Effects of Metal Ions Derived from Core-Shell Electrocatalyst on Cell Durability

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Introduction

The utilization of core-shell catalysts and the replacement of existing system materials to inexpensive alternatives are the promising means of cost reduction in the proton exchange membrane fuel cell (PEMFC) system. However, the elution of metal ions from these materials may jeopardize the cell and membrane durability. In our previous research [1], the influence of Cu^{2+} and Al^{3+} impregnation was examined by power generation tests. The Al^{3+} impregnation compromised the durability, whereas Cu^{2+} improved it when the impregnated concentration was 1000 ppm. In the current study, 10% Cu^{2+}, Al^{3+}, Fe^{2+}, Ni^{2+}, Ag^{+}, and Pd^{2+} were impregnated to investigate magnified effect of metal ions in three durability tests. The cell and membrane durability was evaluated by analyses and was discussed based on oxidation reduction potential (ORP).

Experimental

Following the procedures of the previous study, Cu^{2+}, Ag^{+}, and Pd^{2+} (ORP>0) and Ni^{2+}, Fe^{2+}, and Al^{3+} (ORP<0) were substituted for 10% of sulfonic acid groups in each membrane [1,2]. An open circuit voltage (OCV) durability test under low humidity (15% R.H.) was conducted on the 10% Cu^{2+} cell and a cell without metal ions (Non-metal). Another OCV durability test at a high temperature (120 °C) was performed on the Non-metal and 10% Cu^{2+}, Ag^{+}, and Pd^{2+} cells. The Non-metal and 10% Cu^{2+}, Al^{3+}, Fe^{2+}, Ni^{2+}, Ag^{+} cells were tested by power generation at 0.2 A/cm^2. In addition, fluoride ion (F^{-}) in the discharged water and energy-dispersive X-ray spectroscopy (EDS) spectra were analyzed.

Results and Discussions

Figures 1-3 show the chronological change of OCV or cell voltage obtained in the tests. 10% Al^{3+}, Ni^{2+}, and Fe^{2+} (ORP<0) accelerated cell voltage drop, yet 10% Cu^{2+}, Ag^{+}, and Pd^{2+} (ORP>0) inhibited the drops of OCV and/or cell voltage. Negative ORP ions, except Fe^{2+} that had no effect, also deteriorated membrane durability based on F^{-} analyses, although positive ORP ions improved it. Moreover, the absolute values of ORP correlated with the degree of the effects. The durability enhancement of positive ORP ions is speculated to occur due to the deposition of these meal ions in the membrane ($M^{n+} + n/2*H_2 \rightarrow M + nH^{+}$; M= metal and H^{+}= hydrogen ion), so that the produced H^{+} neutralizes harmful H_2O_2 [3]. The production of H_2O_2 is also reduced when the metal ions deposit at the catalytic layer (CL), which was supported by the existence of metal particles at both the anode and cathode CLs based on the EDS spectra.

Conclusion

The impregnation of 10% Cu^{2+}, Ag^{+}, and Pd^{2+} improved the durability, although 10% Ni^{2+}, Fe^{2+}, and Al^{3+} cells generally showed accelerated deterioration. Hence, it is likely that the direction and degree of effect caused by metal ions can be predicted by ORP values.

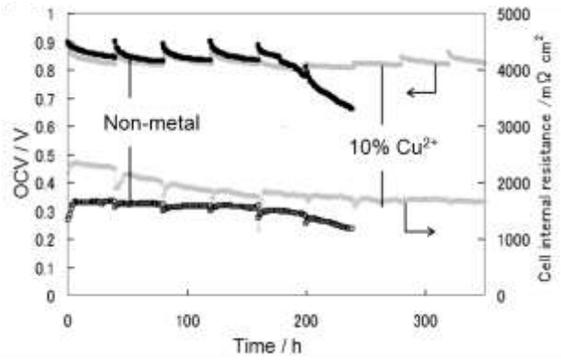

Figure 1. Chronological change of OCV and cell internal resistance during open circuit operation of the Non-metal and 10% Cu^{2+} cells (cell temp.=90 °C and dew point=47.5 °C).

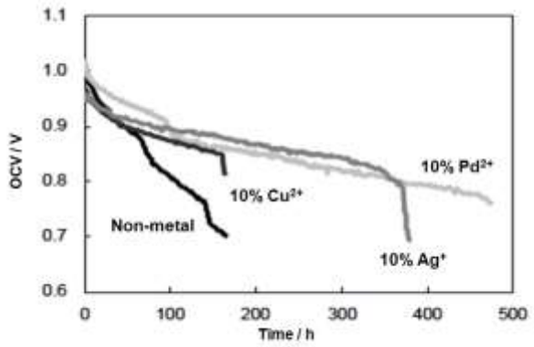

Figure 2. Chronological OCV change during open circuit operation of the Non-metal and 10% Cu^{2+}, Ag^{+}, and Pd^{2+} cells (cell temp.=120 °C, anode dew point=95 °C, and cathode dew point=60 °C).

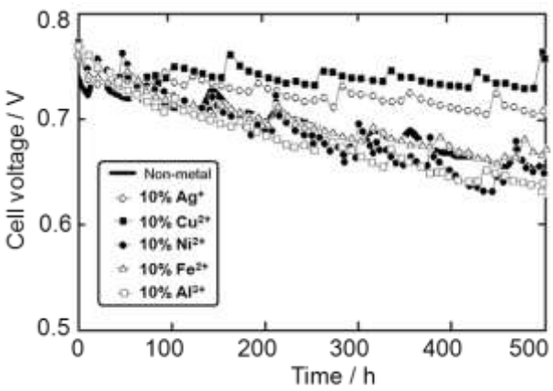

Figure 3. Chronological cell voltage change of the Non-metal and 10% Ag^{+}, Cu^{2+}, Ni^{2+}, Fe^{2+}, and Al^{3+} cells during the long-term power generation test at 0.2 A/cm^2 (cell temp.=80 °C and dew point=65 °C).

Acknowledgements

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References

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