Nanophase Catalyst Layer for Direct Methanol Fuel Cells

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Abstract : Nanophase catalyst layer for direct methanol fuel cell has been fabricated by magnetron sputtering method. Catalyst metal targets and carbon were sputtered simultaneously on the Nafion membrane surface at abnormally higher gas (Ar/He mixture) pressure than that of normal thin film processing. They could be coated as a novel structure of catalyst layer containing porous PtRu or Pt and carbon particles both in nanometer range. Membrane electrode assembly made with this layer led to a reduction of the catalyst loading. At the catalyst loading of 1.5 mg PtRu/cm^2 for anode and 1 mg Pt/cm^2 for cathode, it could provide 45 mW/cm^2 in the operation at 2 M methanol, 1 Bar Air at 80°C. It is more than 30% increase of the power density performance at the same level of catalyst loading by conventional method. This was realized due to the ultra fine particle sizes and a large fraction of the atoms lie on the grain boundaries of nanophase catalyst layer and they played an important role of fast catalyst reaction kinetics and more efficient fuel path. Commercialization of direct methanol fuel cell for portable electronic devices is anticipated by the further development of such design.

초 록 : 마그네트론 스퍼터링 방법에 의하여 Nanophase의 촉매층을 형성하여 Direct Methanol Fuel Cell(DMFC)에 적용하였다. 일반적인 박막 증착 방법보다 높은 압력 (Ar/He 혼합기체)에서 금속 Target과 탄소 Target을 동시에 스퍼터링하여 내피온막 위에 직접 코팅함으로써 기공성 있는 PtRu 혹은 Pt 및 탄소입자를 포함한 새로운 구조의 촉매층을 형성하였다. 본 방법에 의하여 1.5 mg/cm^{2}의 PtRu(Anode) 및 1 mg/cm^2 Pt(Cathode) 로딩으로 2M Methanol, 1 Bar 공기, 80°C 조건에서 45 mW/cm^{2}의 출력을 얻을 수 있었으며, 이는 기존의 상용방법에 의하여 제조된 전극보다 같은 조건에서 30%의 성능향상을 제시한 것이다. 이는 Nanophase 촉매층 구조로 인하여 초미세 분말을 적용하였고, 많은량의 원자들이 입계에 배열하게 됨으로써 촉매반응을 원활하게 하고, 연료의 공급을 효율적으로 해준것에 기안한것으로 판단된다. 그러므로, 본 연구의 결과를 응용할 경우 DMFC를 휴대용 전자기기에 적용함에 있어서 성능향상 및 가격경쟁력 확보에 도움을 줄것으로 기대된다.

Key words : Nanophase, Sputtering, Catalyst layer, DMFC

1. Introduction

The development of environmentally benign, cost effective and efficient small fuel cells is one of the greatest challenges for materials scientists, industrial designers and portable electronics manufacturers. Portable applications of small fuel cells will be available by the technical achievement of PEMFC (Proton Exchange Membrane Fuel Cell) or DMFC (Direct Methanol Fuel Cell) since they are the fuel cells that can be operated in the ambient condition. Recently, the materials and processes for compact and light weight PEMFC operating at room temperature and atmospheric pressure without any peripheral such as compressor or humidifier has been developed for portable power sources.[1] Its energy density over 120 Wh/kg (including metal hydride can) showed the potential of its application to laptop computer.[2] However, fuel storage is still the bottleneck for the commercialization due to its volume and the problem of refilling. Thus, fuel cells employing liquid organic fuels are attractive as portable applications since the aqueous solution for fuel is oxidized at the anode while oxygen in the air is reduced at the cathode and the most developed liquid feed fuel cell is the DMFC.[3,4] It is competitive and even superior to advanced rechargeable batteries such as lithium polymer or sulfur batteries in the view of energy density and recharging matter. And, as the new concept of mobile multimedia devices (PDA, wearable computer etc.) is becoming realized, more powerful energy storage device is required and DMFC would be the solution for these applications. There are several technical problems concerning the realization of this technology into the market. The major issues are : (i) more efficient methanol oxidation catalyst design, (ii) methanol tolerant catalyst for cathode, (iii) methanol crossover resistant membrane, (iv) liquid diffusion electrode, (v) air breathing electrode, and (vi) compact cell pack design with methanol solution storage.

Novel catalyst layer design has to be proposed for more efficient MEA (Membrane and electrode assembly), so that both of the volume of cell pack and material cost of DMFC could be reduced. An estimation of power output and material cost has been simulated. By the conventional DMFC technologies, $20 is expected per cell pack (1000 mW for cellular phone), which is rather expensive comparing with

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battery pack and over 50% of this cost is coming from the catalyst (6 mg PtRu/cm^2 and 3 mg Pt/cm^2 for anode and cathode, respectively). Although at this large amount of catalyst loading, only 50 mW/cm^2 of power output is available when the cell is operated in 2 M methanol solution and air at room temperature. At this performance, only 10 mW/cm^2 could be achieved in the monopolar cell pack condition with air breathing operation instead of requiring 30 mW/cm^2 for talking mode in the cellular phone within the size of conventional rechargeable battery pack.

Recently, improvements of power performance were reported by utilizing sputtering method for catalyst coating.[5] An attempt to apply the catalyst layers by sputter deposition directly on both of membrane and electrode led an increase of catalyst utilization by two orders of magnitude and showed the possibility of reduction of the anode catalyst loading below 4 mg/cm^2 used in conventional MEA processing.[6] This paper also describes sputter deposited catalyst layer, but somewhat novel design of catalyst metals and carbon was studied for more efficient electrochemical reaction and fuel path in the catalyst layer by utilizing nanophase structures. Nanophases are materials with at least one dimension in the nanometer range, generally less than 100 nm. Because of their unique combinations of mechanical, physical and magnetic properties, they have received considerable attention in the past decade.[7,8] This novel structure was achieved by abnormally higher gas pressure of sputtering source (10^2 to 10^3 Pa) than normal thin film processing (10^{-1} to 10^{-2} Pa). Nanophase layer of catalyst and carbon processed with this method was characterized by TEM (Transmission Electron Microscopy), HREM (High Resolution Electron Microscopy) and it was tested as MEA of DMFC for measuring its polarization characteristics.

2. Experimental

2.1 Magnetron Sputtering of PtRu, Pt and Carbon

Nanophase particles of PtRu, Pt and carbon were loosely adhered to the surface of membrane directly by magnetron sputtering process. Shown in Fig. 1, ultra high vacuum chamber was evacuated to 10^{-6} Pa and filled with gas mixture of Ar and He and maintaining 100 Pa. Two-inch diameter PtRu alloy target was sputtered by dc magnetron at 300 W.

Nanophase PtRu was directly coated on the anode side of membrane (Nafion 115). Carbon target was simultaneously sputtered by rf magnetron at 400W and nanophase carbon was freely mixed with sputtered PtRu particles and deposited on the membrane surface. The membrane was fully dried by gel dryer before loading on the supporting jig in the chamber. Pt and carbon targets were also co-sputtered by the same method on the cathode side of membrane after flipping the membrane-supporting jig. The sputtering time and power could control the particle size and the loading amount of catalyst and carbon. Active area of catalyst on the membrane was decided by masking the membrane and it was 10 cm^2 in this experiment. The microstructure of nanophase catalyst layer was characterized by TEM (H-9000NA, Hitachi).
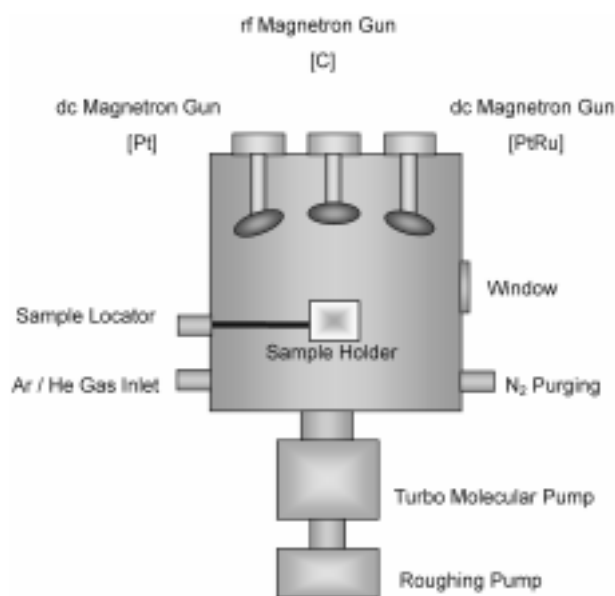

Fig. 1. UHV Chamber with Catalyst and Carbon Sputtering System.

These catalyzed membranes were sectioned by ultramicrotomy method,[9] so that the specimens of 60 nm thick could be prepared at the stroke rate of 1 mm/sec during the sectioning.

2.2 MEA Process and Polarization Test

Catalyzed membrane containing nanophase PtRu-C on the anode, Nafion 115 membrane for electrolyte and nanophase Pt-C on the cathode was hot pressed with 200 kgf/cm^2 of hydraulic pressure at 125°C for 3 minutes between the diffusion electrodes of both sides. Diffusion electrode was prepared with microporous layer of carbon/Teflon composite powder on the either side of porous carbon paper (Toray 060). The MEA (membrane and electrode assembly) was situated in the cell fixture and polarization characteristics were measured by fuel cell test station (GT500, Globetech) combined with electric load (Model 890, Scribner).

3. Result and Discussion

DC or RF magnetron sputtering at such high pressure was possible since the width of the dark space in the plasma is inversely proportional to the gas pressure so that the number of collisions between accelerating ions and gas atoms in the dark space is independent of the gas pressure. And it could provide the formation of porous and nanophase particles on the surface of membrane or electrode rather than the formation of a dense thin film. Also with the co-sputtering of carbon target, multi-phase of catalyst metals and carbon particles were coated directly on the interface of electrochemical catalytic reaction. This process enabled the catalyst layer containing catalyst and carbon particles both in nanometer range, so that a unique properties of MEA could be achieved due to its larger portion of catalytic reaction and more efficient liquid methanol or gaseous oxidant flow. Conventional catalyst supporting material such as carbon is now also in nanophase
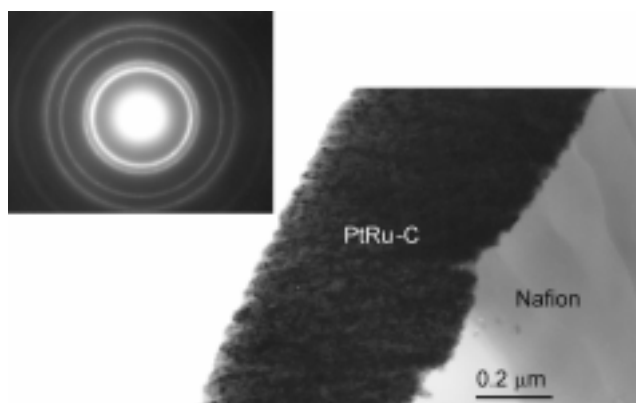
Fig. 2. Diffraction pattern from PtRu and TEM microstructure of cross-section of catalyst layer (PtRu-C) on the membrane.
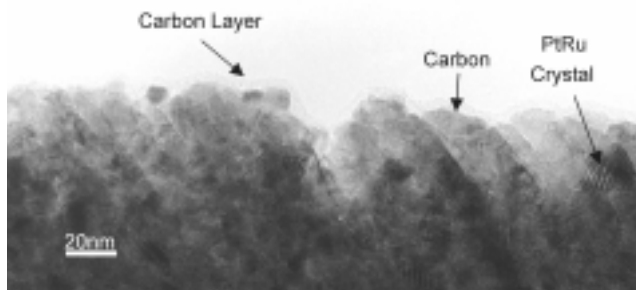

Fig. 3. HREM Microstructure of nanophase catalyst layer.

as the same size of catalyst so that the thickness of catalyst layer can be reduced. Because of the small particle sizes, a large fraction of the atoms (as high as 50%) lie on the grain boundaries. As a result, grain boundaries and interfaces played an important role of fast kinetics of catalyst reaction and

   Shown in Fig. 2 are the diffraction pattern from the dark field of nanophase catalyst and the microstructure of PtRu and carbon on the membrane. As seen on these micrographs, fine particles of catalyst and carbons are well dispersed and formed 250 nm thick layer. At this thickness, the catalyst loading was measured as 1.5 mg/cm^2. On the cathode, 1 mg/cm^2 of Pt was coated with carbon. Carbon was controlled as 20% by weight of total catalyst layer in both sides. Those individual particle sizes were measured in the Fig. 3 that shows an HREM microstructure of nanophase catalyst layer. Carbon layer on the surface is shown and it would give better electrical contact between catalyst layer and diffusion electrode. Ultra fine particles (5~10 nm) of PtRu and carbon was well dispersed and the nanocrystaline structure of PtRu is also shown in the micrograph. Because of the sputtering at high pressure, this catalyst layer was deposited loosely with pores in orthogonal direction of fuel path. And, it is thought that co-sputtering with carbon retarded the directional growth of PtRu. However, further studies on the gas pressure and the optimal combination of Ar/He will provide more appropriate structure of catalyst layer.

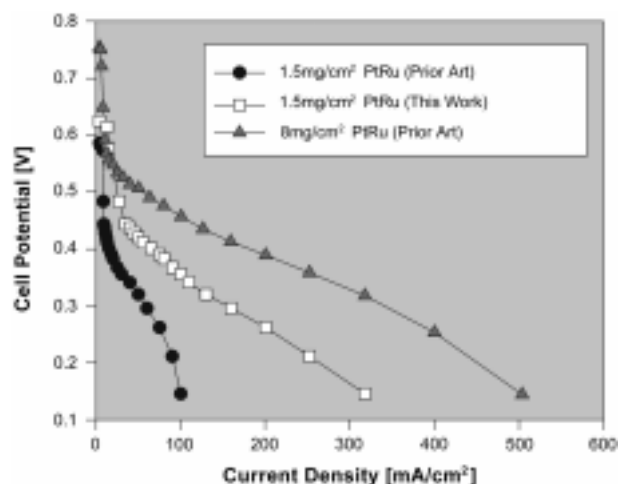   Polarization characteristics of MEA made of this catalyst

Fig. 4. Polarization characteristics of MEA made of nanophase catalyst layer in DMFC (Operating conditions: 2 M Methanol, 1 Bar Air, 80°C).
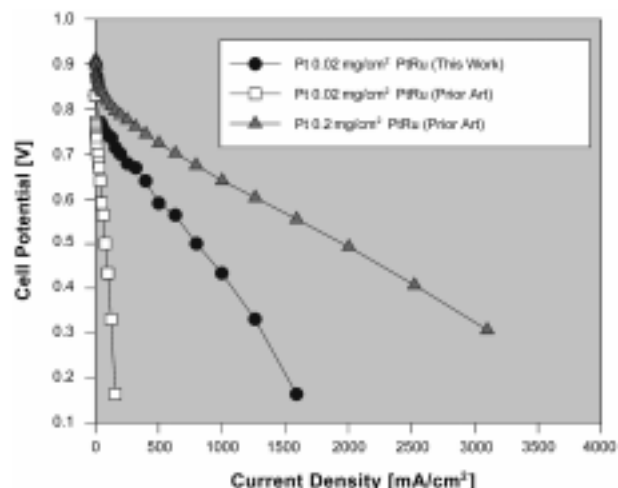

Fig. 5. Polarization characteristics of MEA made of nanophase catalyst layer in PEMFC (Operating conditions: Hydrogen/Oxygen, 1 Bar, 80°C)

layer are shown in Fig. 4. As seen on this curve, the MEA with catalyst electrode by spray coating of PtRu/C (prior art) showed near 300 mA/cm^2 at 0.3 V. At this prior art, the utilization of catalyst is still lower than expected, so that a large amount of precious catalyst has to be loaded. Nanophase catalyst layer that has nanophase carbon and PtRu of 1.5 mg/cm^2 showed 150 mA/cm^2. This power output showed the possibility of lowering the amount of catalyst loading as comparing to the performance of MEA having same amount of catalyst by prior art. The more efficient fuel path and reaction kinetics owing to the lowerd charge transfer resistance by novel nanophase catalyst layer is thought to be the role of this achievement. Comparing with the MEA having the same amount (1.5 mg/cm^2) of catalyst by prior art, this method provided the fast activation at the lower current range and the reducing the polarization by diffusion at the high current range due to the efficient fuel path. This effect is more sig-

nificant when this method is applied to the MEA (anode Pt catalyst loading 0.2 mg~0.02 mg by spray coating and this method) for PEM fuel cell operated by gaseous fuel, hydrogen, and it is shown in the Fig. 5.

4. Conclusion

The proposed nanophase catalyst layer has promising characteristics in the process and power performance. At the low amount of catalyst loading (1.5 mg PtRu/cm^2 for anode and 1 mg Pt/cm^2 for cathode), the power density of 45 mW/cm^2 at 80°C was achieved and ended up with 15 mW/cm^2 at room temperature. However, DMFC is still far away from the competence to the Li batteries as a commercial product. Further studies on the interface chemistry of catalyst layer and optimization of processing conditions will suggest the more improved microstructure that is good for either electrochemical catalytic reaction and the efficient fuel path. In this way, material cost and power density would not be the barrier for the realization of small DMFC for a power source of portable electronic devices.

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