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# The Effect of Two-Layer Cathode on the Performance of the Direct Methanol Fuel Cell

**Chanho Pak†, Seung Jae Lee, Seol-Ah Lee and Hyuk Chang**

Fuel Cell Program Team, Materials and Devices Research Center, Samsung Advanced Institute of Technology,
P.O. Box 111, Suwon, Gyunggi-do 440-600, Korea

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**Abstract**−To reduce the effect of methanol permeated from the anode, the structure of the cathode was modified from a single layer with Pt black catalyst to two-layer with PtRh black and Pt black catalysts, respectively. The current density of the direct methanol fuel cell (DMFC) using the two-layer cathode was improved to 228 mA/cm$^2$ compared to that (180 mA/cm$^2$) of the DMFC using the single layer cathode at 0.3 V and 303 K. From the cyclic voltammograms (CVs), it is indicated that the amount of adsorbates on the metal catalyst in the two-layer cathode is less than that of adsorbates in the single layer cathode after methanol test. In addition, the adsorbates were removed very rapidly by electrochemical oxidation from the two-layer cathode. It is suggested from *ex situ* X-ray absorption near edge structure analysis that the d-electron vacancy of Pt atom in the two-layer cathode is not changed by the methanol test. Thus, Pt is not covered with the adsorbates, which agrees well with the results of CV.

Key words: Direct Methanol Fuel Cell, Two Layer Cathode, PtRh, Pt, Methanol Crossover

## INTRODUCTION

Direct methanol fuel cell (DMFC) is a promising power source for portable electronic devices that require high energy density [Chang et al., 2002; Thomas et al., 2002] due to its features, which are high efficiency, low emission, and convenient charging or quick refueling. However, to commercialize the DMFC as real power source, many technical issues need to be resolved.

Among the all issues to solve, the anode catalyst with high methanol oxidation activity, the membrane with the low methanol and water permeability [Lee and Yi, 2004] and the cathode catalyst with the methanol tolerance are crucially required. To decrease the methanol crossover through the membrane, several methods have been studied. Such approaches are hybridization by making the inorganic particle in the membrane, nano composite with inorganic materials and proton conducting polymers, and metal thin films coated on the membrane [Kim et al., 2002; Ma et al., 2003; Miyake et al., 2001; Park, 2004]. However, as long as a proton is transferred with the aid of water dissociation at the polar groups in the membrane channel, the absolute 0% crossover of methanol is not attainable. Thus, the total cell potential is decreased due to the mixed potential caused by the simultaneous redox reaction of a proton and a methanol in the cathode. In addition, the oxidation of methanol at the cathode produces CO, which can be poisonous over the Pt catalyst. Thus, fast removal of excess methanol in the cathode is necessary to obtain high performance of DMFC.

Recently, Wei et al. reported that the performance of DMFC was improved by adopting multi-layers to the anode and the cathode electrodes [Wei et al., 2002]. The thin film electrode with under 5 μm thickness containing a PtRu/C catalyst, Nafion® or PTFE and $(NH_4)_2C_2O_4$ as the pore forming agent was prepared by hot press method. This additional layer was located between the catalyst layer and the membrane at both anode and cathode side. It was suggested that the thin film layer containing PtRu/C catalyst before the cathode could first oxidize the methanol permeated from the anode, and then eliminate the harmful effect of the methanol crossover on the Pt catalyst of the cathode.

Other bimetallic catalysts, such as PtSn [Morimoto et al., 1998], PtMo [Mukerjee et al., 1999] and PtRh [Koch et al., 1976; de Souza et al., 2002; Ross et al., 1975] systems, can also show high activities for the methanol oxidation and have been studied as anode catalysts of the DMFC and CO tolerant catalysts for the proton exchange membrane fuel cell. However, the PtRh catalyst was only studied for methanol oxidation long time ago [Koch et al., 1976; Ross et al., 1975]. It was suggested that the PtRh system exhibited higher activity than that of Pt alone [Ross et al., 1975]. Recently, de Souza and coworkers reported that the electrochemical oxidation of ethanol of the PtRh electrode showed higher activity than that of Pt and Rh monometallic catalyst. They also reported that the activity of PtRh catalyst was dependent on the alloy composition [de Souza et al., 2002].

In this paper, it is shown that the insertion of new catalyst layer with PtRh catalyst between membrane and Pt catalyst layer in the cathode increases the performance of the DMFC. It was suggested that the improved performance of the two-layer electrode compared to the single layer electrode containing only Pt catalyst is attributed to the fast removal of adsorbed species on the catalyst surface in the cathode. This agreed well with the results obtained from the cyclic voltammetry and *ex situ* X-ray absorption near edge structure.

## EXPERIMENTAL

Commercial PtRu black and Pt black catalysts were purchased from Johnson Matthey. Nafion® 115 membrane was obtained from DuPont. The PtRh black catalyst, which has 2 : 1 atomic ratio, was synthesized by the solution reduction method as follows [Lee et al., 2003]: Each of $H_2PtCl_6$ and $RhCl_3$ was dissolved in doublely

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†To whom correspondence should be addressed.
E-mail: Chanho.Pak@samsung.com

deionized (DI) water. After 2 h stirring, aqueous solutions of $H_2PtCl_6$ and $RhCl_3$ were mixed and stirred for two more hours. The aqueous solution containing a reducing agent such as $NaBH_4$ was added into the above solution. A black powder was produced and dispersed in the solution. After hydrogen gas was fully evolved, the precipitated black powder was rinsed by DI water to remove the excess $NaBH_4$ and other remaining contaminants. After freeze-drying of washed black powder, the PtRh black catalyst was obtained.

The catalyst ink was prepared by dispersing the black catalyst in the alcohol solution with ionomers. The catalyst ink was sprayed onto the carbon paper to form the electrode. Four cathodes were prepared. First is the single layer with Pt black catalyst (3 mg/cm$^2$ Pt) as the reference cathode (Pt-MEA). Second and third are the two-layer cathodes, which consist of one layer with Pt catalyst (3 mg/cm$^2$ Pt) on the diffusion layer, and the other layer with PtRh catalyst (1 mg/cm$^2$ and 2 mg/cm$^2$ PtRh) (PtRh1-MEA and PtRh2-MEA, respectively) covered on the layer containing Pt catalyst. Fourth is the single layer cathode using the PtRh catalyst (3 mg/cm$^2$ PtRh) for the sole purpose of comparison (Rh-MEA). The anode was prepared by using PtRu black catalyst with 8mg/cm$^2$. The combination of different cathode, membrane and same anode provides the four different kinds of membrane electrode assembly (MEA).

The single cell test was conducted by using the MEA with 10.5 cm$^2$ of the reaction area at 303 K with 2 M-methanol solution and the air. Potential vs. current density plots were obtained by potentiodynamic measurement from open circuit voltage to 0.1 V.

The cyclic voltammetry was carried out using the same single cell set-up before and after the electrochemical reaction with methanol. To investigate the catalyst behavior with respect to the methanol oxidation, nitrogen was passed through the cathode for 1 h before and after the methanol reaction. At the same time, nitrogen was passed through the anode and was swapped with hydrogen to serve as the RHE (reference hydrogen electrode) reference and the counter electrode. The cyclic voltammetric measurements were made in the potential range of 0.05 to 0.9 V vs. RHE at a sweep rate of 20 mV/s.

After the electrochemical experiment, X-ray absorption spectra of Pt $L_{III}$ were recorded by *ex-situ* with transmission mode at beamline 7C at the Pohang Accelerator laboratory (PAL) using Si (311) double-crystal monochromator. The analysis of X-ray absorption spectra was performed by the standard procedure [Teo, 1986]. In the X-ray absorption near edge structure (XANES), the first inflection points of all samples were adjusted and aligned to the edge energies of the Pt foil.

## RESULTS AND DISCUSSION

The X-ray diffraction (XRD) as shown Fig. 1 of PtRh black catalyst was conducted by the X-ray powder diffractometer using Cu $K_\alpha$ source. There is no evidence of peaks related to Rh oxide and Rh in the XRD pattern. The PtRh (220) diffraction peaks in the PtRh catalyst were shifted slightly to 68.35° from that (67.52°) of Pt (220) from JCPDS (Joint Committee on Powder Diffraction Standards) card, which indicated that PtRh alloy was formed. The average crystalline size is determined as 3.4 nm from the PtRh (220) reflection by using Scherrer's equation [Arico et al., 1996].

Fig. 2 shows the single cell performance with 2 M-methanol and air displaying the effect of different cathodes. These curves are obtained at 303 K using the 2 M-methanol with 3 times of stoichiometric amount and excess air. The current densities measured at 0.3 V were 180, 201, 228 mA/cm$^2$ for Pt-MEA, PtRh1-MEA, and PtRh2-MEA, respectively. The overall performance of the single cell was improved by modifying the structure of the cathode from the single layer to the two-layer as well as increasing the amount of PtRh catalyst in the additional layer. Thus, it is easy to explain that the improved performance of MEA with the two-layer cathode was caused by increasing the total amount of Pt in the cathode electrode. However, as shown in Fig. 2 a, the Rh-MEA with cathode having only PtRh black catalyst (3 mg/cm$^2$) displayed very low performance curve compared to that of the Pt-MEA, which suggests the pure PtRh alloy catalyst has very low activity for the oxygen reduction reaction. So, it is suggested that the increase in the performance of PtRh-MEAs is related to the additional layer of the PtRh black catalyst on the Pt catalyst layer.

To elucidate the effect of the additional PtRh layer on the performance of the DMFC, cyclic voltammetry was measured before and after 2 M-methanol test. Fig. 3 shows the anodic portions of

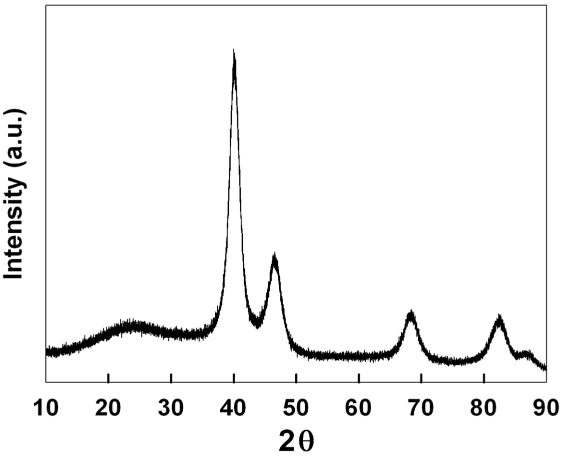

**Fig. 1. XRD of PtRh black catalyst.**

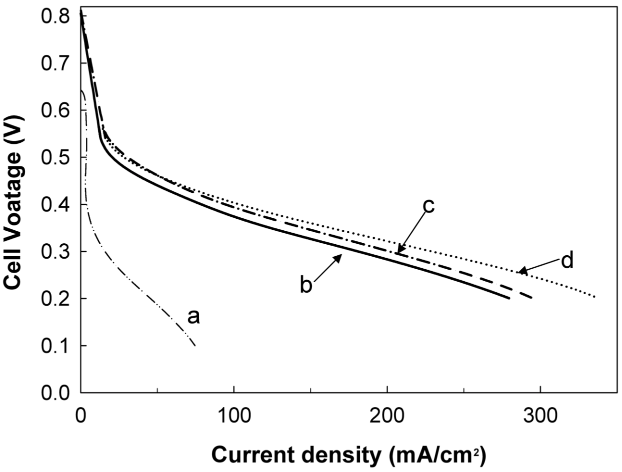

**Fig. 2. Cell voltage as a function of current density for DMFC single cell with (a) Rh-MEA, (b) Pt-MEA, (c) PtRh1-MEA and (d) PtRh2-MEA at 303 K. See the text for a detailed description.**

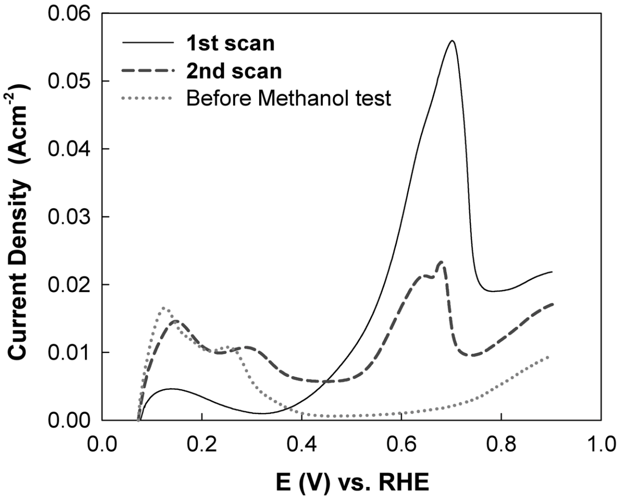

**Fig. 3. Cyclic voltammogram at 20 mV/s on DMFC single cell from the cathode in the Pt-MEA before and after methanol test at 303 K.**

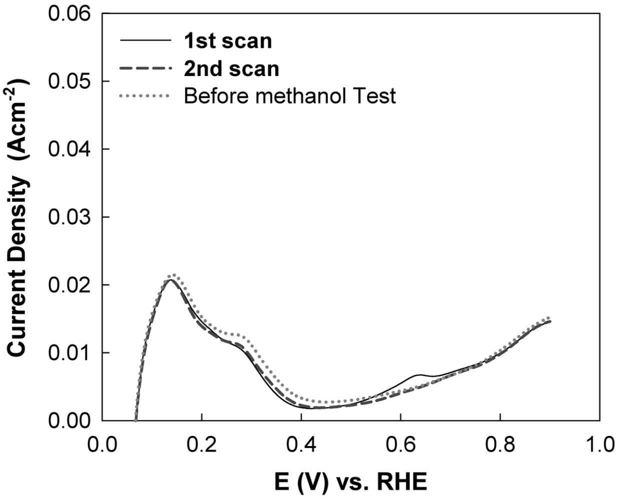

**Fig. 4. Cyclic voltammogram at 20 mV/s on DMFC single cell from the cathode in the PtRh1-MEA before and after methanol test at 303 K.**

the cyclic voltammograms (CVs) corresponding to the CO oxidation process of the single layer Pt cathode before and after the methanol test. Before the test, the typical CV of Pt catalyst was displayed [Elliott et al., 1999; Umeda et al., 2003]. Two desorption peaks of H atom were observed in the range of 0.05 V to 0.4 V as shown in Fig. 3. The electrochemically active surface area of the Pt catalyst in the cathode was obtained from the total charge required for the hydrogen desorption from the catalyst surface assuming a value of 220 μC/cm$^2$ for the oxidation of atomic hydrogen [Lee et al., 1998]. Before the 2 M-methanol test, the active surface area of the Pt catalyst in the cathode in the Pt-MEA was 11.9 m$^2$/g. The active surface area was decreased to 2.0 m$^2$/g after the 2 M-methanol test. As shown in Fig. 3, desorption peaks corresponding to adsorbates on the metal surface were observed between 0.5 and 0.8 V in the CV. So, the decrease in the active surface area can be attributed to the adsorbed species on the Pt surface during the methanol test. The adsorbed species would be intermediates such as $CH_2OH$-, CHOH-, COH-, CHO- or carbon monoxide [Lee et al., 2003; Markovic et al., 1995], which are produced by the oxidation of methanol permeated through the membrane on the Pt surface in the cathode of MEA. In Fig. 3, a weak shoulder was observed at around 0.65 V during the oxidation of adsorbates on the Pt surface. Moreover, a large desorption peak was displayed at around 0.7 V. In general, CO oxidation on the Pt surface occurs in the range of 0.7 V to 0.74 V in the CV [Friedrich et al., 2002; Lee et al., 1999]. Thus, it is indicated that another species in addition to CO was adsorbed on the Pt surface during the oxidation of methanol permeated from the anode. Another species is indicated obviously from CV obtained during the second scan. Two oxidation peaks were observed at 0.65 V and 0.68 V, respectively. The second peak could be assigned to the oxidation of the CO and the first peak could be assigned to another intermediate species. However, the total area of desorption peaks from the adsorbates between 0.6 V to 0.8 V was decreased significantly. It means the adsorbates can be removed by the electrochemical oxidation from the Pt surface.

Fig. 4 shows CV of the cathode in the PtRh1-MEA before and after 2 M-methanol test. Before the test, it was very similar to that of the cathode in the Pt-MEA. The active surface area of the metal catalyst in the PtRh1-MEA was 13.1 m$^2$/g, which is slightly larger than that of the Pt-MEA cathode. At the first scan of the CV after the test, significant differences were observed between the cathode in the Pt-MEA and PtRh1-MEA, respectively. After the methanol test, the active surface area of the metal catalyst in the PtRh1-MEA was decreased slightly to 12.6 m$^2$/g, which indicates that the adsorption of intermediates on the metal catalyst in the cathode of PtRh1-MEA is not significant.

The desorption peak from adsorbates in the range of 0.5 V and 0.8 V is very small compared to that of the cathode in the Pt-MEA as shown in Fig. 3. The peak from the oxidation of adsorbates is centered on 0.62 V. Assignment of this peak is difficult because alloying of Pt with other metal atoms could reduce the oxidation potential of CO to below 0.6 V [Friedrich et al., 2002]. The CV from the cathode in PtRh1-MEA was almost recovered to the original CV after the second scan as shown in Fig. 4. On the other hand, desorption peak of the adsorbates on the Pt surface in the Pt-MEA remained after many scans as shown in Fig. 3. It is suggested that the removal of the adsorbates is faster at the cathode of the PtRh1-MEA than the cathode in the Pt-MEA. In the literature, PtRh shows the enhanced activity for methanol oxidation than the Pt alone and this behavior was correlated with the ease of oxygen adsorption on the Rh metal [Ross et al., 1975]. It is also well known that Rh is used in the three-way catalyst to remove CO and NO simultaneously under low concentration of oxygen [Bedrane et al., 2002]. Also, Rh has very suitable oxygen bond energy [Santra et al., 2002] within the 320-390 kJ mol$^{-1}$ to activate the oxygen, which could oxidize the CO in the oxygen atmosphere [Novakova et al., 2001]. Recently, de Souza and coworkers reported that alloying Rh with Pt improved the selectivity for $CO_2$ of the electrochemical oxidation of ethanol [de Souza et al., 2002]. Taking into account from the above results and properties of Rh described in the literatures, it is suggested that the improvement of the single cell performance by modifying the structure of the cathode is attributed to the enhanced oxidation of

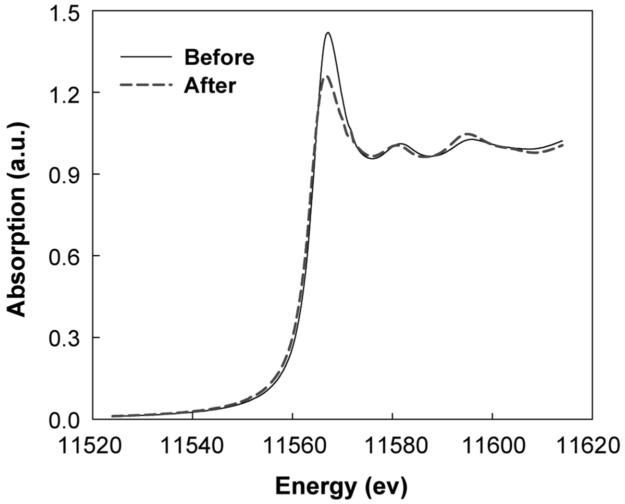

**Fig. 5. XANES spectra at Pt $L_{III}$ edge before and after 2 M-methanol test of the cathode in the Pt-MEA.**

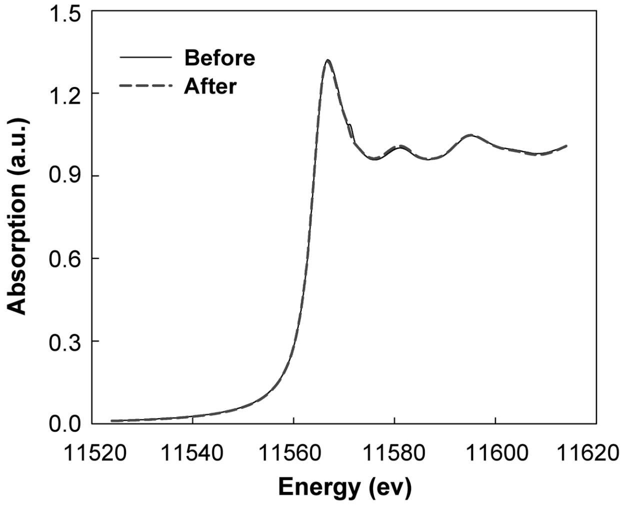

**Fig. 6. XANES spectra at Pt $L_{III}$ edge before and after 2 M-methanol test of the cathode in the PtRh1-MEA.**

the methanol permeated from the anode and the fast removal of contaminants, especially CO, produced during the methanol oxidation. Thus, the Pt catalyst in the cathode of the PtRh1-MEA can maintain the activity for the oxygen reduction reaction.

In Figs. 5 and 6, the XANES spectra at Pt $L_{III}$ edge from cathodes of the Pt-MEA and PtRh1-MEA are shown before and after 2 M-methanol test. The white line is defined as the large peak appearing right after the absorption edge. This is caused by the electron transition from core 2p states to unoccupied 5d states of Pt atom. Thus, the area of the white line is related to the electron density of valence state of Pt atom. This area is usually changed by alloying Pt with other metal atom or by adsorbed species on Pt atom [O'Grady et al., 2001; Russell et al., 2001; Viswanathan et al., 2002]. For the cathode in the Pt-MEA, the white line of Pt edge was decreased after the methanol test as shown in Fig. 5, which indicates that an adsorbed species still existed on the surface of the Pt. However, the white line of Pt edge from the cathode of PtRh1-MEA was not changed before and after the methanol test as shown in Fig. 6. Such result indicates the electronic state of Pt is not affected by the oxidation of the methanol permeated from the anode. It was also suggested that there are no adsorbates on the Pt atom, which agrees well with the results from the CV.

## CONCLUSION

Improved performance in the DMFC was observed when the structure of cathode in the MEA was changed from the single layer having a Pt catalyst to the two-layer structure having an additional PtRh catalyst layer coated on the Pt catalyst layer. From the cyclic voltammetry, the differences between the single layer electrode and the two-layer electrode were the active surface area of the metal catalyst after the methanol test and the removal speed of adsorbates from the metal. The active surface area for the cathode in the Pt-MEA was decreased from 11.9 to 2.0 $m^2/g$ after the methanol test. However, those from the cathode in the PtRh1-MEA were almost maintained as 13.1 and 12.6 $m^2/g$ after the methanol test. Also, it was suggested that the adsorbates were removed very rapidly in the cathode of the PtRh1-MEA than the cathode of Pt-MEA.

In the case of Pt atom at the cathode in Pt-MEA, d vacancy investigated by XANES was decreased by the adsorption of intermediates produced from the methanol oxidation. However, d vacancy of Pt atom at the cathode in PtRh1-MEA was not affected by the methanol test. This result was agreed well with the result from the CV.

It is suggested that the DMFC performance is improved by the oxidation of the methanol permeated from the anode and the recovery of bare Pt surface by the fast removal of adsorbates in the additional PtRh layer in the cathode of the PtRh1-MEA, which is located between the membrane and the Pt catalyst layer.

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