

Short communication

Current density dependence on performance degradation of direct methanol fuel cells

Min Ku Jeon, Ki Rak Lee, Kwang Seok Oh, Dae Sik Hong, Jung Yeon Won, Shuang Li, Seong Ihl Woo*

Department of Chemical and Biomolecular Engineering & Center for Ultramicrochemical Process Systems, Korea Advanced Institute of Science and Technology, 373-1, Yuseong, Daejeon 305-701, Republic of Korea

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Abstract

A stability test on direct methanol fuel cells (DMFCs) was carried out at current densities of 100, 150, and 200 mA cm⁻². Each test lasted for 145 h in the three cases. X-ray diffraction, energy dispersive spectroscopy, and scanning electron microscopy were used for analysis of the membrane electrode assemblies (MEAs). The maximum power densities were 93.9, 79.9, and 55.1% of the initial value after operation at 100, 150, and 200 mA cm⁻², respectively. A PtRu black catalyst with an original particle size of 3.3 nm was used for the anode electrode. For the MEAs operated at 100, 150, and 200 mA cm⁻², the PtRu particle sizes increased from the original size to 3.4, 3.9, and 4.2 nm, respectively, while a Pt black catalyst used for the cathode electrode did not change in size. Dissolution of the Ru was observed, and the ratio of (Pt:Ru) changed from (53:47) in the case of the fresh MEA, to (54:46), (56:44), and (73:27) for the MEAs after operation at 100, 150, and 200 mA cm⁻², respectively. The equivalent weight of the NafionTM membrane increased from a weight of 1264 g for a fresh membrane, to a weight of 1322, 1500, and 1945 g with the increases in operating current density to 100, 150, and 200 mA cm⁻², respectively.

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1. Introduction

Direct methanol fuel cells (DMFCs) are currently being widely studied for possible applications as portable power sources, such as in personal digital assistant devices, cellular phones or notebook computers, because of their high energy density and the easy handling of a liquid fuel [1]. Intensive study on the DMFCs including the activity increase of electro-catalysts [2], the search for and analysis of catalysts by new methods [3–6], the synthesis and modification of membrane materials [7], and the optimization of MEA preparation methods [8] have been carried out, and a large amount of progress regarding the performance of MEAs has been achieved over the last decade. Now that the commercialization of DMFCs has commenced, however, long-term stability, a key factor which can potentially determine the success or failure of DMFC usage,

has not yet been sufficiently investigated. In a few relevant studies, Yi et al. have reported a 30% performance degradation after a 75 h operation [9], while Thomas et al., demonstrating a 2000 h operation, suggested that the performance degradation found in his study originated from a slow drop in anode activity [10]. However, there have been very few reports on the current density dependence of the performance degradation.

In the present study, a long-term stability test of a DMFC was carried out at different constant current densities of 100, 150, and 200 mA cm⁻² each for 145 h. Pt and PtRu black catalysts, which are state-of-the-art catalysts in DMFCs, were used as cathode and anode catalysts, respectively. The MEAs were analyzed by X-ray diffraction (XRD) for particle size and for the study of any phase change. Composition changes in the PtRu catalyst were studied by using energy dispersive spectroscopy (EDS). Scanning electron microscopy (SEM) was used for analysis of surface morphology. The change of SO₃H in the NafionTM membrane was determined by a back-titration method.

* Corresponding author. Tel.: +82 42 869 3918; fax: +82 42 869 8890.
E-mail address: siwoo@kaist.ac.kr (S.I. Woo).

2. Experimental

2.1. Preparation of MEA

Pt black HiSPEC1000 (Johnson Matthey, UK) catalyst ink and PtRu black catalyst HiSPEC6000 (Johnson Matthey, UK) catalyst ink were prepared with deionized water, isopropyl alcohol and a Nafion ionomer solution as cathode and anode catalysts, respectively. The catalyst inks were repeatedly put through sonication and stirring to ensure a homogeneous mixing; they were then sprayed on PTFE films until the loading of the catalysts was measured to be 2 mg cm^{-2} . The sprayed PTFE films were dried for 24 h and hot-pressed for 3 min with a NafionTM 115 membrane at 120°C at 1000 psi in order to transfer the catalyst layers of the PTFE films to the Nafion membranes. The MEAs were tested with a 4 cm^2 active area cell. The cells were activated with a methanol solution set at 55°C overnight before the test.

2.2. Operation and analysis of MEA

Each single cell was operated at different constant current densities of 100, 150, and 200 mA cm^{-2} . Methanol (1 M) and dry oxygen were fed into the anode and cathode at a flow rate of 1 ml min^{-1} and 100 cc min^{-1} , respectively. The cells were maintained at 55°C for 145 h. An XRD analysis was carried out before detaching the catalysts from the used MEAs. Titration of the NafionTM films was performed after detaching the catalysts from the MEAs. The separated films were dried in a vacuum at 60°C for 12 h and then immersed in a NaOH solution for 24 h. The NaOH solution was titrated by using an HCl solution.

3. Results and discussion

Fig. 1 shows the polarization curves before and after operation for 145 h at (a) 100, (b) 150, and (c) 200 mA cm^{-2} . The open circuit voltage (OCV) did not show significant changes in the cases of the 100 and 150 mA cm^{-2} operations, while that of 200 mA cm^{-2} operation dropped from 0.617 to 0.475 V ($\pm 0.5\%$), indicating a significant increase of methanol crossover. Maximum power densities were reduced to 93.9, 79.9, and 55.1% of the initial value after operation at 100, 150, and 200 mA cm^{-2} , respectively, for 145 h. This result shows that the performance degradation of DMFCs was accelerated with an increase in the operating current density.

Fig. 2 shows the XRD pattern of (a) Pt (cathode) (b) PtRu (anode) catalysts, respectively, as a function of the operating current density. For the Pt catalysts, a formation of a new phase or a peak shift was not observed. In addition, the full-width at half maximum (FWHM) did not change with the operating current density, indicating that there was no agglomeration of the Pt catalysts during operation. The particle size, calculated using the Debye–Scherrer equation, was on average 9.1 nm for the all samples. In contrast to the Pt catalyst, a peak shift to lower 2-theta was observed in the PtRu catalysts. The peak at 40.4° moved to 40.3 , 40.2 and 39.8° ($\pm 0.04^\circ$) when operated at 100, 150, and 200 mA cm^{-2} , respectively. In addition, the average

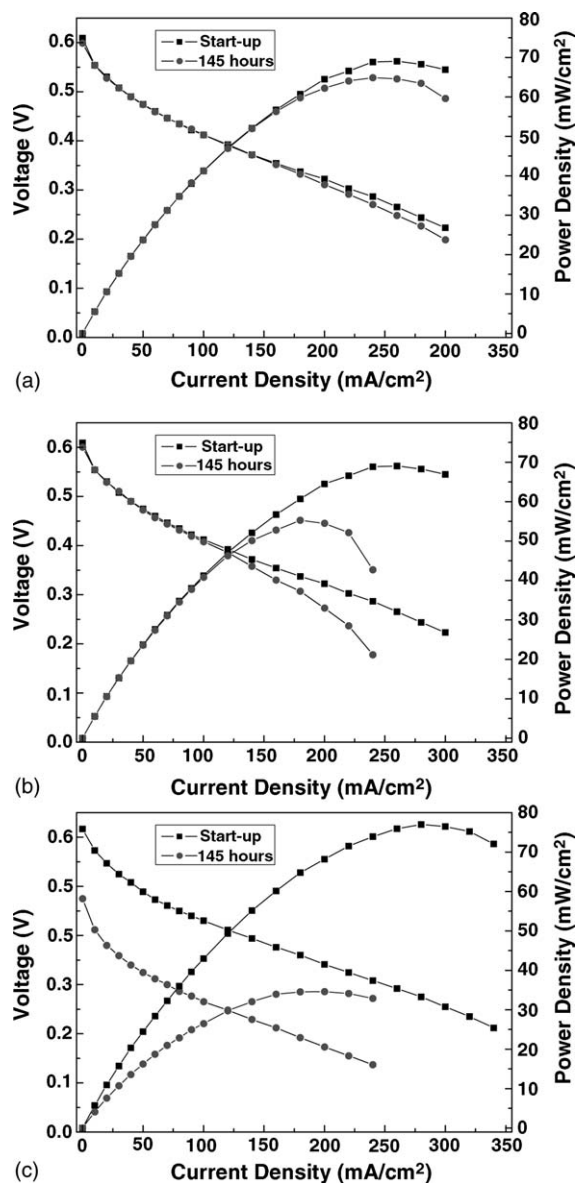


Fig. 1. Performance of single cells before and after operation for 145 h at (a) 100, (b) 150, and (c) 200 mA cm^{-2} .

particle size increased from 3.3 nm to 3.4, 3.9 and 4.2 nm ($\pm 1\%$) after operation at 100, 150, and 200 mA cm^{-2} , respectively. This agglomeration of PtRu particles means that there was a decrease in surface area, which resulted in a decrease of power density. The particle size difference in the Pt and PtRu catalysts was the main cause of the different sintering characteristics, because the small PtRu particles are easier to move than the large Pt particles. Agglomeration of catalysts, also reported in previous studies, occurred in this study as well. In the previous study, the average particle size of the PtRu/C catalysts increased from 7.1 to 15 nm, while the change in the Pt/C catalysts was not significant, after operation at 100 mA cm^{-2} for 75 h [9].

In the EDS analysis, the ratio of (Pt:Ru) changed from (53:47) in the case of the fresh MEA, to (54:46), (56:44), and (73:27) ($\pm 0.1\%$) for the MEAs operated at 100, 150, and 200 mA cm^{-2} , respectively. This result shows that dissolution of Ru occurred

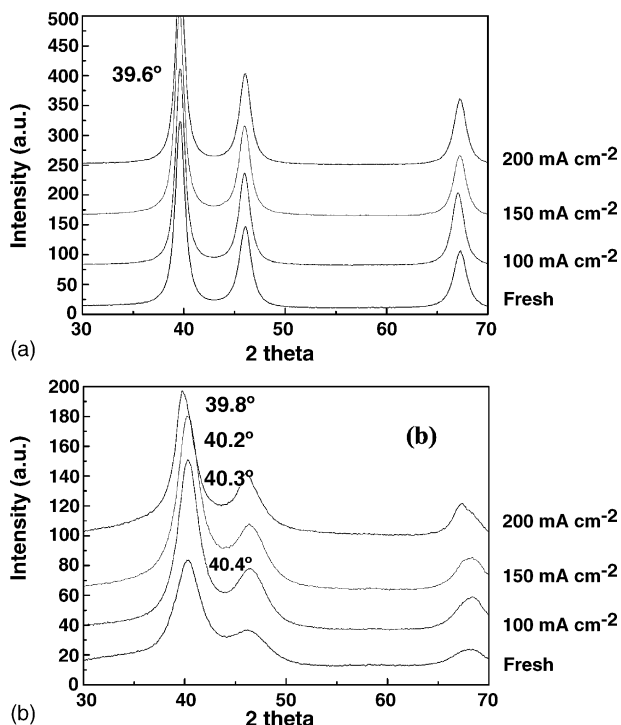


Fig. 2. X-ray diffraction results of (a) Pt (cathode) and (b) PtRu (anode) catalysts.

during the operation and that the rate of the dissolution was accelerated with each increase in operating current density. This change of anode electrode is in good agreement with a previous report, which suggested that the origin of the performance degradation is a slow drop in the anode activity [10]. An especially fast dissolution of the MEA operated at a current density of 200 mA cm⁻² explains the significant degradation of power density. The main cause of the Ru dissolution is considered to

be the formation of formic acid as a by-product. In a methanol oxidation reaction, formaldehyde and formic acid are the principal by-products, and formic acid can react with Ru [7]. A higher current density means a higher power density in the operation condition of this paper. Therefore, a high current density indicates a fast methanol oxidation reaction and the formation of formic acid. Dissolution of Ru was also reported in previous studies, where it was shown that dissolution of Ru occurs in an OCV condition and is accelerated by applying current [11].

Fig. 3 shows the SEM results of the Pt black catalysts: (a) fresh, and after operation at (b) 100, (c) 150, and (d) 200 mA cm⁻² for 145 h. A change in surface morphology was not observed for the Pt black catalysts. Fig. 4 shows the SEM results of the PtRu black catalysts: (a) fresh, and after operation at (b) 100, (c) 150, and (d) 200 mA cm⁻², each for 145 h. In spite of the Ru dissolution and the reduced performance, the dispersion of the catalyst particles still exhibited a very good particulate property.

Proton conductivity of the Nafion membrane originates from the SO₃H. A change of equivalent weight (eq. wt.), defined as the required weight of Nafion for 1 mol of SO₃H, was determined by a back-titration method. The eq. wt. increased from 1264 g for a fresh NafionTM, to 1322, 1500, and 1945 g for the MEAs operated at 100, 150, and 200 mA cm⁻², respectively. This result shows that the NafionTM membranes lost SO₃H during the operation, and that the rate of the SO₃H loss was faster in higher current densities.

In summary, performance degradation in the DMFCs was accelerated with an increase in operating current density. An increase in particle size, and dissolution of Ru was observed from the PtRu catalysts. In addition, the eq. wt. of the NafionTM membrane increased with the increase in operating current density. Since a DMFC is a complicated electrochemical system, these

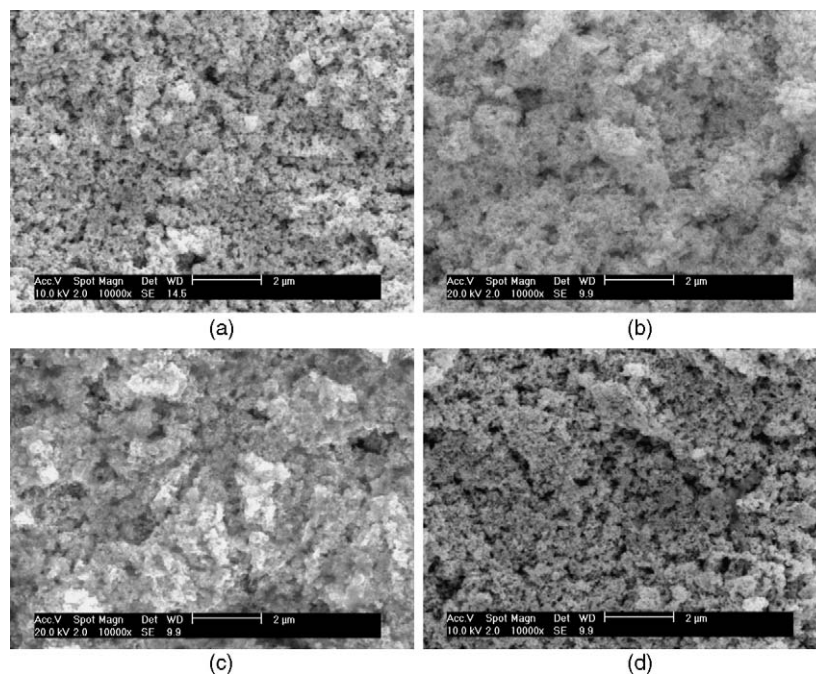


Fig. 3. Scanning electron microscopy images of Pt (cathode) catalysts: (a) fresh and after operation at (b) 100, (c) 150 and (d) 200 mA cm⁻² each for 145 h.

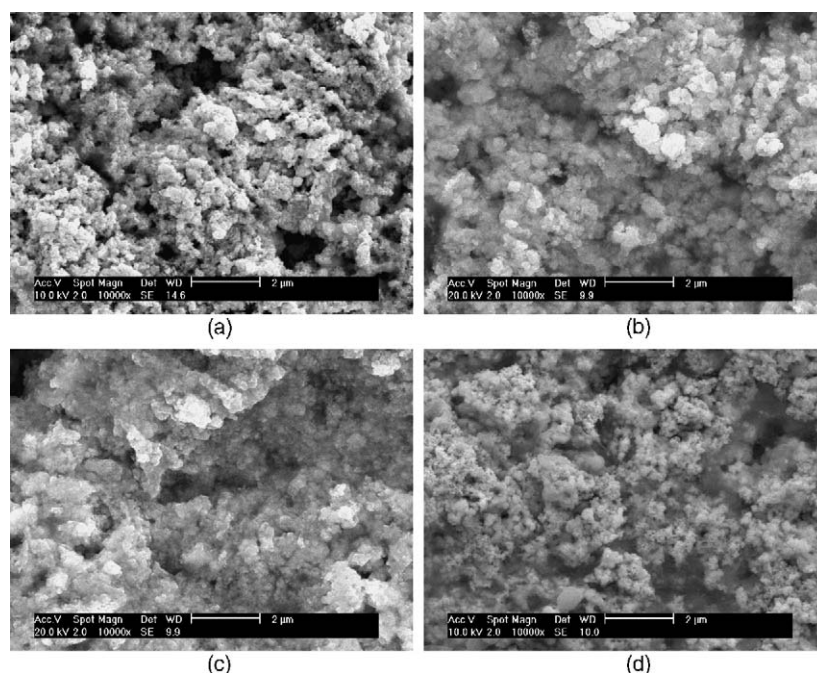


Fig. 4. Scanning electron microscopy images of PtRu (anode) catalysts: (a) fresh and after operation at (b) 100, (c) 150 and (d) 200 mA cm⁻² each for 145 h.

changes cannot explain the origin of the performance degradation completely; however, they are considered to be the main cause of the performance degradation and of the operating current density dependence.

4. Conclusions

Performance degradation of direct methanol fuel cells was studied at different operating current densities. Maximum power density decreases to 93.9, 79.9, and 55.1% of the initial value were obtained after operation for 145 h at 100, 150, and 200 mA cm⁻², respectively. An agglomeration of the anode catalyst (PtRu) was observed, while there was no change in the cathode catalyst (Pt). Dissolution of Ru was studied by an EDS, and the rate of dissolution was found to accelerate with an increase in operating current density. Finally, the equivalent weight of the NafionTM membrane increased with the increase in operating current density.

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