## §8. Hydrogen Pump Characteristics of an Intermediate Temperature Type Proton Conducting Oxide

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In a future nuclear fusion plant, hydrogen isotope recovery for fuel cycle is one of the important issues. An electrochemical hydrogen pump using a proton-conducting oxide is one of the candidate materials for hydrogen recovery. Some sintered oxides based on $CaZrO_3$, $SrZrO_3$ or $BaZrO_3$ etc show protonic conduction in hydrogen containing atmosphere at high temperature, if the zirconium in the oxides is partially replaced by some aliovalent cation. The ceramics of these oxides can be used as a solid electrolyte for various electrochemical devices such as hydrogen sensors, fuel cells, hydrogen pumps etc. Hydrogen pump using proton conducting oxide has attractive advantages such as: hydrogen extraction from both hydrogen molecules and hydrogen compounds; control by electric current; no pressurization, etc. In the previous research, $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ (CZI), and $SrZr_{0.8}In_{0.2}O_{3-\alpha}$ (SZI), which were used for the one-end closed tube of the test hydrogen pump, were chosen as the proton-conducting ceramic, because alkaline earth zirconates such as $CaZrO_3$ and $SrZrO_3$ are, in general, chemically more stable and stronger in mechanical strength than alkaline earth cerate ceramics. As the results, in spite of the fact that the conductivity of SZI is higher than that of CZI, the hydrogen pump performance of SZI was lower than that of CZI.[1] The reasons were suggested as follows; the decrease of the proton conductivity of SZI, chemical reduction of SZI due to the increase of oxide-ionic conduction at elevated temperature. Although the oxide-ionic conduction is restrained under lower operation temperature, the proton conductivity also decreases. In the present study, therefore, we selected $BaZrO_3$ type proton conducting oxide, which would exhibit higher proton conductivity than that of CZI and SZI even intermediate temperature below 700 K. Their hydrogen pump properties were studied from a view point of the behavior of charge particles in the proton conducting oxide.

We carried out the performance tests of the one-end-closed tube made of $BaZr_{0.955}Y_{0.03}Co_{0.015}O_{3-\alpha}$ with wide electrode area. The shape of the test tube was 12 mm inner diameter, 1.5 mm thickness and 200 mm length. The platinum electrode was attached on both sides of the test tube and the effective area on the cathode electrode was approximately 47 $cm^2$. In this experiment, wet argon gas, which contained water vapor of 1.2 kPa and hydrogen of 4 kPa, was fed to the anode at 100 $cm^3$/min. Wet argon gas contained with water vapor of 1.2 kPa was fed to the cathode at 100 $cm^3$/min. The change of water vapor in the cathode would indicate the behavior of oxide ion in the proton conducting oxide. The test tube was heated up to 723 K by an electric furnace. Then, the constant current was passed through between the electrodes by a galvanostat. The gas components were measured by an child mirror hygrometer and a gas chromatograph.

Figure 1 shows the results of hydrogen pump as a function of current with temperature dependence between the range of 623K and 723K. A slope of voltage decreased with temperature rise. It shows that a total conductivity of proton conducting oxide increases with temperature. On the other hands, hydrogen concentration in the cathode increased with current. It almost equaled to the theoretical value calculated by Faraday's low regardless of temperature. It seems that the transport number of proton is unity. Water vapor in the cathode, however, decreased, while water vapor in the anode increased with current. The decrease of water vapor in the cathode implies that water vapor was decomposed into hydrogen and oxygen. Furthermore, the increase of water vapor in the anode implies that hydrogen gas in the anode reacted with oxygen which would be formed by the proton conducting oxide. It indicates that oxide ionic conduction exhibited and oxide ion migrated in the proton conducting oxide in spite of lower temperature less than 723 K.

The exhibition of oxide ionic conduction would reduce the proton conductor as an oxide material and promote the deterioration of hydrogen pump performance. Therefore, as the results of a series of studies using alkaline earth zirconates type proton conducting oxide, it is found that $CaZr_{0.9}In_{0.1}O_{3-\alpha}$, which was not exhibited oxide ionic conduction at the temperature below 923K, is most suitable for practical use.

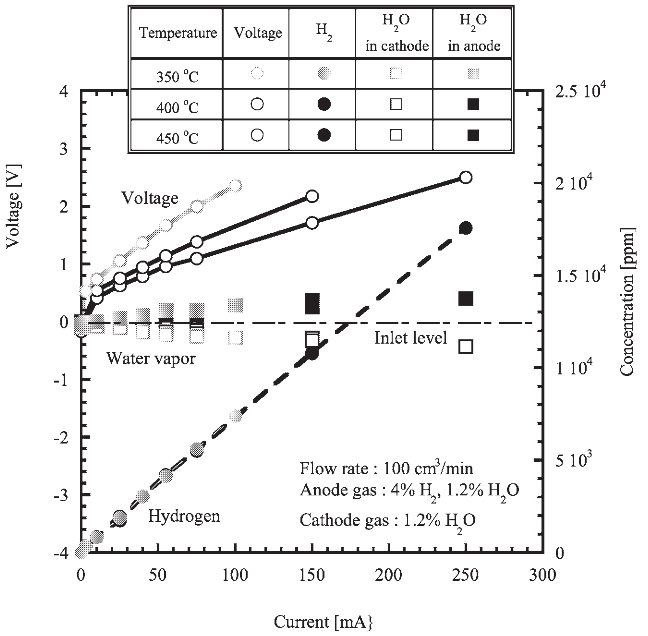


Fig. 1: Temperature dependence of voltage, water vapor and hydrogen concentration as a function of current.

1) Tanaka, M. et al.: Fusion Sci. Technol., **54** (2008) 479.