Structural Analysis for Manganese Ion in Organic Solvent by XAFS

Hiroshi Ohzono*(5227), Hideaki Ohyama, Shinji Ozaki[1](4142), Kenji Fujiwara[2](5660), Juichi Sasada(5752), Toshio Mori(7168), Masao Takahashi[3](1285)

Matsushita Battery Industrial Co., Ltd., [1] Matsushita Technoresearch Inc.,
[2] Matsushita Electric Industrial Co., Ltd.,
[3] The Institute of Scientific and Industrial Research, Osaka University

Manganese oxide has been used as battery material. The industrial application of manganese oxide has penetrated the battery market as a product, for example manganese dry battery, alkali manganese dry battery, lithium battery, and lithium rechargeable battery, etc. In these batteries, when manganese oxide reacts with electrolyte solution, manganese ion melts into electrolyte solution. Since organic solvent is especially used as electrolyte solution with lithium battery and lithium rechargeable battery, it is thought that the configuration of manganese ion that melts into organic solvent is important when discussing the chemical reaction in lithium battery and lithium rechargeable battery.

As the technique of performing the structural analysis of the metal ion in solution, there are X-ray diffraction analysis, neutron diffraction analysis, X-ray Absorption Fine Structure (XAFS) analysis, etc. We have attempted to apply the fluorescence XAFS analysis to structural analysis of manganese ion, because the concentration of the manganese ion that melts into electrolyte solution is very low.

Solutions, which soaked two kinds of manganese oxide in which synthetic method differs in propylene carbonate in appropriated time, were used.

XAFS spectra of Mn-*K* edge were measured at BL16B2 station of SPring-8. The fluorescence X-ray from samples were detected by the Lytle detector.

Figure 1 shows the Mn-*K* edge XANES (X-ray Absorption Near Edge Structure) spectra of sample solution A and B. The solid line and dashed line in Fig. 1 corresponds to sample A and B, respectively. As shown in Fig. 1, sample A has the large amount of jumps of an absorption edge. It is found that there are more amounts of manganese, which melted into solution in the sample A. This result and the quantitative analysis by ICP-AES are consistent with each other. We notice that these spectra show the same energy position of absorption edge. The result indicates that this manganese to be equal chemical state.

Further work is required to obtain the structural analysis of manganese ion in details. In order to measure the EXAFS spectra; we will attempt to improve the experimental set up, especially to modify the detector system.

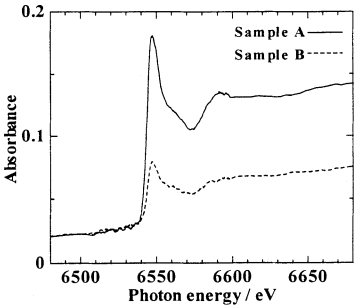

Fig. 1 Mn-*K* edge XANES spectra

High-temperature XAFS Study on $LaMnO_3$-related Materials for Fuel Cell

Tohru Yamamoto(3959)*, Shinichi Noguchi(4618), Hiroshi Deguchi(4133)[a] and Masaki Horiuchi(4926)[b]

Central Research Institute of Electric Power Industry (CRIEPI)
[a]Technical Research Center, Kansai Electric Power Co., INC.
[b]Engineering Section, Kanden Kakou Co., LTD.

Substituted *perovskite-type* oxides have been attempted widely to utilize as an electrode material in solid oxide fuel cell applications, combustion catalysts for hydrocarbon oxidation reactions, etc. In this study, the local structures around La, Sr and Mn in $(La_{1-x}Sr(Ca)_x)MnO_3(0\leq x\leq 0.5)$ solid solutions were analyzed by XAFS spectroscopy using the high-temperature sample attachment.

X-ray absorption spectra(XAS) have been obtained in the BL-16B2 station. The XAS near La, Sr and Mn K-edge were measured by the ordinary transmission method. Sample temperature was controlled in a range 25～700℃. The sample chamber has the ability to heat the sample up to 1500℃ and equips with the gas feeder which is controllable oxygen partial pressure in the range $Po_2=10^{-6}$～1 atm. The XAS data was analyzed using *REX* [*Rigaku co. ltd.*], *WinXAS 97* [*T. Ressler, J. Physique IV, 7, C2-269(1997)*] and *FEFF-8* [*A.L. Ankudinov et al., Phys. Rev. B, 7565(1998)*].

Figure 1 shows the RDF for La K-edge XAFS of $La_{0.8}Sr_{0.2}MnO_3$. The RDF in this study agree with that derived from *Rietveld* analysis(*F. Izumi and T. Ikeda, Mater. Sci. Forum, 321-324 (2000) 198*). Figure 2 shows the temperature dependence of La-K edge RDF of $La_{0.7}Sr_{0.3}MnO_3$. Although the decay of the XAFS oscillation was observed along with the increase of temperature, the RDF around the La was able to identify in this temperature range. The detailed analysis is in progress.

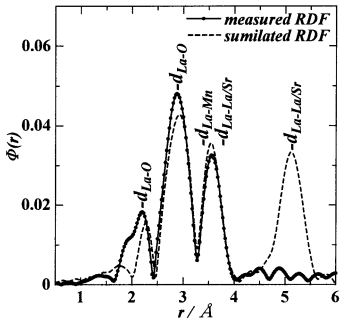

Fig 1. RDF for La-K edge XAFS of $La_{0.8}Sr_{0.2}MnO_3$(room temp.). Solid and dashed lines represent measured and calculated RDF, respectively.

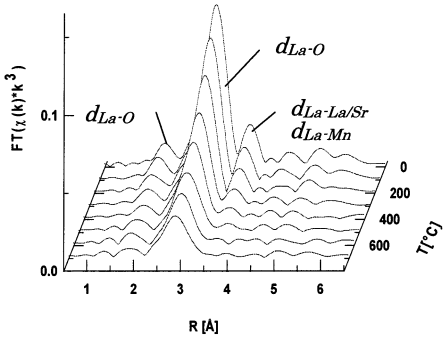

Fig.2 Temperature dependence of La-K edge RDF of $La_{0.7}Sr_{0.3}MnO_3$. These measurements were carried out in the temperature range 25～700℃ in air.