## Ni/Proton Conductor Cermet Anode for Intermediate-Temparature Solid Oxide Fuel Cells

Takuya Kosaka, Minoru Inaba, Akimasa Tasaka, Hiroyuki Yoshida,* and Toru Inagaki*

*Faculty of Engineering, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan*
**Technical Research Center, The Kansai Electric Power Company, Inc., Amagasaki, Hyogo 661-0974, Japan*

Intermediate-temperature solid oxide fuel cells (SOFCs) operated at reduced temperatures have been attracting more and more attention in these days, owing to many reasons. Nickel/oxide-ion conductor cermets are widely used for the anodes of solid oxide fuel cells (SOFCs). However, anode activity of the cermets significant drops at intermediate temperatures < 800°C, and should be improved. At the anode cermets, hydrogen is oxidized to form water through the following elementary steps:

$$H_2 \rightarrow 2\,H\bullet \quad \text{(at Ni surface)} \qquad [1]$$
$$2\,H\bullet \rightarrow 2\,H^+ + 2\,e^- \qquad [2]$$
$$2\,H^+ + O^{2-} \rightarrow H_2O \qquad [3]$$

Steps [2] and [3] simultaneously proceed only at the interface of electrode, electrolyte, and reactant gas, so-called triple phase boundaries (TPBs), in the anode cermets. If the electrolyte in the cermet has proton conductivity as well as oxide-ion conductivity as is seen in high temperature proton conductors, these elementary steps can be greatly modified. The protons formed in Step [2] can migrate in the electrolyte together with oxide ions, and Step [3] can proceed at the surface of the proton conductor as shown in Fig. 1. In studies on hydrogen pumps based on high-temperature proton conductors, it has been reported that Steps [1] and [2] are very fast.[1) ] Hence, if Step [3] is facile, the total reaction rate will be greatly improved, resulting in a low overvoltage at the anode.

Rare earth ion doped barium cerate, $BaCe_{1-x}M_xO_{3-\alpha}$ (M = Y, Yb, Nd, and Sm, etc.) is known to be proton and oxide ion mixed conductor in hydrogen-containing atmospheres[1, 2)]. In the present study, $BaCe_{0.9}Sm_{0.1}O_{3-\alpha}$ (BCS10) was used as a model cermet material. BCS10 was prepared by a solid-state reaction and a citrate process, and characterized by X-ray diffraction (XRD). The conductivity of the sintered body was measured in various atmospheres by AC impedance spectroscopy, and typical results are shown in Fig. 2. The conductivity of BCS10 in dry Ar mainly originates from oxide-ion conduction because of hydrogen free atmosphere. The conductivity in dry and humidify $H_2$ was deviated from that in dry Ar at temperatures below 873 and 1023 K, respectively. This behavior corresponds to the appearance of proton conduction as described by reactions [4] and [5].

$$H_2 + 2\,O_O^{\times} + 2\,h^{\cdot} = 2\,OH_O^{\cdot} \qquad [4]$$
$$O_O^{\times} + V_O^{\cdot\cdot} + H_2O = 2\,OH_O^{\cdot} \qquad [5]$$

Fig. 3 represented discharge curves of a fuel cell, which consisted of a Ni/BCS10 anode cermet, a Sc-stabilized zirconia (ScSZ) electrolyte, and a platinum cathode, in the range of 1273-873 K. The fuel was in humidified $H_2$ and the oxidant was air. Though clear improvement by proton conductance was not observed in this figure, stable discharge was possible even in the temperature range where proton conduction was predominant (below 1023 K). Destruction of Ni/BCS10 anode cermet by evolution of $H_2O$ at the electrolyte/BCS10 interface did not take place. Further tests for the effect of proton conduction are now being under investigation.

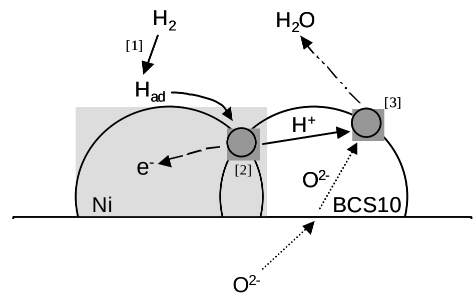


**Fig. 1.** Reaction sites for hydrogen oxidation reaction at Ni/proton conductor cermet anode.

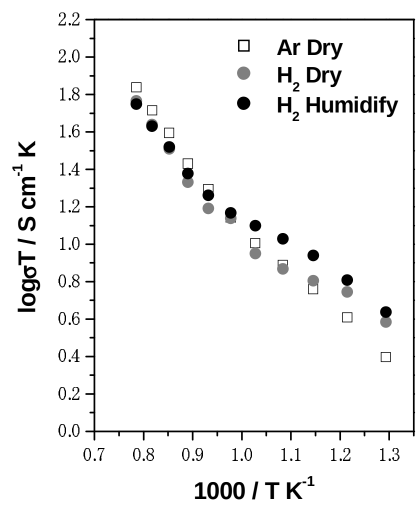


**Fig. 2.** Arrhenius plots of total conductivity of BCS10 prepared by solid-state reaction in dry Ar, $H_2$ and humidified $H_2$ in the temperature range of 773-1273 K.

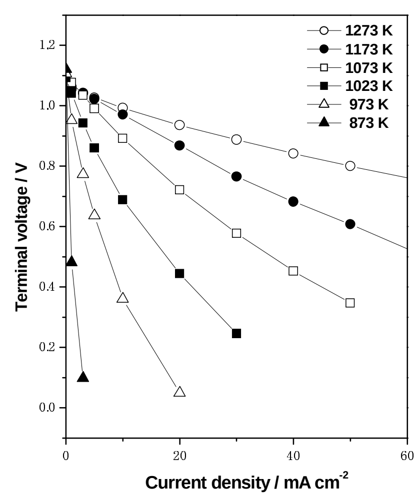


**Fig. 3.** Cell voltage-current density curves for test cell using Ni/BCS10 anode at various temperatures.

**References**
(1) H. Iwahara, T. Yajima, T. Hibino, and H. Ushida, *J. Electrochem. Soc.*, **140** (1993) 1687.
(2) H. Iwahara, T. Yajima, and H. Ushida, *Solid State Ionics*, **70/71** (1994) 267.