§6. Study on Proton Transfer under Electrochemical Hydrogen Pump Using $SrZrO_3$-base Oxide

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In the field of nuclear fusion engineering, tritium recovery from the gas stream such as blanket sweep gas or vacuum exhaust gas is one of the important issues. The candidate material of the tritium recovery is a palladium membrane diffuser for chemical purification of hydrogen. To provide a driving force for hydrogen to permeate through the membrane, the considerable difference between pressure of feed hydrogen and pure hydrogen is necessary. It is also necessary to pass through the catalyst bed for cracking of water vapor and hydrocarbons.

Some perovskite-type oxides such as $SrCeO_3$ and $CaZrO_3$, $SrZrO_3$ etc, which were doped with Yb^{3+}, Y^{3+} and In^{3+} etc, exhibit proton conduction in hydrogen-containing atmosphere at high temperature. Such proton conducting oxides have the potential of recovering hydrogen isotopes. We have proposed to apply a proton conducting oxide as a promising material instead of the palladium membrane diffuser. In the previous reports[1], we have evaluated the performance of the hydrogen pump by $CaZrO_3$-base oxide with lower conductivity among such oxides. As the result, this method was proved the effective for hydrogen recovery from the mixed gas of hydrogen gas, water vapor and methane. However, the improvement of the hydrogen pump performance was necessary for the practical use. In order to increase the hydrogen extraction, we applied $SrZrO_3$-base oxide with higher conductivity than $CaZrO_3$-base oxide in this study. We carried out the performance tests of the one-end-closed tube made of $SrZr_{0.9}In_{0.1}O_{3-\alpha}$ with wide electrode area. The shape of the test tube was 12 mm inner diameter, 0.72 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 42 cm^2. In this experiment, wet argon gas was fed to the anode and dry argon gas was fed to the cathode at 100 cm^3/min, respectively. The test tube was heated up from 673K to 873K by an electric furnace. Then, the constant current was passed through between the electrodes by a galvanostat.

Figure 1 shows the temperature dependence of proton transport number, which is the fraction of the protonic current to the total current, and voltage at constant current under the water vapor electrolysis. The proton transport number was less than unity. It may show that mixed conduction of not only proton also oxide-ion and electron-hole exhibited at higher temperature. Under the existence of oxygen gas generated by water vapor electrolysis, it is well known that the electron hole and proton are generated by the following defect equilibrium reactions:

$$H_2O+V^{\cdot\cdot}_o \rightleftarrows 2H^{+}+O^{x}_o$$

$$V^{\cdot\cdot}_O+1/2O_2 \rightleftarrows 2h'+O^{x}_o$$

where H^+ is a proton, $V^{\cdot\cdot}_O$ is an oxygen vacancy, h' is an electron hole, O^x_o is an oxygen ion on a normal lattice site. As a result, both hole and proton exist in the oxide and the hole migrates with proton by passage of an electric current. This is the reason why the proton transport number became less than unity. The transport number of proton had a maximum around 823 K. It might show that proton conduction decreased in order to be decreased the solubility of the proton at high temperature. On the other hands, voltage decreased with increase in temperature, i.e. the overall conductivity of $SrZr_{0.8}In_{0.1}O_{3-\alpha}$ increased with temperature. It indicates that a high temperature is not necessarily required in order to increase the hydrogen extraction of $SrZr_{0.8}In_{0.2}O_{3-\alpha}$, although a larger electric current can pass through the oxide at elevated temperature.

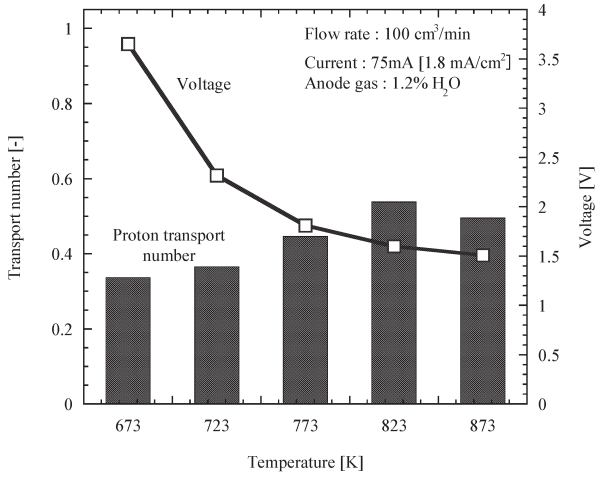

Fig. 1: Temperature dependence of proton transport number and voltage under the constant current.

Reference

1) Tanaka, M. et al.: J. Nucl. Sci. Technol. **41** (2004) 61.