Crystal structure and ionic conductivity of Ga system oxides for solid electrolyte of fuel cell

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Gallate-based oxides are regarded as promising candidates for the electrolyte of SOFC, because of their high conductivities and high chemical stabilities. In the oxides, partial substitution of aliovalent cations introduces oxygen vacancies and/or protons, and results in significant oxide ion and/or proton conduction above 500 K. Thus, it is important to clarify their crystal structures and nuclear densities of the oxide ion and the protons at elevated temperature. Due to the difficulty in structural analysis on such light atoms, however, there are not enough knowledge on them. In order to make these clearer, we focused on La0.8Sr0.2Ga0.8Mg0.2O3-d (LSGM) and La0.8Sr0.2Ga0.8Mg0.115Co0.085O3-d (LSGMC) as oxide ion conductor and La0.9Ba1.1GaO4 (LBG) as proton conductor, and investigated them with neutron diffraction measurements.

We obtained LSGM and LSGMC powders by heat-treating precursors prepared by AGC SEIMI CHEMICAL CO., LTD. LBG was synthesized with solid-state reaction using each oxide or carbonate as a starting material. As for the products, we characterized their phases by XRD, compositions by EDX, and oxygen nonstoichiometry by microbalance. Conductivity measurements were also performed at elevated temperatures. In order to clarify the crystal structures, neutron diffraction patterns were measured using HERMES of IMR at the JRR-3M, and these patterns were analyzed with the Rietan-2000. The measurements were performed at 298~680 K. The nuclear densities were also estimated based on MEM using the PRIMA

From XRD patterns, it was considered that both LSGM and LSGMC had a single phase of the perovskite-type structure and the lattice constants became smaller by Co substitution. Taking the ionic radii of Mg and Co into account, the results reflect that Co occupies 4c (Ga, Mg) site. Rietveld analysis using neutron diffraction patterns indicated that both LSGM and LSGMC could be attribute to orthorhombic Pnma at 298~680 K. The oxygen content calculated from the site occupancy decreased with increasing temperature in LSGMC while that was essentially independent of temperature in LSGM. These behaviors are consistent with results of oxygen nonstoichiometry measurements. Based on the refined structure, we estimated the nuclear densities with MEM. As a result, it was indicated that the oxygen nuclear density began to spread as temperature increased and that such a tendency was more significant in LSGMC than LSGM. This may correspond with higher conductivity of LSGMC than LSGM. From the difference between the nuclear densities at 298 K and 680 K in LSGMC, it was suggested that oxygen at O1 site diffused toward the neighboring O2 site and vice versa.