§2. A Study for Hydrogen Isotope Separation and Sensing Using Proton Conducting Oxide

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Introduction

Assuming the use for hydrogen isotope sensing, hydrogen pumps and steam electrolyzers using “proton-conducting oxides” has been investigated. Proton conducting oxides typically belong to $\text{ABO}_3$ perovskites to which aliovalent cation doping is conducted. The oxides operate even at 600°C and are thus useful as electrolytes for electrochemical devices working at around the temperature. Particularly for the application to steam electrolysis $\text{SrZr}_{0.5}\text{Ce}_{0.4}\text{Y}_{0.1}\text{O}_{3-\alpha}$ ($\alpha$ is the molar amount of oxygen vacancy caused by the aliovalent cation doping and incorporation of water molecules into the oxide ion vacancies) has been the optimized composition: denoted below as $\text{SZCY541}$ [1]. So far, a thin film of $\text{SZCY541}$ fabricated on the substrate of $\text{NiO/}$SZCY541 composite was found to work with reduced ohmic resistance and hence high energy efficiency [2]. In this study, the effect of volumetric fraction of NiO/SZCY541 in the composite on the steam electrolysis properties was examined.

Experiment

SrCO$_3$, ZrO$_2$, CeO$_2$, Y$_2$O$_3$ were used as starting materials to prepare $\text{SZCY541}$. The appropriately weighed amounts were mixed and fired in air at 1200°C [1]. The obtained $\text{SZCY541}$ powder was mixed with NiO powder with volume fraction from 4/6 to 6/4, and sintered at 1400°C. The electrical conductivity of the composite specimen reduced in hydrogen (resulting in Ni/SZCY541) was measured. The composite in pellet form with 14 mm diameter and 0.5 mm thickness (Fig. 1a) was used as a cathode substrate. $\text{SZCY541}$ paste composed of the powder, ethyl cellulose and a solvent was screen printed on to the NiO/SZCY541 cathode substrate (Fig. 1b) and co-fired at 1400°C to prepare thin $\text{SZCY541}$ layer on the substrate (Fig. 1c). A paste of Sm$_{0.5}$Sr$_{0.5}$CoO$_3$ was hand painted as the anode in 6-mm-diameter circle on the surface of $\text{SZCY541}$ thin film (opposite to the substrate; Fig. 1d). The specimen was attached to the electrochemical cell housing (NorEcs ProboStat) with Pylex glass gasket and heated at 950°C to obtain the final chemical cell of steam electrolysis (Fig. 2). Steam at 20% diluted with Ar gas was supplied to the anode at 600°C and a direct current was sent to the cell. Hydrogen generation was evaluated by gas chromatography and overvoltage character was measured by a current interrupt method, respectively.

Results and Discussion

$\text{Ni/SZCY541}$ composite with a volume fraction of 4/6 showed low electronic conductivity, suggesting insufficient volume or Ni causing poor network formation. Those with fractions of 5/5 and 6/4 had enough conductivity and were used as the substrate of electrolysis cells. The result of electrolysis experiments is shown in Fig. 3. Electrode overpotential of the cell with Ni/$\text{SZCY=6/4}$ is lower than that with 5/5, suggesting larger amount of reaction cites at the Ni/$\text{SZCY}$ interface. In contrary, the cell with Ni/$\text{SZCY=6/4}$ had a higher Ohmic loss than the other, probably due to the higher resistivity of the cathode substrate. The latter factor, the Ohmic losses, has larger effect the total i-V characteristics, and as a result, the cell with Ni/$\text{SZCY=5/5}$ showed the best performance. On the basis of the above discussion, a tubular cell is being constructed with jigs shown in Fig. 4.