Valence State of Cerium Ion Radical Quencher in Polymer Electrolyte Membrances

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Polymer electrolyte fuel cells (PEFCs) are expected to be widely utilized in automotive applications, where long-term operation is an essential performance requirement. One of the degradation factors of PEFCs is the breakdown of the perfluorosulfonic acid electrolyte membrane. In particular, the hydrogen peroxides generated during the cell loading react with impurities in the electrolytes to form radicals such as the hydroxyl radical (HO•). These radicals attack the polymer chains, causing significant chemical degradation of the polymer electrolyte membrane (PEM). In practical applications, cerium species are added to PEM as a radical quencher to absorb the radicals and suppress chemical degradation [1]. Mechanism for the absorption of radical species by the redox reaction of Ce^{3+}/Ce^{4+} has been proposed [2]. However, there are few reports on the electronic structure analysis of cerium ions in PEM. In this study, we have analyzed the electronic structure in cerium-containing PEM by Ce L3-edge X-ray absorption spectroscopy.

Cerium-containing polymer electrolytes with a thickness of 12 μm (GORE-SELECT® MEMBRANEM788.12) was used for the analysis. Ce L3-edge X-ray absorption near-edge structure (XANES) of the PEM was measured in a fluorescence yield mode using a 3-elements solidstate detector at the BL-3 beamline with an Si(220) monochromator at the SR Center, Ritsumeikan University. For the reference, cerium oxide powder was also measured. XANES of standard samples, $Ce(NO_3)_3 \cdot 6H_2O$ [3] and CeO_2 [4] were utilized by MDR XAFS DB.

Figure 1 shows Ce L3-edge XANES of the PEM and CeO₂. For the XANES of the PEM, the absorption edge is observed at 5725 eV. On the other hand, the doublet absorption edges are observed around 5729 and 5736 eV for CeO₂. The spectrum of CeO₂ is consistent with the database. Slight structure differences may be attributed to differences in the measurement facilities. The spectrum of the PEM is similar to that of Ce(NO₃)₃·6H₂O, implying that the cerium ions in the PEM are trivalent. However, there is also a slight peak near 5737 eV in the PEM spectrum. This peak is not detected in Ce(NO₃)₃· 6H₂O and is close to the absorption edge energy of CeO₂, possibly due to the presence of a small amount of tetravalent cerium ions in PEM and/or different coordination structure around cerium ion than that of $Ce(NO_3)_3 \cdot 6H_2O$.



Fig. 1 Ce L3-edge XANES spectra of the cerium contained PEM and CeO_2 with $Ce(NO_3)_3 \cdot 6H_2O$ and CeO_2 database.

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References

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