Crystal structure and ionic conduction path of Ln2Ni1-xCuxO4+d for solid oxide fuel cells

Yasushi Idemoto and Naoto Kitamura
Departme nt of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba 278-8510

Recently, solid oxide fuel cell (SOFC) has drawn much attention, and many researches on the device have been carried out. Lanthanum nickelate-based materials with the K2NiF4-type structure are considered as promising candidates for cathodes of SOFC. It is well-known that excess oxygens are incorporated at interstitial sites in the rock-salt La2O2 layer and the oxygens can be a conduction species in the lanthanum nickelate-based materials. Due to the difficulty in an analysis on crystal structures at elevated temperature, however, it is still ambiguous how the host crystal structure affects excess oxygen sites and their conduction path.

From such background, we investigated Ln2Ni1-xCuxO4+d with the K2NiF4-type structure in this work. By using neutron diffraction patterns, crystal structures of the materials at high temperature were refined with the Rietveld method, and their nuclear density distributions were also estimated by the maximum entropy method (MEM).

We synthesized LaNi0.8Cu0.2O4+d with a solution method using citric acid as an additive. Phase identification of the sample was carried out by XRD, and the composition was evaluated by ICP. Conductivity of the sample was also measured at elevated temperature. In order to study the crystal structure in detail, we measured neutron diffraction patterns at the temperature range from 298 to 673 K using HERMES of IMR at the JRR-3M[1], and analyzed the patterns with the Rietan-FP[2]. We also estimated nuclear density of the sample by MEM technique with PRIMA program[3].

It was confirmed with X-ray diffractions that LaNi0.8Cu0.2O4+d had a single phase of the K2NiF4-type structure. From ICP measurement, it was indicated that metal composition of the sample was almost equal to the nominal one.

As for the lanthanum nickelate-based sample, Rietveld analysis using neutron diffractions was performed. In the analysis, we assumed the space group as I4/mmm and excess interstitial oxygens in the rock-salt layer. As a result, it was found that lattice constants of the material increased as temperature increased. The content of the excess oxygen, which was calculated from the occupancy, became lower with increasing temperature although their sites were essentially independent of temperature. Because bond valence sum of (Ni,Cu) site became lower at higher temperature, it was considered that the effective negative charge of the excess oxygens was compensated by an oxidation of Ni and/or Cu. From the nuclear density distribution at elevated temperature, it was suggested that oxygens at the interstitial site and an apex site of the perovskite layer moved significantly compared with the other oxygens.

[1] K. Ohoyama, T. Kanouchi, K. Nemoto, M. Ohashi, T. Kajitani, Y. Yamaguchi, Jpn. J. Appl. Phys. 37, 3319 (1998) .
[2] F. Izumi, and T. Ikeda, Mater. Sci. Forum, 321, 198 (2000).
[3] F. Izumi and R. A. Dilanian, "Recent Research Developments in Physics, "Vol.3, Part II, Transworld Research Network, Trivandrum (2002), pp.699-726.