



Degradation of Membrane Electrode Assemblies utilizing PtRu Catalysts under High Potential Conditions



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H I G H L I G H T

- The degradation of MEAs utilizing PtRu was studied by using an accelerated test.
- Ru crossover from anode to cathode significantly influenced the cell performance.
- The amount of Ru deposition in cathode isn't proportional to that of Ru dissolution.
- A recovery method for MEA in which Ru is deposited in cathode was investigated.
- A recovery method can recover cathode performance to a remarkable extent.

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We investigated the degradation of membrane electrode assemblies (MEAs) utilizing PtRu catalysts by way of an accelerated anode degradation test (anode potential cycling) that simulated localized fuel starvation. We predicted that anode potential would be high (approx. 1.4 V vs. RHE) when localized fuel starvation occurred during start-up of the stack. Although the dissolution of Ru in the anode increased with increasing upper potential limits in anode potential cycling that simulated localized fuel starvation, the Ru crossover from anode to cathode and Ru deposition in the cathode reached a maximum at an upper potential limit of 1.2 V. In addition, we investigated a method for restoring the performance of MEAs deteriorated by Ru deposition. With this method more than 90% of cathode performance (H_2-O_2 voltage) and 79% of H_2 -Air voltage can be recovered.

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1. Introduction

Proton Exchange Membrane Fuel Cells (PEMFCs) show great promise as energy sources of the future. They convert chemical energy to electrical energy with significantly greater efficiency than conventional combustion processes and are environmentally friendly. We have been developing residential 1 kW co-generation systems utilizing PEMFCs [1–3] and installing them in Japan (over 1000 systems/year). Cost and durability are the keys to commercial success. At present, however, there is limited information available on the failure modes of PEMFCs, and the causes and mechanisms of degradation have not yet been clarified.

Catalyst degradation is one of the most important issues associated with PEMFCs. Generally speaking, the cathode catalysts consist of Pt or Pt–Co metal alloys supported on high surface area

carbon. Many researchers have reported on the degradation of these catalysts. Migration [4,5] and dissolution–redeposition [6–8] of Pt have been reported as major Pt/C degradation mechanisms. Moreover, degradation of the carbon support is also known to shorten the lifespan of a PEMFC [9,10].

Limitations in current reforming technology make it difficult to produce clean hydrogen cost-effectively, so the presence of CO in the fuel gas is normally unavoidable in reformat-based fuel cell systems. When pure Pt is used as the anode catalyst for a fuel cell system running on fuel gas that contains CO, functionality is reduced significantly due to poisoning by CO. It has been reported that CO-tolerance of the catalyst improves when Pt is alloyed with another metal or metals such as Ru, Sn, Fe, Mo or Au [11–19]. Ru-containing catalysts, such as PtRu alloy and PtRu metal oxides, are generally used as anode catalysts due to their ability to remove the adsorbed CO reaction intermediates that form during electrochemical oxidation of CO-containing hydrogen [11–14]. Even though the performance potential is greater with PtRu catalysts than with Pt and other Pt alloy catalysts, we must factor in the degradation of Ru when using PtRu

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catalysts. In MEAs utilizing PtRu catalysts, it is thought that there are two primary mechanisms of degradation. One is dealloying and dissolution of Ru in the anode, which reduces Ru concentration in the PtRu and leads to a decline in CO-tolerance. Compared to Pt, Ru is unstable, especially under high potential conditions [20,21]. The other is Ru crossover, a phenomenon in which dissolved Ru moves from anode to cathode through the membrane. The effects of Ru contamination on the kinetics of the oxygen-reduction reaction (ORR) have also been reported previously [22–24]. For instance, Gancs et al. observed an 8-fold decrease in ORR kinetics with 18% Ru coverage in an O₂-saturated 0.5 mol dm⁻³ H₂SO₄ solution [22]. Ru deposited on the cathode was also found to lower the ability of the cathode to tolerate methanol, which is known to crossover from the anode to the cathode in DMFCs [23]. However, little had been reported on the fact that Ru crossover is a key degradation mechanism in PEMFCs using reformate-based fuel, in which there can be problems of air getting into the anode, or of localized fuel starvation.

Recently, Cheng et al. reported a 40% drop in ORR current at 0.9 V with 20% Ru deposition, and in addition to the impact on cathode performance, a significant drop in CO tolerance was found with Ru degradation. They detected Ru deposited in the cathode using CO stripping voltammetry and double-layer capacitance of cyclic voltammetry [24–26]. Although these studies of Ru crossover assumed an anode potential of less than 0.9 V (vs. RHE) in the start/stop cycle, we think the potential of the start/stop cycle in the stack could be significantly higher, especially in conditions of localized fuel starvation, and thought a method to recover the performance of cathodes degraded by Ru deposition was needed.

In this study, we investigated the degradation of MEAs utilizing PtRu catalysts by way of an accelerated anode degradation test that simulated localized fuel starvation. Moreover, a method for recovering the performance of MEAs deteriorated by Ru deposition was examined.

2. Experimental

2.1. Preparation of MEA

The membrane electrode assembly (MEA) was prepared by hot pressing both the anode and the cathode catalyst onto a membrane. Both catalyst layers consisted of a catalyst and a Perfluorocarbon sulphonic acid polymer (PFSA) electrolyte. The cathode catalyst was PtCo/C (Pt:Co = 3:1 (atomic ratio), Pt content: 50%, Tanaka Kikinzoku Kogyo, Tokyo Japan) and the anode catalyst Pt–Ru/C (Pt:Ru = 2:3 (atomic ratio), Pt content: 30%, Tanaka Kikinzoku Kogyo, Tokyo Japan). A PFSA membrane with a thickness of 50 μm was used as the electrolyte material. The MEA was 25 cm² in active area.

2.2. Single cell test

The fuel cell experiments were performed in a single cell and carried out at 70 °C (cell temperature: $T_{cell} = 70$ °C), atmospheric pressure, and 100% inlet relative humidity (anode dew-point temperature, $T_{da} = 70$ °C, cathode dew-point temperature, $T_{dc} = 70$ °C). The fuel-air utilization ratios were 75% and 55%, respectively, and the current density was 0.3 A cm⁻². The fuel used was a simulated reforming gas (SRG), consisting of 80% H₂, 20% CO₂ and 0–50 ppm CO (H₂ balance), or pure hydrogen. 0.5% air was added to the fuel for the air bleed test.

2.3. Accelerated anode degradation test

The accelerated anode degradation tests and cyclic voltammetry (CV) were conducted using a potentiostat with a power unit (HZ-5000 system, HOKUTO DENKO, Japan). Anode potential cycling was

used as the accelerated anode degradation test. The single cell test and CVs were performed before and after the accelerated anode degradation test. CVs were measured under H₂ (anode, 100 mL min⁻¹) and N₂ (cathode, 100 mL min⁻¹) at a scan rate of 5 mV s⁻¹. The stable CVs were recorded after potential scanning for 3 cycles.

2.4. Characterization of catalyst layer

Cross-sectional samples of the catalyst layers after the accelerated anode degradation tests were analyzed using scanning electron microscopy (SEM, H-3500, Hitachi-hitech, Japan) and energy dispersive X-ray spectrometry (EDS, E-max 50, Horiba Japan). The concentrations of metals in the catalyst layer were measured by SEM–EDS.

3. Results and discussion

3.1. Simulation of localized fuel starvation

In the stack in which air had been fed into the anode, localized fuel starvation occurred temporarily in some of the cells in the stack during start-up. The anode potential of these cells keeps increasing until fuel reaches the anode. This temporarily leads to voltage reversal, a condition in which anode potential is higher than cathode potential. In this study, a simulation test of voltage reversal, in which voltage was forcibly applied between the anode and cathode (both of which were filled with air) using a potentiostat, was conducted in order to determine the anode and cathode potentials. A three-electrode cell equipped with reversible hydrogen electrode (RHE) was used in this experiment, and both anode and cathode potential are shown versus those of the RHE.

Fig. 1 shows the anode and cathode potentials when voltage is applied between the anode and cathode at room temperature in the air/air condition. All plots in Fig. 1 show the potential 2 s after applying voltage. The anode and cathode potentials were clarified by this experiment; when the voltage reversal was –600 mV, anode potential was 1.43 V (vs. RHE). Generally speaking, the duration of the voltage reversal caused by localized fuel starvation was less than a few seconds, and almost all voltage reversals were more than –600 mV [27–29]. Hence, the upper potential limit and the scan rate of potential cycling in this study were set at 1.4 V (vs. RHE) and 500 mV s⁻¹, respectively.

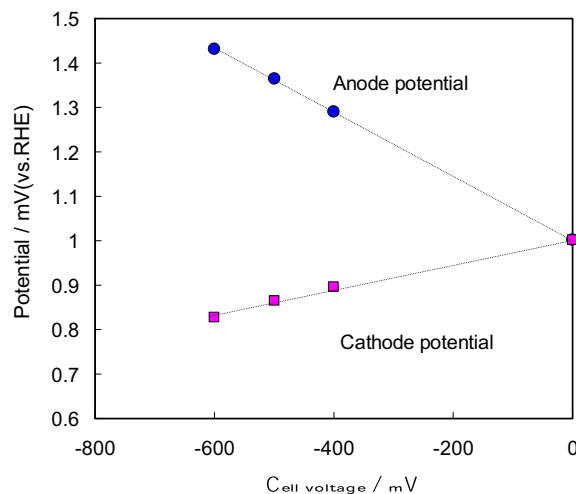


Fig. 1. Anode and cathode potentials when voltage is applied between anode and cathode at room temperature. Anode: air; Cathode: air, no gas supply.

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