Electronic conductivity of ZrO_2-CeO_2-$ScO_{1.5}$ solid solutions

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ZrO_2-CeO_2-$YO_{1.5}$ (ZCY) solid solutions have higher surface catalytic activity for oxygen exchange reaction than ZrO_2-$YO_{1.5}$(YSZ) and CeO_2-$YO_{1.5}$ (YDC) electrolytes[(1)]. The high catalytic activity is strongly related to the physical properties such as electronic conductivity in ionic or mixed electric/ionic conductors. On the other hand, ZCYs have lower oxide ion conductivity than YSZ[(2)], which is not preferable when the material is used as electrode materials for SOFCs. The improvement of the conductivity of CeO_2-ZrO_2 based solid solutions should be achieved by changing the dopant from $YO_{1.5}$ to $ScO_{1.5}$ because the oxide ion conductivity of a scandia stabilized zirconia (ScSZ) electrolytes is a couple of times higher than YSZ. In this study, the electronic conductivity of $[(ZrO_2)_{1-x}(CeO_2)_x]_{0.8}(ScO_{1.5})_{0.2}$ (ZCS20, x = 0, 0.1, 0.2) was directly measured by a DC polarization method with a modified Hebb-Wagner's type ion blocking cell.

ZCS20 solid solutions were prepared by a conventional solid state reaction method. Appropriate amounts of ZrO_2(TOSOH, TZ-0), CeO_2(WAKO, 99.9%) and Sc_2O_3 (Daiichi Kigenso Kagaku Kogyo, 99.9%) powders were weighed and mixed by ball-milling method. The mixture was shaped into disks, pressed by CIP at 390 MPa, and sintered at 1773 K in air for 5 h. The obtained pellets were ground and polished. The thickness and diameter of the pellet was about 1 mm and 17 mm, respectively. Porous platinum electrodes with platinum current collectors and leads were attached on the centers of both surfaces of the pellet.

The setting of our ion blocking cell was drown in our previous paper[(3)]. The oxygen partial pressure around the blocking cell was usually fixed at 1 kPa during the measurement. A constant voltage was applied between the reversible and the blocking electrode as the oxygen was transferred from the blocking to the reversible electrodes in order to avoid a gas leakage from the glass seal due to the increase of pressure around the blocking electrode. When the voltage(E_{app}) is applied to the sample, the current changes until an ionic current is fully blocked. In the steady state, the measured current is electronic current(I_e). The electronic conductivity (σ_e) was determined by the equation as follows,

$$\sigma_e = \frac{L}{A}\left(\frac{\partial I_e}{\partial E_{app}}\right) \qquad (1)$$

where A and L are the electrode area and the thickness of sample pellets, respectively. The electronic current was observed as a function of applied voltage. The oxygen partial pressure at the blocking electrode and the sample, $P(O_2)$, was calculated by using the following equation,

$$E_{\mathrm{app}} = \frac{RT}{4F}\ln\frac{P_{out}(O_2)}{P(O_2)} \qquad (2)$$

where R, T, F and $P_{out}(O_2)$ are the gas constant, the sample temperature, the Faraday constant and the oxygen partial pressure around the reversible electrode, respectively. The electronic conductivity was evaluated as a function of oxygen partial pressure using the equations 1 and 2.

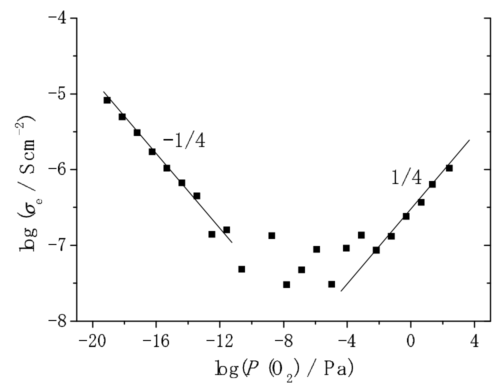

Figure 1. Electronic conductivity of 11.1mol% Sc_2O_3-88.9mol% ZrO_2 as a function of $P(O_2)$ at 1073 K.

Figure 1 shows a typical electronic conductivity plot obtained for a ScSZ electrolyte (ZCS(x = 0), 11.1 mol%-Sc_2O_3 doped ZrO_2.) at 1073 K. The electronic conductivity depended on the $P(O_2)^{1/4}$ in $P(O_2) > 10^{-2}$ Pa, and therefore, the dominant carrer of the electronic conduction is electronic hole in this $P(O_2)$ region. On the other hand, the electrical conductivity indicated the dependence on $P(O_2)^{-1/4}$ in $P(O_2) < 10^{-13}$ Pa. This dependency means that the electron is the dominant conductive specie in the lower $P(O_2)$ region. The electronic conductivity was slightly higher than that of YSZ in our previous study.

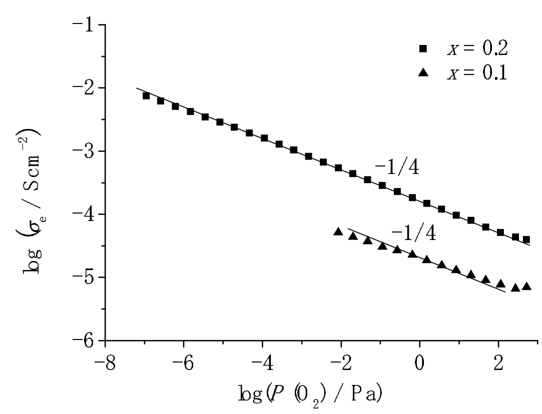

Figure 2. Electronic conductivity of $[(ZrO_2)_{1-x}(CeO_2)_x]_{0.8}(ScO_{1.5})_{0.2}$ (x = 0.1, 0.2) at 1073 K.

Figure 2 shows the electronic conductivity of ZCS20 solid solutions of x= 0.1 and 0.2 at 1073 K. The electronic conductivity remarkably increased by doping ceria to ScSZ. The slope of the plot was -1/4 in a certain $P(O_2)$ range, which indicates the electron is the dominant conductive specie in this $P(O_2)$ range. The $P(O_2)$ range with -1/4 slope was narrow for ZCY of x = 0.1, and was extremely enhanced by increasing CeO_2 concentration in ZCS20s from x = 0.1 to 0.2. These properties were similar to that of ZCY solid solutions at 1273 K[(3)].

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