

Degradation Study of MEA for PEMFC Under Low Humidity Conditions

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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. 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 and confirmed the formation of radicals in the catalyst layers. We have also confirmed the formation of H₂O₂ on the Pt electrode. In this paper, we will report the results of these studies.

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 $\sim 2 \mu\text{V/h}$) at a current density of 1A/cm² and at 100 % relative humidity at 80°C. On the other hand, an obvious degradation was reported under the low humidity condition (i.e., the voltage decay rate was $\sim 100 \mu\text{V/h}$).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, and 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. 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. 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. Rapid voltage decay was observed under the accelerated OCV condition (i.e., low humidity condition). This voltage decay was attributed to the degradation of the MEA.

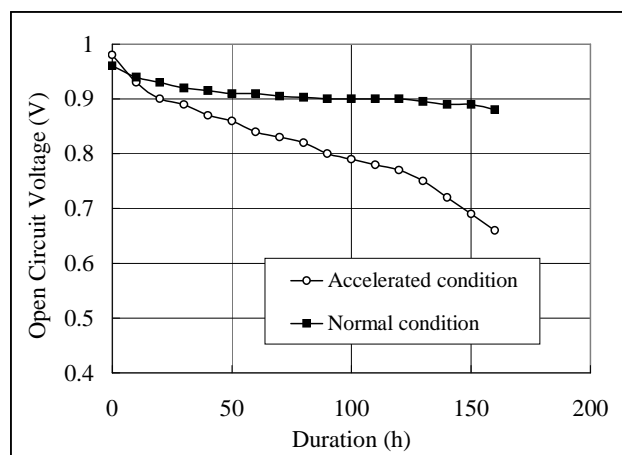


Fig.1 Durability of MEA under OCV conditions

The chemical degradation of the ion exchange ionomer is believed to proceed via a peroxide radical attack.³ In order to ascertain the degradation mechanism, 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, and the signals observed at 327 mT were assigned to carbon radicals. A probable carbon radical formation mechanism will be discussed.

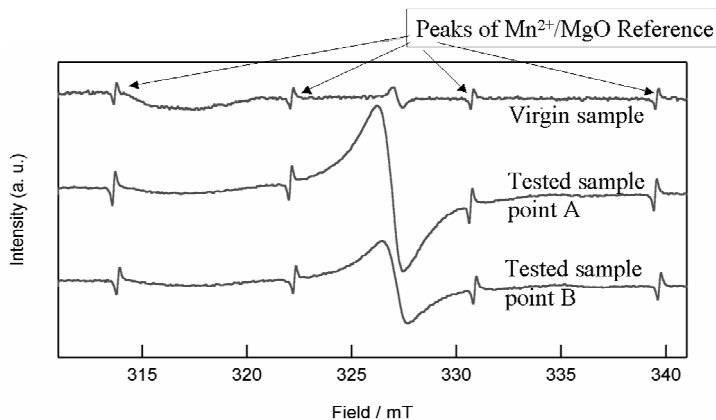


Fig.2 ESR spectra of the MEA

References

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- (2) Report of Sanyo Electric Co., Ltd. to the New Energy Development Organization (2002)
- (3) A.B. LaConti, M. Hamdan and R.C. McDonald, "Mechanisms of Membrane Degradation for PEMFCs" *Handbook of Fuel Cells: Fundamentals, Technology, and Applications, Vol 3*, W. Vielstich, A. Lamm, and H.A. Gasteiger, Editors, Wiley, New York, NY, 2003.