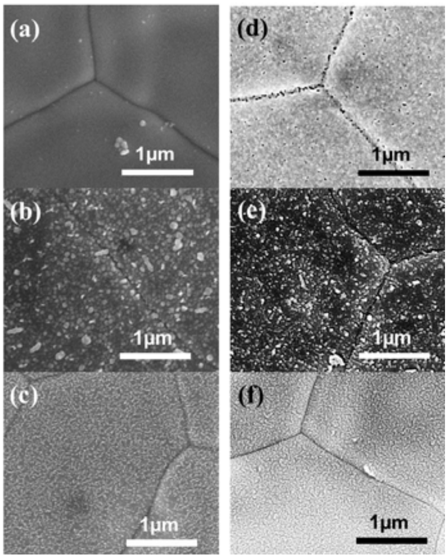

Fig. 1 SEM images of sputtered Pt with (a) 1Pa, (b) 5Pa, and (c) 10Pa of oxygen, and thermally reduced layers of (d) the 1Pa Pt, (e) the 5Pa Pt, and (f) the 10Pa Pt.

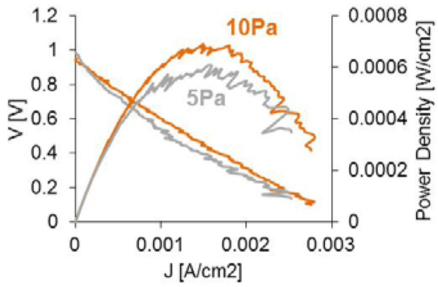

Fig. 2 I-V data of SOFCs with the nano-porous Pt sputtered at 5 and 10Pa of oxygen with post-annealing in high vacuum (10^{-6}Torr) at 400ºC.

Acknowledgements

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References

1. R. Doshi, V. L. Richards, J. D. Carter, X. P. Wang and M. Krumpelt, J. Electrochem. Soc., 146, 1273 (1999).
2. C. R. Xia and M. L. Liu, Solid State Ionics, 144, 249 (2001).
3. C. R. Xia, F. L. Chen and M. L. Liu, Electrochemical and Solid-State Letters, 4, A52 (2001).
4. J. H. Shim, C. Chao, H. Huang and F. B. Prinz, Chem. Mater., 19, 3850 (2007).
5. P. Su, C. Chao, J. H. Shim, R. Fasching and F. B. Prinz, Nano Letters, 8(8), 2289 (2008).