

Hydrogen Peroxide Formation as a Degradation Factor of Polymer Electrolyte Fuel Cells

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Durability is one of the most important issues in commercialization of polymer electrolyte fuel cells (PEFCs). A long life over 90,000 hours (= 10 years) is required for PEFC stacks in the small-scale cogeneration systems; however, sufficient durability to meet this demand has not been established. Various mechanisms are being considered for the deterioration of the cell stacks during a long operation. Hydrogen peroxide formation, which is formed electrochemically or chemically during operation, is one of the potential deteriorating factors of PEFCs.¹ In the present study, we investigated H₂O₂ formation as a degradation factor of PEFCs.

1. Durability tests of perfluorosulfonic acid ion-exchange membranes against hydrogen peroxide

Durability tests of Nafion 117 membranes with various counter ions against hydrogen peroxide solution were carried out. Decomposition of H⁺-type Nafion was very slow even at 80°C in 30% hydrogen peroxide solution; however, the presence of transition-metal ions such as Fe²⁺, Fe³⁺, and Cu²⁺ greatly enhanced its decomposition as shown in Fig. 1.

2. Hydrogen peroxide formation on Pt/C catalysts

20 wt.% Pt/C catalysts (E-TEK) were dispersed on glassy carbon (GC) disk electrode, and oxygen reduction reaction (ORR) and the formation of hydrogen peroxide as a by-product were investigated by the rotating ring-disk electrode (RRDE) technique. Hydrogen peroxide formation was greatly affected by the agglomeration of Pt/C catalysts on GC. A large amount of hydrogen peroxide was formed when Pt/C was highly dispersed as shown in Fig. 2. These results revealed that series 2-electron reduction (H₂O₂ formation), which is negligible on clean bulk Pt surface, does exist on Pt particles supported on carbon. However, in agglomerated state, water is predominantly formed through apparent 4-electron reduction, which results from the series 4-electron reduction or catalytic decomposition of H₂O₂ at nearby Pt/C catalysts in the agglomerates.

3. Gas crossover and its effects on degradation of MEAs

The amount of crossover hydrogen, which was measured by an electrochemical method, increased with increasing cell temperature, humidification, and gas pressure. A typical amount of crossover hydrogen was about 0.8 mA cm⁻² at a cell temperature of 80°C under ambient pressure. This fact indicated that heat evolution by gas crossover was negligible. During an open-circuit test of a H₂/Ar cell, hydrogen crossover increased with time as shown in Fig. 3. In addition, fluoride ion, which is a decomposition product of the electrolyte, was detected in the water in the condensers. A small amount of hydrogen peroxide was detected as well. These facts indicated that hydrogen peroxide, which causes deterioration of the electrolyte, was formed by catalytic

reactions of hydrogen and oxygen.

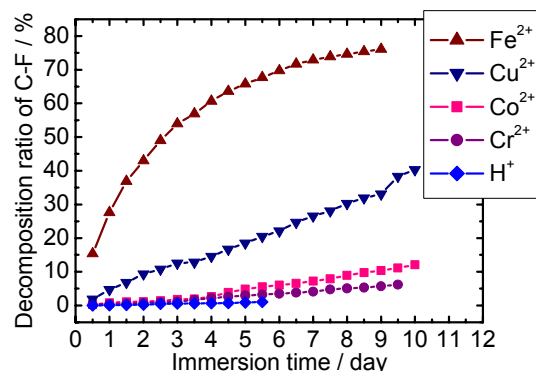


Fig. 1. Variation of fluoride ion elution from Nafion 117 (1 x 1 cm²) immersed in 30% H₂O₂ at 80°C.

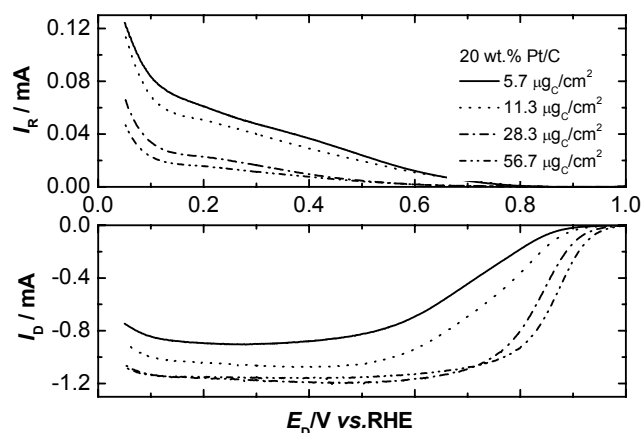


Fig. 2. Hydrodynamic voltammograms for oxygen reduction in 1 M HClO₄. Disk electrodes: 20 wt.% Pt/C loaded with different amounts on GC, Ring electrode: Pt. Rotating rate: 900 rpm.

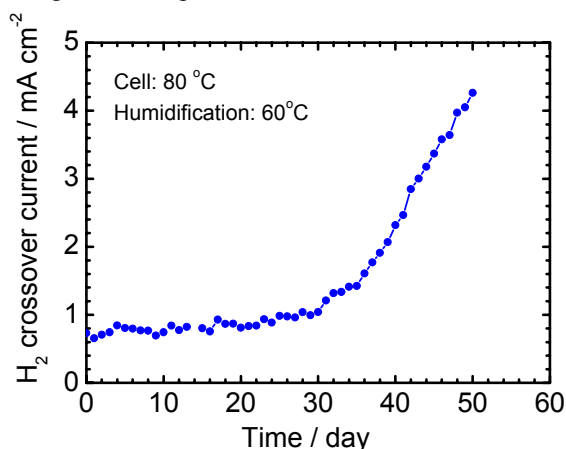


Fig. 3. Variation of H₂ crossover current during an open-circuit test of a H₂/Air single cell (25 cm²). Cell temp.: 80°C, humidification 60°C.

This work was supported by Research and Development of Polymer Electrolyte Fuel Cells from New Energy and Industrial Technology Development Organization (NEDO), Japan.

References

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