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Radiation enhanced diffusion of hydrogen in perovskite-type oxide ceramics under reactor irradiation

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Abstract

Electrical conductivity of yttrium-doped perovskite-type barium-cerium oxide ceramics ($BaCe_{0.9}Y_{0.1}O_{3-\delta}$), implanted with 10 keV H_2^+ ions, was measured in situ under fission reactor irradiation. An increment of the electrical conductivity, called radiation induced conductivity (RIC), was observed with increasing ionizing dose rate. The RIC for the specimen with implanted H at 1.1 kGy/s and irradiation temperatures 473–673 K was higher by about four orders of magnitude than the base conductivity without radiation at 0 Gy/s, and was about two orders of magnitude higher than that without H. The RIC is attributed to electronic excitation as well as hydrogen enhanced diffusion. The RIC greatly depended on the irradiation temperature, but was insensitive to the fast neutron fluence in the range $3.3–7.4 \times 10^{23}$ n/m^2. The results show that the radiation induced defects, produced by neutron collisions, and radiolysis have no influence on the electronic and protonic conduction.

1. Introduction

Perovskite-type oxide ceramics have potential for use as burning-plasma diagnostic components, tritium monitors, tritium collectors and tritium breeding materials of blankets in nuclear fusion reactors. It is expected that high levels of hydrogen isotopes will be trapped in the insulating materials by ion bombardment from plasma or production due to Li-neutron nuclear reaction during a long term D–T discharge. Moreover, the behavior of the trapped hydrogen isotopes will be enhanced by several radiation induced phenomena such as radiation induced conductivity (RIC), radiation induced electromotive force (RIEMF) and radiation induced electrical degradation (RIED) [1–6] which has previously been reported. It is extremely important to understand how trapped hydrogen isotopes behave in insulating materials exposed to the radiation environment.

In the present study, the electrical conductivity of perovskite-type oxide ceramics was measured in situ at irradiation temperatures below 473 K (first cycle: 29 reactor full power days) and 673 K (second cycle: 27 reactor full power days) under fission reactor irradiation, and radiation induced phenomena on electronic and protonic conductivity in the ceramics are discussed.

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2. Experiments

A 10 at.% Y doped $BaCeO_3$ ($BaCe_{0.9}Y_{0.1}O_{3-\delta}$) material which had a typical perovskite-type structure and the highest proton conductivity [7] was used in the present experiments. The dimension of the specimen was 8 mm diameter and 1 mm thick. After surface etching of the specimen using Ar^+ ion sputtering in a high vacuum, zirconium metal (Zr) was deposited on one side of the specimen using an electron beam-sputtering device. Hydrogen atoms were implanted into the Zr film using a 10 keV H_2^+ ion beam at 473 K. The fluence was about 5.0×10^{21} H/m^2 and the projected range of 5 keV H^+ in Zr is about 25 nm. In order to make hydrogen atom transport by chemical reaction easily, zirconium oxide (ZrO_2) was deposited on the other side of the specimen. The thickness of both Zr and ZrO_2 films was about 1.0 μm. Moreover, two platinum electrodes of 3.0 mm diameter and

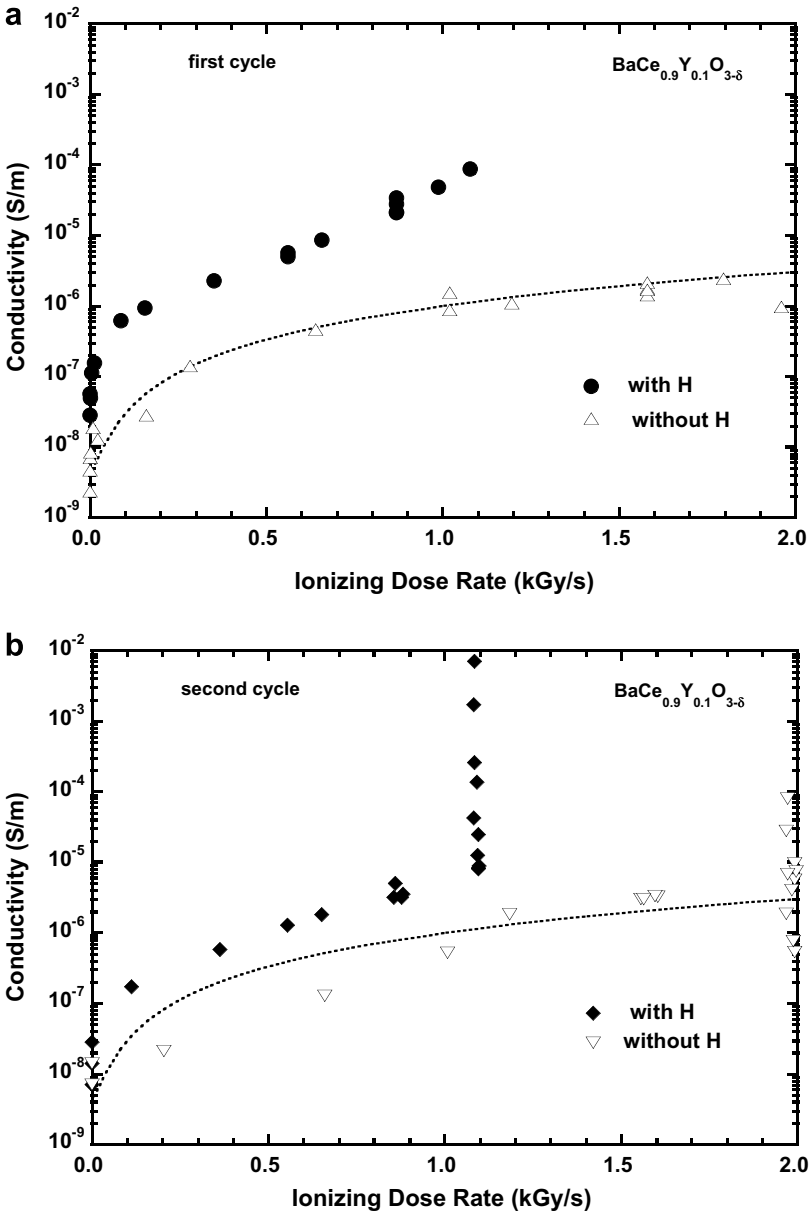

Fig. 1. Conductivities for $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ with and without H as a function of ionizing dose rate in the (a) first and (b) second reactor cycles.

1.0 mm thick were connected on both sides of the specimen with silver conductive paint. The specimens with and without H were accommodated in a fixture (sub capsule) made of copper and alumina, used in a guard ring geometry, and were installed in a specially designed irradiation rig. The irradiation rig was filled with helium gas at a pressure of 1.0×10^5 Pa and inserted in the vertical direction to the ground in the core of the Japan Materials Testing Reactor (JMTR) at the Oarai research establishment of Japan Atomic Energy Research Institute (JAERI).

Electrical conductivity measurements were carried out by recording DC-currents while applying DC-voltages of ± 30 V during the reactor irradiation. The DC electric field was disconnected during irradiation, except for the short times needed for the measurements [6].

The reactor power was raised sequentially up to 50 MW. When the reactor power reached 50 MW, the irradiation temperatures for the specimens with and without H increased up to 448 and 473 K for the first cycle, respectively, and 572 and 673 K for the second cycle, respectively, adjusted by introducing or evacuating He gas in the irradiation rig, in order to change the heat conduction. The ionizing dose rate, due to mainly gamma-ray irradiation, for the specimens with and without H were 1.1 and 2.0 kGy/s, respectively, at the reactor full power of 50 MW. The fast ($E > 1.0$ MeV) and thermal ($E < 0.683$ eV) neutron fluxes for the specimens with and without H were 6.8×10^{16} and 1.6×10^{17} n/m^{2}s, respectively, and 8.0×10^{17} and 1.6×10^{18} n/m^{2}s, respectively. The reactor full power days in the first and second cycles were 29 and 27 days, respectively. The resultant ionization doses and the fast neutron fluences for the specimens with and without H were 5.3×10^3 and 9.7×10^3 MGy and about 3.3×10^{23} and 7.4×10^{23} n/m^2, respectively.

3. Experimental results and discussion

The currents measured at the several voltages applied for the specimens with and without H increased as the ionizing dose rate increased. Although the specimen temperature is elevated by gamma-ray heating, the increment of the irradiation temperature has little influence on the increment of the current. The current for the specimen with H is proportional to the applied voltage and is asymmetric at positive and negative voltages. On the other hand, the current for the specimen without H exponentially increased with increasing applied voltage. The differences of the current–voltage characteristics with and without H may possibly be due to

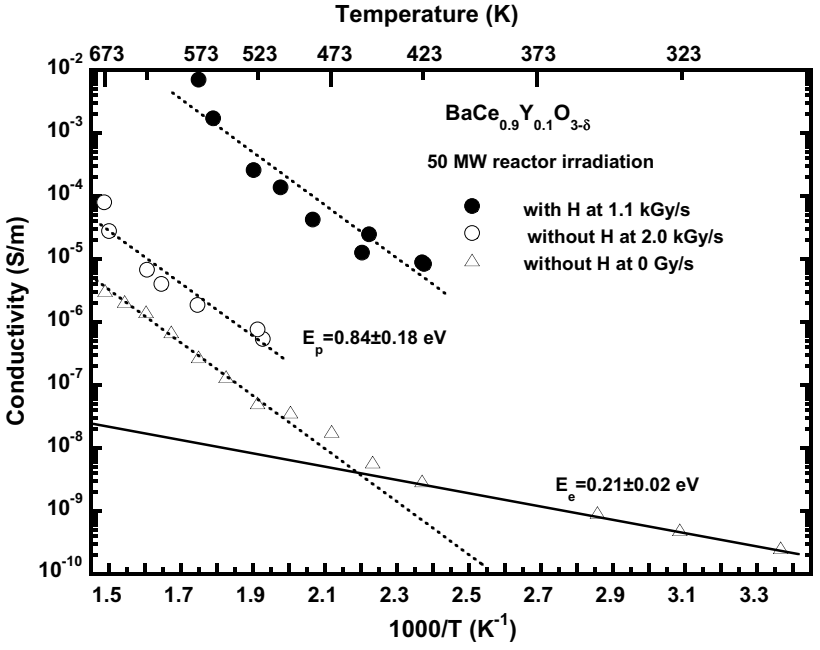

Fig. 2. Arrhenius plot of the conductivity for $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ with and without H against the irradiation temperature.

trapping of H at the cathode electrode by hydrogen migration.

Fig. 1(a) and (b) show electrical conductivity for the specimens with and without H, respectively, as a function of ionizing dose rate during the first and second cycles. The conductivity was calculated using Ohm's law with the currents from applied voltages 0 to +10 V and the specimen volume. The conductivity increased with increasing ionizing dose rate, namely it is RIC. The values at the ionizing dose rate of 1.1 kGy/s were 2–4 orders of magnitude higher than that without radiation. The RIC with H is higher compared to that without H. The theoretical values of RIC, σ_{RIC}, based on an electronic excitation model, can be expressed as $\sigma_{RIC} = \sigma_0 + KR^d$ [4,5], where σ_0, K, R and d are the base conductivity, the value of the proportionality constant, the ionizing dose rate and the value of the dose rate exponent, respectively. As shown with the dotted curves in Fig. 1(a) and (b), values for these param-

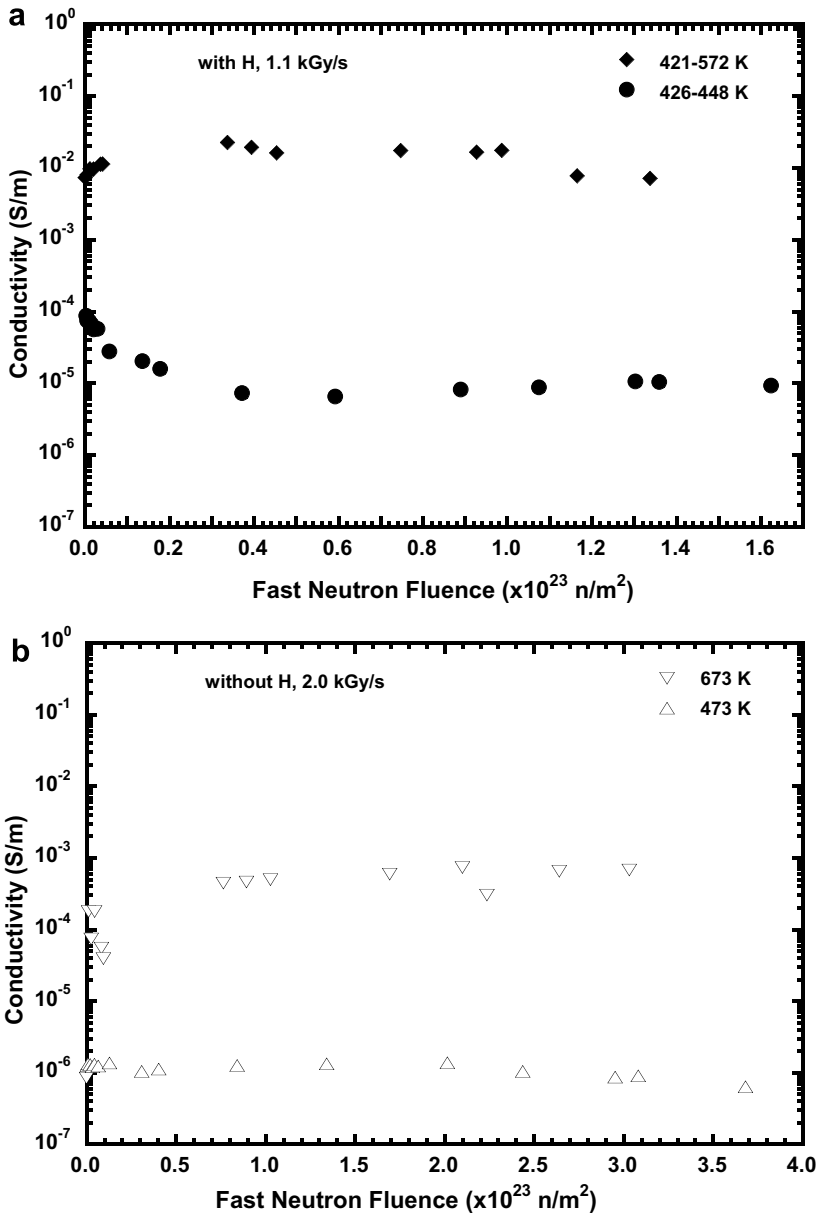

Fig. 3. Fast neutron fluence dependence of the conductivity for $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ (a) with H at 426–448 and 421–572 K and (b) without H at 473 and 673 K.

eters were determined by fitting to the experimental data as a function of the ionizing dose rate as follows; $\sigma_0 = 4.7 \times 10^{-9}$ S/m, $K = 3.0 \times 10^{-8}$ and $d = 0.9$ for the experimental data of RIC without H. However, the experimental values for RIC with H cannot be expressed with this equation. These facts indicate that the RIC with H may be caused by electronic excitation as well as enhanced diffusion of H due to ionizing irradiation. After irradiation for 29 reactor full power days, the second reactor irradiation experiment was carried out for 27 days. The RIC for specimens with and without H during the second cycle was similar to that during the first one. While the ionizing dose rate was kept at constant values of 1.1 and 2.0 kGy/s for the specimens with and without H, respectively, and irradiation temperature was raised by adjusting the He gas pressure in the irradiation rig. The conductivities increased gradually with increasing temperature, as shown in Fig. 1(b). Fig. 2 shows an Arrhenius plot of the conductivity as a function of $1000/T$, where T is the irradiation temperature, as compared to that without radiation for the specimen not including H. The pre-exponential factor for the conductivity of the specimen with H at high temperatures above 473 K was about three orders of magnitude higher than that without H. The protons dominate the conductivity above 473 K. The increment of the pre-exponential factor corresponds to the increment of the density of conducting protons, excited by radiation energy. The activation energy for conductivity with and without H was determined to be 0.84 ± 0.18 eV, calculated from the slope in Fig. 2, and was the same as without radiation. This value is associated with the potential energy for protonic conduction. Therefore, having the same activation energy with and without radiation shows that the radiation damage due to neutron cascade collisions has no influence on the protonic conduction.

Fig. 3(a) and (b) show the fast neutron fluence dependence of conductivity for the specimens (a) with and (b) without H at ionizing dose rates of 1.1 and 2.0 kGy/s, respectively. The irradiation temperatures for the specimens with and without H were 426–448 and 473 K during the first cycle and 421–572 and 673 K during the second cycle. The RIC increased with increasing irradiation temperature. The temperature dependence of the RIC may show thermal excitation of electrons trapped in the subbands near the conduction band [8]. The RIC hardly changes during the fast neutron irradiation, except for the RIC with H in first cycle, which initially decreased quickly for a brief period and thereafter increased to a constant level. These results indicate that the radiation induced defects such as point defects, dislocations and lattice distortions have no influence on the electronic and protonic conductions. It has been reported that electronic conduction of $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ specimen is modified by sub-band annihilation in the gap between valence and conduction bands due to charge transfer from Ce^{4+} to Ce^{3+}during neutron and electron irradiations, while proton conduction is not modified [8–11]. Therefore, the present results may show that sub-band annihilation due to charge transfer does not occur during the neutron irradiation. It is necessary to investigate individually the damage due to such radiation sources as fast neutrons, electrons and gamma-rays. It can be concluded that the $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ specimen which has the highest proton conductivity is a much stronger insulating material for the radiation damage induced at the fast neutron fluence of 7.4×10^{23} n/m^2.

4. Summary

The RIC of $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ specimens with and without H was observed at irradiation temperatures below 473 K (first cycle: 29 reactor full power days) and 673 K (second cycle: 27 reactor full power days) under fission reactor irradiation. The increment of the conductivity, RIC, in the specimens with H at the maximum ionizing dose rate of 1.1 kGy/s (50 MW reactor power), and without H at 2.0 kGy/s were about two and four orders of magnitude higher, respectively, than the base conductivity without radiation at 0 MW. The difference between the conductivities with and without H is caused by radiation enhanced diffusion of hydrogen, excited due to ionizing processes. The RIC with and without H for the second cycle was almost same as the result for the first one. The radiation defects produced by the neutron fluence of about 3.3×10^{23} n/m^2 do not appear to change the protonic conduction.

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