Hydrogen Permeation through Ru-Doped Perovskites via Mixed Protonic-Electronic Conduction

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Mixed protonic-electronic conductors are useful for hydrogen separation. Some acceptor-doped perovskites are known to have protonic conduction in moist atmospheres at high temperatures. An addition of electronic conduction into the high-temperature proton conductors (HTPCs) will possibly bring desirable hydrogen permeability.

This paper reports that the mixed protonic-electronic conduction appears in some perovskite-type HTPCs on doping Ru, i.e., $BaCe_{0.9-x}Y_{0.1}Ru_xO_{3-\alpha}$ (x=0-0.1) and $SrZr_{0.9-x}Y_{0.1}Ru_xO_{3-\alpha}$ (x=0-0.125).

The samples were prepared by a normal solid state reaction route. They had a single phase of orthorhombic perovskite-type structure and were sufficiently dense to avoid mechanical gas leakages. The ionic transport number and hydrogen permeability was measured by and electrochemical cell with disk specimens (0.5 mm thick) at 800ºC. X-ray absorption spectroscopy was measured at room temperature for the Ru-doped and undoped materials annealed in moist reducing atmosphere at 800ºC to examine their electronic structures.

The EMF of hydrogen concentration cell measured for $BaCe_{0.9-x}Y_{0.1}Ru_xO_{3-\alpha}$ (800ºC) deviated lower than that calculated from the Nernst equation, indicating that the ionic transport number decreases with increasing amount of Ru in moist reducing atmospheres. Figure 1 shows the permeation rate of hydrogen (swept by moist argon gas) through the materials from 1-100% hydrogen. The maximum hydrogen flux was 6.47×10^{-8} mol/s cm^2 (x=0.1), equivalent to the internally short-circuited current density of 12.5 mA/cm^2. The change in water vapor pressure in the outlet of the sweep gas reveals that both proton and oxide-ion work as ionic charge carriers by about even contributions, i.e., $t(H^+)/t_i \sim t(O^{2-})/t_i \sim 0.5$; this fraction is unchanged from the base HTPC.

The hydrogen flux is proportional to the difference in the logarithm of the hydrogen partial pressure in hydrogen-supplying compartment from that in the hydrogen-permeating compartment, $\ln(p_{H2,supp}/p_{H2,perm})$, indicating that the permeation occurs due to the ambipolar diffusion. These results suggest that the Ru doping adds a kind of electronic conduction to the proton conductor of Y-doped $BaCeO_3$.

Figure 2 shows soft X-ray absorption spectroscopy (XAS) spectra of $BaCe_{0.9-x}Y_{0.1}Ru_xO_{3-\alpha}$ (x=0 and 0.075). In case that the specimens were untreated after sintering in moist air, the spectra of both Ru-doped and undoped specimen have peaks just below the top of the valence band (V.B.). The XAS is directly related to the unoccupied density of states, so that the peaks are attributable to the density of hole state. The Ru-undoped specimen annealed in moist 1% H_2 have no peak at the hole state. However, in the Ru-doped case, the hole peaks (indicated by arrow) remains even after the treatment in the reducing atmosphere. This fact suggests that the electronic species for the mixed conduction will be attributed to the electron hole formed in the Ru-doped materials.

$SrZr_{0.9-x}Y_{0.1}Ru_xO_{3-\alpha}$ basically shows similar tendency both in the electrochemical and spectroscopic results, although the hydrogen permeability was less than that of the Ru-$BaCeO_3$.

The following is a possible explanation for the hole formation: Ru-4d orbitals split into three t_{2g} and two e_g orbitals at the 6-cordination site and the t_{2g} orbitals can locate near the top of the valence band. Ru presumably has an oxidation state of 3^+ ($4d^5$) in reducing atmospheres, so that the t_{2g} subband is partially vacant and accepts electrons from the the valence band. As a result, the hole thus created is mobile through the oxygen sublattice.

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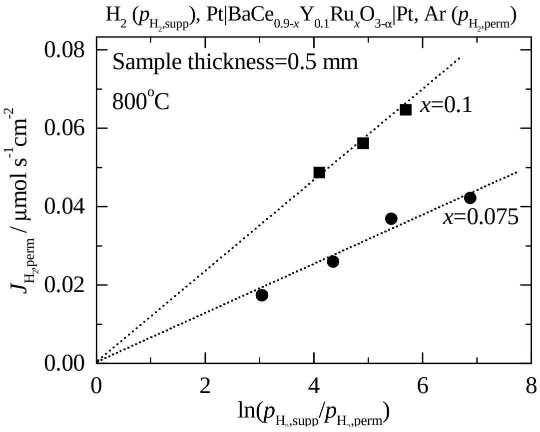

Fig. 1 Hydrogen permeation through $BaCe_{0.9-x}Y_{0.1}Ru_xO_{3-\alpha}$ (x=0.075 and 0.1) at 800ºC as a function of the logarithm of the hydrogen pressure ratio (hydrogen supply side to permeate side). The sample thickness=0.5 mm.

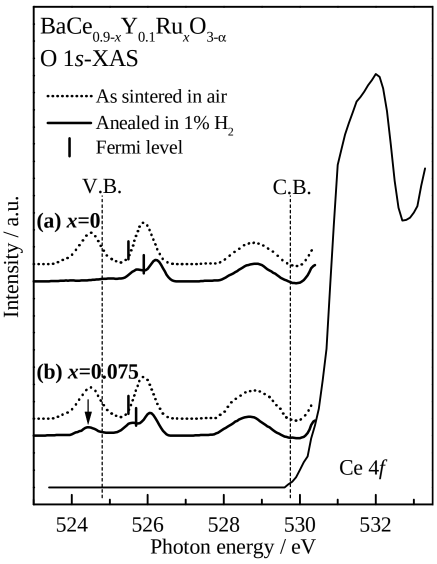

Fig. 2 XAS spectra of $BaCe_{0.9-x}Y_{0.1}Ru_xO_{3-\alpha}$ (x=0, 0.075), overview and 10-time magnified spectra around the band gap region; the dashed lines: of the specimens as sintered in air, solid lines: of the specimens after annealed in moist 1% H_2 at 800ºC for 10h.