Structural Disorder and Diffusional Pathway of Oxide Ions in a Doped Pr2NiO4-Based Mixed Conductor

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Mixed oxide-ionic and electronic conducting ceramics (MIECs) are attracting much interest as materials for oxygen separation membranes. Oxygen can permeate through MIECs membranes when a gradient of oxygen chemical potential exists. A2BO4-based oxides with K2NiF4-type structure have extensively been studied as new mixed ionic-electronic conductors, where A and B are cations. The development of improved MIECs requires a better understanding of the mechanism of ionic conduction, and crucial to this is a comprehensive knowledge of the crystal structure. It was speculated that the oxide ion conduction in the A2BO4-based oxides occurs by diffusion of excess oxide ions along the rock-salt-type AO layers. However, the diffusion path of oxide ion has not been determined yet. Pr2NiO4-based oxides have high oxygen permeability and high diffusivity of oxide ions. Here, we report for the first time the diffusion path of oxide ions in a K2NiF4-type mixed conductor (Pr0.9La0.1)2(Ni0.74Cu0.21Ga0.05)O4+d (PLNCG), through a high-temperature neutron powder diffraction study (M. Yashima, M. Enoki, T. Wakita, R. Ali, Y. Matsushita, F. Izumi and T. Ishihara, " Structural Disorder and Diffusional Pathway of Oxide Ions in a Doped Pr2NiO4-Based Mixed Conductor ", J. Am. Chem. Soc. (Communications), 139, [9] 2762-2763 (2008).). We chose this chemical composition, because it exhibits high oxygen permeability. The present result would give hints for the design of K2NiF4-type conductors.

A PLNCG sample was prepared by a solid-state reaction method at 1300 oC for 6 h in air. Neutron powder diffraction data of PLNCG were in situ measured at 606.6 oC and 1015.6 oC using a furnace and a 150 detector system HERMES at a neutron wavelength of 1.82646 . Neutron diffraction patterns at both temperatures indicated a K2NiF4-type structure with I4/mmm space group. Neutron-diffraction data were analyzed by a combination of Rietveld analysis, the maximum-entropy method (MEM), and MEM-based pattern fitting (MPF). A computer program RIETAN-2000 was utilized for the Rietveld analysis and MEM-based whole pattern fitting, and VESTA for visualization of nuclear density (scattering-length density) distribution. It is known that MPF makes it possible to determine nuclear densities in compounds containing disordered chemical species from neutron diffraction data.

Rietveld refinements of the neutron diffraction data of PLNCG at 606.6 oC and 1015.6 oC were successfully performed on the basis of the K2NiF4-type structure with I4/mmm space-group symmetry. It was found that PLNCG has a crystal structure consisting of (Ni,Cu,Ga)O6 octahedron and (Pr,La)-O layers. Refined occupancy factors indicated the excess oxygen of d = 0.0154(3) in (Pr0.9La0.1)2(Ni0.74Cu0.21Ga0.05)O4+d, which is ascribed to the interstitial O3 atom. The O3 atom is located at a 16n site, i.e., (x, 0, z) where x = 0.666(19) and z = 0.223(9) at 1015.6 oC. The oxy-

gen atom at the O2 site (4e; (0, 0, z); z = 0.1752(4) at 1015.6 oC) exhibits highly anisotropic thermal motion (U11 = U22 = 0.115(3) 2 and U33 = 0.021(3) 2), which leads to the migration of oxide ions to the nearest-neighbor interstitial O3 positions. The striking feature in the nuclear density distribution is the curved O2-O3 diffusion path. This feature is ascribed to the repulsion between (Pr,La) and O atoms. In fact, the distance between the (Pr,La) and O atoms are kept approximately constant along the diffusion paths. This fact suggests that the large-sized cations such as Pr and La ions at the A site in the A2BO4-type conductor are effective in improving the oxide-ionic conduction on the A-O layer. The conduction path is along the <100> directions near the O2 site and roughly along the <301> directions around the center of the paths. The nuclear-density distribution also shows the two-dimensional (2D) network of the O2-O3-O2 diffusion paths of oxide ions. The 2D feature is consistent with the anisotropic transport of oxide ions in La2NiO4+d. The nuclear density on the diffusion path at 1015.6 oC is larger than that at 606.6 oC, which is consistent with the improved oxygen permeability at higher temperatures.