

Electron and Hole Conductivity of $\text{ZrO}_2\text{-CeO}_2\text{-YO}_{1.5}$ Solid Solutions

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$\text{ZrO}_2\text{-CeO}_2\text{-YO}_{1.5}$ solid solutions have lower ionic conductivity than yttria stabilized zirconia(YSZ) or yttria doped ceria(YDC)[1]. On the other hand, the surface catalytic activity for oxygen exchange reaction is promoted in the $[(\text{ZrO}_2)_{1-x}(\text{CeO}_2)_x]_{0.9}(\text{Y}_2\text{O}_3)_{0.1}$ (ZCY, $x = 0.1\sim 1$) solid solutions[2]. The surface catalytic activity is related to the physical properties of these solid solutions. One of the most important properties is the ionic and the electronic conductivity. In this study, the electronic conductivity of ZCY solid solutions at 1073K is measured directly by DC-polarization method with Hebb-Wagner's ion blocking cell(3, 4) as functions of the oxygen partial pressure($P(\text{O}_2)$) and the composition.

ZCY solid solutions were prepared by solid state reactions among ZrO_2 (TOSOH, TZ-0), CeO_2 (WAKO, 99.9%) and Y_2O_3 (WAKO, 99.9%), as reported in our previous report[5]. The homogeneous single phase of fluorite structure was confirmed by X-ray diffraction analyses and the relative density was above 95% for all sintered specimens.

The ion blocking cell is schematically shown in Fig. 1. The DC-polarization measurements were performed with potenti/galvanostat (Type 2020, TOHO TECHNICAL RESEARCH). When the voltage was applied to the samples, the current changed until the steady state was established. In the equilibrium state, the measured current is electronic current(I_e), governed by electrons and holes in the samples.

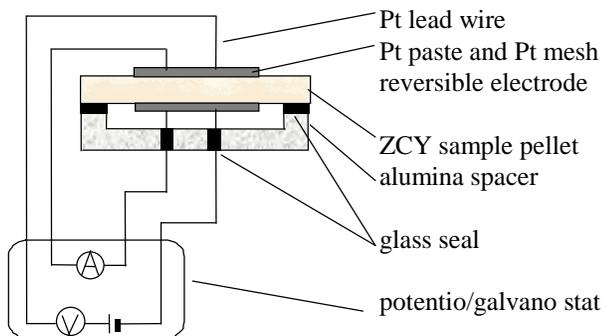


Fig. 1. Schematic view of polarization cell.

The electronic conductivity(σ_e) can be obtained from the I_e versus applied voltage(E_{app}) curve with the following equation,

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

where A and L are the electrode area and the thickness of sample pellets, respectively. The oxygen partial pressure at the inner electrode and the sample, $P(\text{O}_2)$ was calculated by using the following equation,

$$E_{app} = \frac{RT}{4F} \ln \frac{P_{out}(\text{O}_2)}{P(\text{O}_2)} \quad (2)$$

where R , T , F and $P_{out}(\text{O}_2)$ are the gas constant, the sample temperature, Faraday constant and oxygen partial pressure around the outer electrode, respectively.

Figure 2 shows the derived electronic conductivity of ZCY($X = 0.1\sim 0.5$) at 1073 K as a function of $P(\text{O}_2)$. The electronic conductivity depends on the $P(\text{O}_2)^{-1/4}$ in $P(\text{O}_2) > 1$ atm, so that the dominant species of the electronic conduction is determined as electron. On the other hand, the electrical conductivity of ZCYs with high Ce contents($X = 0.7\sim 1.0$) deviate from the $P(\text{O}_2)^{-1/4}$ dependence in $P(\text{O}_2) > 10^{-4}$ atm as shown in Fig. 3. Furthermore, ZCY without Zr content($X = 0$) indicates the dependence on $P(\text{O}_2)^{1/4}$ in $P(\text{O}_2) > 10^{-2}$ atm. This dependency means that the hole conduction is dominant in the high $P(\text{O}_2)$ region. The hole conduction was not observed obviously in our previous study at 1273 K[5]. Considered from the appearance of the hole conduction with decreasing temperature, the activation energy of hole conduction is lower than that of electron conductivity.

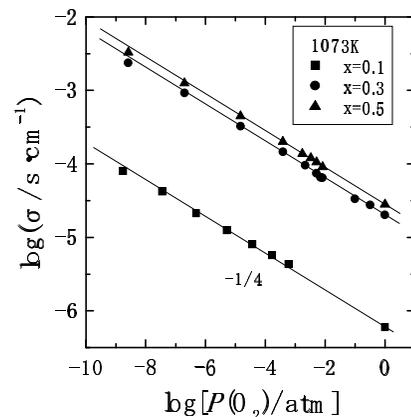


Fig. 2 Electronic conductivity of ZCY($X=0.1\sim 0.5$)

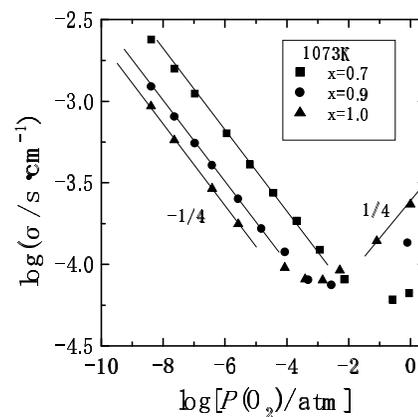


Fig. 2 Electronic conductivity of ZCY($X=0.7\sim 1.0$)

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