DEGRADATION STUDY OF MEA FOR PEMFC UNDER LOW HUMIDITY CONDITIONS

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ABSTRACT

The degradation study of the MEA for PEMFC under low humidity conditions was conducted. The MEA degradation was observed during low humidity open circuit voltage tests. In order to investigate the degradation mechanism, we conducted ESR studies of the degenerated MEA, and confirmed the formation of radicals in the catalyst layers. The MEA degradation mechanism that includes the radical formation reaction was verified.

INTRODUCTION

In the development of the Proton Exchange Membrane Fuel Cells (PEMFC), durability of the membrane electrode assembly (MEA) is one of the vital issues especially for stationary power sources. Recently, it was reported that the degradation of the MEA occurred under low humidity conditions, whereas no obvious degradation was observed under high humidity conditions.1,2 In order to develop durable MEAs, it is inevitably important to understand the degradation mechanism of the MEA. It is commonly believed that chemical degradation of the ion exchange ionomer proceeds via peroxide radical attack.3 However, there has been no direct evidence of radical formation in the MEA. We have conducted an ESR study of the degenerated MEA. In this paper, we will report the results of this degradation study.

EXPERIMENTAL

Perfluorosulfonic acid membrane Flemion® SH50 (thickness: 50 μm, ion exchange capacity: 1.1 meq./g) was used as the membrane. A solution of Flemion® (ion exchange capacity: 1.1) was used as the catalyst coating ionomer. The cathode catalyst was 50% Pt supported on Ketjenblack EC, and the anode catalyst was 54% Pt-Ru (1:1.5) supported on Ketjenblack EC. The catalyst layers were prepared by creating
suspensions of the Flemion® ionomer solution with the catalyst powders and spreading the resulting slurries onto a substrate. The MEAs were prepared by hot-pressing the catalyst layers onto the membranes. The geometric area of the electrodes was 25 cm².

The open circuit voltage (OCV) tests were conducted under different conditions. During the OCV tests, there was no current flow through the MEA, whereas hydrogen and air were fed to the cell. Under a normal OCV condition, hydrogen and air were both humidified to 100% relative humidity. Under an accelerated OCV condition, dry air was fed to the cathode.

The crossover hydrogen was measured by flowing hydrogen gas to the anode and nitrogen gas to the cathode, and the hydrogen concentrations in the nitrogen gas were then analyzed using a gas chromatograph.

The ESR studies of the MEAs were conducted with a JEOL ESR Spectrometer JES-TE300. After the accelerated OCV test, the MEAs were dried in air. They were then cut into 2mm by 10mm pieces and put into a measuring cell. The ESR measurements were conducted at liquid nitrogen temperature.

RESULTS AND DISCUSSION

We reported the durability of MEA under high humidity conditions.1 The MEA showed good durability for over 4000hs (i.e., the voltage decay rate was ~2 μV/h) at a current density of 1A/cm² and at 100% relative humidity at 80°C. The degradation study of the MEA under low humidity and high humidity conditions were reported, and an obvious degradation was observed under the low humidity condition (i.e., the voltage decay rate was ~100 μV/h), whereas no degradation was observed under the high humidity condition.2 Therefore, we tried to ascertain this result by an accelerated test at low humidity. An open circuit voltage (OCV) test was conducted as an accelerated life evaluation method. Under OCV conditions, the possible reaction at the anode is the reaction between H₂ and crossover O₂ on the anode catalyst. The possible reaction at the cathode is the reaction between O₂ and crossover H₂ on the cathode catalyst. These reactions may generate peroxide radicals, which are widely believed to attack the ion exchange ionomer and degrade the MEA. The details of radical generation will be discussed later. During normal operating conditions (i.e., constant current operations or constant voltage operations), above-mentioned reactions may be retarded for the following reasons. During normal operating conditions, H₂ at the anode and O₂ at the cathode are electrochemically consumed. Then the pressures of H₂ and O₂ in the cell are reduced, which results in the decrease of crossover H₂ and crossover O₂ through the membrane. Also the crossover H₂ and crossover O₂ may react electrochemically on the catalysts. In addition, electrochemically-generated water will help the dry-out situation at the anode. These effects will decrease the formation of peroxide radicals. Therefore, the
OCV tests, especially under low humidity conditions, have the advantage of an accelerated life evaluation method over the normal operating methods.

Figure 1 shows the durability of a MEA under different OCV conditions. Under a normal OCV condition, the voltage decay was relatively small (i.e., OCV decay rate was $\sim 0.2 \text{mV/h}$). On the other hand, a rapid voltage decay was observed under the accelerated OCV condition (i.e., OCV decay rate was $\sim 2 \text{mV/h}$). This voltage decay was attributed to the degradation of the MEA. Also, measurements of the crossover hydrogen through the MEA before and after the OCV tests were conducted to ascertain the degradation of the MEA. Figure 2 shows the concentrations of the crossover hydrogen before and after the OCV tests. We found that the crossover hydrogen significantly increased after the accelerated OCV test, and this was attributed to membrane damage.

In order to clarify this damage, the degradation mechanism of the MEA was investigated. It is commonly believed that chemical degradation of the ion exchange ionomer proceeds via a peroxide radical attack. This mechanism was advocated by LaConti and co-workers. They assumed that the hydroxyl and hydroperoxyl radicals were generated by the reaction between $\text{H}_2$ and $\text{O}_2$, and the MEA degeneration was caused by the attack of these radicals. Their radical formation sequence is listed below.

\begin{align*}
\text{STEP 1 : } & \text{H}_2 \rightarrow 2\text{H} \cdot \text{ (on Pt or Pt/Ru catalyst)} \\
\text{STEP 2 : } & \text{H} \cdot + \text{O}_2 \text{ (diffused through PEM)} \rightarrow \text{HO}_2 \cdot \\
\text{STEP 3 : } & \text{HO}_2 \cdot + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 \\
\text{STEP 4 : } & \text{H}_2\text{O}_2 + \text{M}^{2+} \rightarrow \text{M}^{3+} + \text{HO} \cdot + \text{OH}^{-} \\
\text{STEP 5 : } & \text{H}_2\text{O}_2 + \text{HO} \cdot \rightarrow \text{HO}_2 \cdot + \text{H}_2\text{O}
\end{align*}

This mechanism is possible because these radicals are very reactive and may cause the decomposition of the ion exchange ionomer. However, there has been no direct evidence of the radical formation in the MEA.

In order to ascertain the radical generation in the MEA, we conducted electron spin resonance studies of the degenerated MEA. Figure 3 shows the ESR spectra of the MEA at liquid nitrogen temperature. Large ESR signals at 327 mT were observed with the degenerated MEA. In order to determine the origin of the signals, we conducted the ESR measurement of the degenerated MEA with and without the catalyst layers. Similar ESR signals at 327 mT were detected with the anode layer-detached MEA and also with the cathode layer-detached MEA. However, no ESR signals were observed with the anode and the cathode layer detached MEA, namely, only the membrane of the degenerated MEA. Therefore, we found that these signals originated from the catalyst layers of the degenerated MEA.
The ESR signals observed at 327 mT were isotropic signals with a g-value of 2.003 and a line width of 1.3 mT. Also the signals had no hyperfine structures. From these results, the signals observed at 327 mT were assigned to carbon radicals.\textsuperscript{4,5} It should be mentioned that some carbon radicals on the carbon black were very stable.\textsuperscript{6} The structure and formation mechanism of the carbon radical were considered. In this experiment, carbon black (Ketjenblack EC) was used as the support of both the anode and the cathode catalysts. Figure 4 shows a schematic structure of the carbon black crystallite. Hydrogen or other functional groups are identified on carbon blacks, and hydrogen is bonded directly to carbon atoms (i.e., C-H bonds).\textsuperscript{7}

A probable carbon radical formation mechanism was the hydrogen abstraction by the hydroxyl or hydroperoxyl radicals. Therefore, the ESR signals observed with the degraded MEA were attributed to the carbon radicals that were presumably formed by either the hydroxyl radical or hydroperoxyl radical or both.

Therefore, hydroxyl or hydroperoxyl radical formation during the accelerated test was presumed, and the MEA degradation mechanism that includes the radical formation reaction was clarified.

In this study, however, we could not identify other radical species i.e., the hydroxyl or hydroperoxyl radical, or radicals of the decomposed ion exchange ionomer. In general, the lifetime of radicals are very short, i.e., the lifetime of the hydroxyl or hydroperoxyl radical are on the order of nonoseconds.\textsuperscript{8,9} Therefore, the usage of a spin trap agent will be effective in order to identify the radical species. The large ESR signals observed with the degraded MEA can be considered as a trace of the reactive radical generation in the MEA.

CONCLUSIONS

The degradation study of the MEA for PEMFC using the low humidity OCV test was conducted, and obvious degradation was confirmed. In order to investigate the degradation mechanism, an ESR study of the degenerated MEA was conducted. Large ESR signals at 327 mT were observed within the catalyst layers of the degenerated MEA. The ESR signals were assigned to carbon radicals. The carbon radicals were presumably generated by a reaction of the carbon black and either the hydroxyl radical or hydroperoxyl radical or both. The hydroxyl or hydroperoxyl radical formation during the accelerated test was presumed, and the MEA degradation mechanism that includes the radical formation reaction was supported.
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Normal condition: $T_{\text{cell}}=80^\circ \text{C}, T_{\text{da}}=T_{\text{dc}}=80^\circ \text{C}, \text{H}_2/\text{Air}$, Pressures : 0.1/0.1 MPa,
Accelerated condition: $T_{\text{cell}}=80^\circ \text{C}, T_{\text{da}}=80^\circ \text{C}$, Dry air was fed to the cathode

Fig. 1 Durability of MEA under open circuit voltage test

Fig. 2 Measurement of crossover hydrogen
Fig. 3  ESR spectra of MEAs at liquid nitrogen temperature

Fig. 4  Carbon radical formation mechanism