

## Reaction kinetics on platinum electrode / yttrium-doped barium cerate interface under H<sub>2</sub>–H<sub>2</sub>O atmosphere

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### ABSTRACT

For the evaluation of electrode reaction at H<sub>2</sub>–H<sub>2</sub>O(g), Pt/BaCe<sub>0.95</sub>Y<sub>0.05</sub>O<sub>3-δ</sub>, the electrode impedance and steady-state polarization measurements were examined as the functions of hydrogen partial pressure,  $P_{H_2}$ , steam partial pressure,  $P_{H_2O}$  and hydrogen activity on the electrolyte surface at triple phase boundary (TPB),  $a_H$ , using three-terminal method at 773 and 873 K. The electrode interfacial conductivity strongly depended on  $P_{H_2}$ . From the results of the polarization measurements, the  $a_H$  dependence of the reaction rate can be related to the contribution of adsorbed hydrogen atoms on the BCY surface at TPB. Additionally, the  $P_{H_2}$  dependence of the reaction rate is attributed to the contribution of the adsorbed hydrogen atoms on the Pt surface. In order to explain the  $P_{H_2}$  dependence of reaction rate, we propose the two electrode reaction models by the magnitude of the concentration of adsorbed hydrogen atoms on the Pt surface. The following reaction processes were considered as the rate determining reaction step in H<sub>2</sub>–H<sub>2</sub>O(g), Pt/BaCe<sub>0.95</sub>Y<sub>0.05</sub>O<sub>3-δ</sub>: (i) the surface diffusion of H<sub>ad</sub> (Pt) near TPB, and (ii) the dissociative adsorption of H<sub>2</sub> on the Pt surface at TPB. The reactions (i) and (ii) take place in parallel.

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### 1. Introduction

Proton ceramic fuel cells (PCFCs) are considered to be the promising energy conversion technology with high power generating efficiency in the intermediate temperature range from 673 to 873 K. At this temperature range, PCFCs have the advantages of polymer electrolyte fuel cells (PEFCs) and solid oxide fuel cells (SOFCs) such as high proton conductivity, high fuel utilization, unnecessary of precious metal catalyst and so on. They can be applied not only to stationary power generating system but also to power source of the transportation vehicle [1]. Perovskite-type proton conducting oxides have attracted much attention as electrolyte materials of PCFCs. Especially, BaCeO<sub>3</sub> based proton conducting oxides are promising candidate materials because it is known that they have high proton conductivity and show high performance as fuel cells, hydrogen pumps, hydrogen sensors [1–7].

The electrode reaction mechanisms of proton conducting oxides need to be clarified for their applications to the electrochemical devices such as PCFCs. So far, gas electrode reaction mechanisms of solid electrolyte system have mainly been studied on that of oxide ion conductors [8–13]. In the case of oxide ion conductors, the electrode reaction kinetics has been explained by chemical reaction model. For example, Mizusaki et al. suggested that the rate determining reaction process at the H<sub>2</sub>–H<sub>2</sub>O(g), Pt/YSZ is the exchange of adsorbed species across the TPB between the Pt and the YSZ surface [11]. On the other

hand, the electrode reaction of proton conducting oxides has also been reported [14–21]. Uchida et al. studied on polarization phenomena at the H<sub>2</sub>, Pt | SrCe<sub>0.95</sub>Yb<sub>0.05</sub>O<sub>3-δ</sub> | Pt, air [14] and limiting current in a high temperature hydrogen pump based on SrCe<sub>0.95</sub>Yb<sub>0.05</sub>O<sub>3-δ</sub> with porous Pt electrodes [15]. Additionally, the electrode reaction kinetics of the metal (Ni, Pt, Ag, Au)/Sr<sub>0.995</sub>Ce<sub>0.95</sub>Y<sub>0.05</sub>O<sub>2.970</sub> interface using a point contact electrode technique has been investigated by Kek et al [17]. They suggested the electrode reaction mechanism at the metal electrode/Sr<sub>0.995</sub>Ce<sub>0.95</sub>Y<sub>0.05</sub>O<sub>2.970</sub> is decisively determined by the nature of the electrode and the hydrogen partial pressure. Although the electrode reaction kinetics has been discussed on the basis of chemical reaction process in the ref. [17], the formulation of the electrode reaction mechanism has not been made yet, and the rate determining reaction has not been clarified in detail. Moreover, in many cases, the electrode reaction kinetics of proton conductors has been analyzed using Butler–Volmer equation, which is based on the kinetics of the charge transfer reaction [19–21]. Therefore, we tried to elucidate electrode reaction of proton conducting oxides by proposing the chemical reaction model in detail.

In this study, the electrode reaction kinetics at the H<sub>2</sub>–H<sub>2</sub>O(g), Pt/BaCe<sub>0.95</sub>Y<sub>0.05</sub>O<sub>3-δ</sub> was investigated by the AC impedance and steady-state polarization measurements. From the results of these electrochemical measurements, we attempted to determine the electrode reaction mechanism and the reaction rate equation. In order to elucidate the electrode reaction mechanism, we analyzed the electrode reaction kinetics in various ways and considered the following things specifically: (a) electrode overpotential can be given by either the difference in the hydrogen potential or the difference in the oxygen potential, and (b) the

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reaction processes to be considered as the rate determining step can be the chemical reaction of adsorbed species on the Pt surface, the surface diffusion of adsorbed species on the Pt electrodes and the dissociative adsorption reaction at TPB. As the results of analysis as described above, we report the best results of the analysis in this paper. The electrode reaction process at the  $\text{H}_2\text{-H}_2\text{O}(\text{g})$ , Pt/BaCe<sub>0.95</sub>Y<sub>0.05</sub>O<sub>3- $\delta$</sub>  was concluded to be the electrode reaction mechanism as described later.

## 2. Experimental

### 2.1. Sample preparation

Yttrium-doped barium cerate, BaCe<sub>0.95</sub>Y<sub>0.05</sub>O<sub>3- $\delta$</sub>  (BCY), was prepared as an electrolyte by a solid state reaction method and sintered at 1923 K for 10 h in air. The relative density of sintered disk-shaped sample was higher than 98% of the theoretical value. The disk-shaped pellet was confirmed to be a single phase perovskite by X-ray diffraction analysis. The sample surfaces of 15 mm in diameter were polished with 15, 9, 6, and 3  $\mu\text{m}$  diamond paste, and thickness of the sample was finally 1.57 mm.

Platinum paste electrodes were screen-printed on both sides of sample surfaces as working (WE) and counter (CE) electrodes, whose diameter was 6 mm (electrode area: 0.28 cm<sup>2</sup>). Reference electrode (RE) was pasted on the side surface of a sample disc. The pellet with porous platinum electrodes was sintered at 1373 K for 4 h in air. A platinum wire of 0.3 mm in diameter was wound on the reference electrode as an electric lead.

### 2.2. Electrochemical measurements

For the evaluation of electrode reaction at Pt/BaCe<sub>0.95</sub>Y<sub>0.05</sub>O<sub>3- $\delta$</sub> , the electrode impedance and steady-state polarization current were measured using three-terminal method under controlled  $\text{H}_2\text{-H}_2\text{O}$  atmospheres at 773 and 873 K. Schematic illustration of the experimental setup is shown in Fig. 1. The symmetrical electrochemical cell was set in a reaction chamber with three gas compartments separated for each electrode. Humidified  $\text{H}_2\text{-Ar}$  gas mixtures were prepared independently for each compartment and introduced into three compartments. In order to keep constant potential distribution

of water vapor within the electrolyte, the water vapor pressure,  $P_{\text{H}_2\text{O}}$ , was controlled to be the same for all compartments. Hydrogen partial pressure,  $P_{\text{H}_2}$ , of WE and CE was varied from 0.001 to 1 bar (0.1% $\text{H}_2\text{-Ar-100}\%$  $\text{H}_2$ ) while the reference electrode was exposed to the fixed  $\text{H}_2\text{-Ar}$  gas ( $P_{\text{H}_2} = 0.01$  bar).

The impedance measurements were performed with applied AC amplitude of 10 mV in the frequency range from 10 mHz (or 1 mHz) to 1 MHz using a frequency response analyzer (NF Co., FRA 5096) and a potentiostat (TOHO TECHNICAL RESEARCH, potentiostat/galvanostat 2000).

The steady-state polarization current was measured by a potentiostatic method. The electrode overpotential,  $E$ , was calculated by subtracting overpotential of electrolyte resistance around open circuit voltage (OCV),  $R_{\text{OCV}}$ , from the applied potential between WE and RE. The electrolyte resistance between WE and RE was determined by the high frequency intercept of the complex impedance plots around OCV.

Additionally, the electrode impedance in anodic and cathodic polarization was measured at 773 K under  $P_{\text{H}_2} = 0.01$ , 1 bar and  $P_{\text{H}_2\text{O}} = 0.012\text{-}0.027$  bar.

## 3. Results and Discussion

### 3.1. Electrode interfacial conductivity and steady-state polarization current

Fig. 2 shows the results of the observed electrode impedance around OCV at 873 K. The electrode interfacial resistance,  $R_E$ , is deduced from the difference of resistance between high frequency intercept and low frequency intercept of the observed electrode impedance. The electrode interfacial conductivity,  $\sigma_E$ , is calculated by the following equation:

$$\sigma_E = 1 / (AR_E) \quad (1)$$

where  $A$  is the electrode area of the working electrode.

Fig. 3 (a) and (b) show  $\sigma_E$  as a function of  $P_{\text{H}_2}$  and  $P_{\text{H}_2\text{O}}$  at 773 and 873 K, respectively. As shown in Fig. 3, the  $\sigma_E$  strongly depends on  $P_{\text{H}_2}$ . The log  $\sigma_E$  increases against log  $P_{\text{H}_2}$  with the slope of the plot between 1/2 and 3/4. On the other hand, it is found that the  $\sigma_E$  is almost

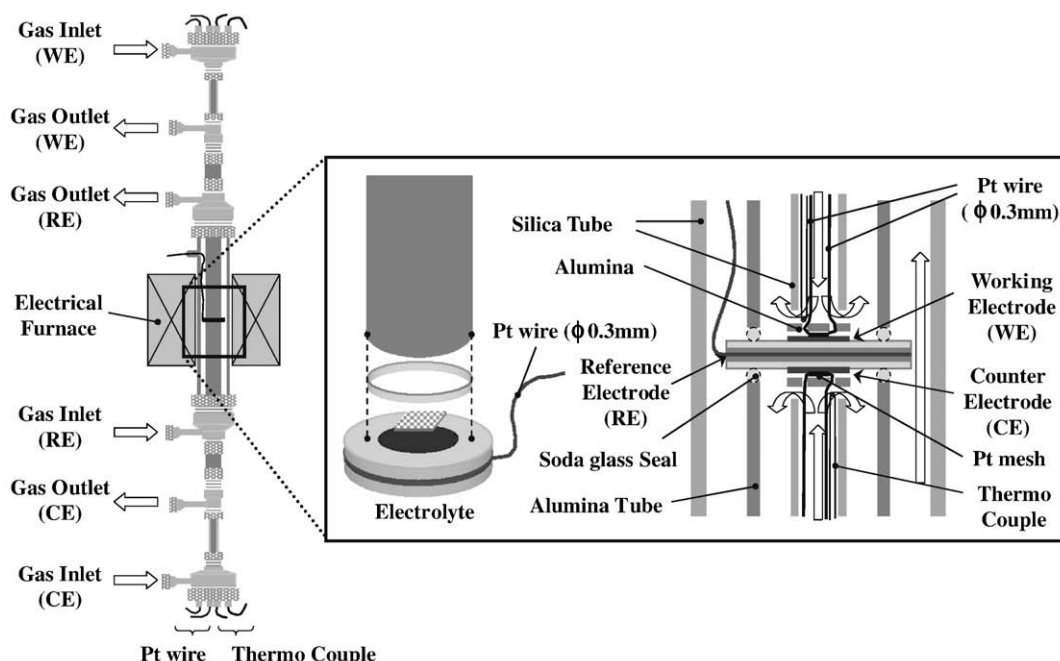


Fig. 1. Schematic illustration of the experimental setup.

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