Communication

Evaluating surface protonic transport on cerium oxide via electrochemical impedance spectroscopy measurement

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A B S T R A C T

Surface protonic transport on cerium oxide (CeO_2) was investigated using electrochemical impedance spectroscopy (EIS). CeO_2 pellets showing low relative density: approximately 60%, was prepared for the purpose. The structure and morphology of the prepared CeO_2 pellets were confirmed from XRD and SEM measurements. Results show that the pellets had a pure cubic phase, with open pores on which water can be adsorbed. Electrochemical impedance spectroscopy measurements were taken to evaluate the surface protonic transport on CeO_2 as a function of temperature and as a function of partial pressure of water (P_{H2O}) at 400 °C. Investigations of the temperature dependence of the conductivity revealed that only the conductivities of surface grain bulk (σ_{intra}) and surface grain boundary (σ_{inter}) increased with decreasing temperatures under wet conditions ($P_{H2O} = 0.026$ atm). The P_{H2O} dependence of surface conductivities (σ_{intra} and σ_{inter}) revealed that σ_{intra} increases strongly with P_{H2O} at 400 °C. These findings provide evidence that water adsorbates play an important role in surface protonic transport on CeO_2 at low temperatures. Surface protonic transport at low temperatures can contribute to the expansion of applications for electrical and catalytic processes.

1. Introduction

Cerium oxide (ceria) is well known as a material exhibiting mixed conductivity of oxide ions [1–5] and electrons [1,2,6] over a range of temperatures, e.g. 150–1000 °C. Consequently, ceria and doped ceria is widely used for chemical and electrical energy conversion processes such as hydrogen production [7], automotive catalysis [8], CO_2 reduction [9], and solid oxide fuel cells [10]. In addition, nanoceramics of ceria doped with acceptors such as Sm [11] and Gd [12] have attracted attention because it is suggested that water can be incorporated into the lattice oxygen vacancy to show proton conduction in these oxides at low temperatures (<400 °C). At such low temperatures, the dependence of steam pressure on resistivity was also investigated with film-shaped bare CeO_2 to understand the influence of steam addition on protonic conduction [13].

Recently, proton conduction via adsorbed water onto oxides, so-called "surface protonics", has also been widely investigated for nanocrystalline oxides such as Y-stabilized ZrO_2 (YSZ) [14,15], TiO_2 [16], and CeO_2-based oxides [17–19], exhibiting surface protonic conduction under wet conditions. Actually, the total conductivity increases from a certain temperature at around 150–300 °C with decreasing temperatures. At lower temperatures, water adsorption onto the oxides is favorable.

Water exudation from nanocrystalline oxides is observed. Therefore, we may conclude that a layer of adsorbed water with hydrogen bonding forms, yielding a high protonic conductivity at low temperatures. The surface proton transport mechanism is proposed to change from the Grotthuss mechanism to the vehicle mechanism with increasing thickness of the adsorbed water layer. By the Grotthuss mechanism, a proton hops from one —O—H species to a nearest available oxide ion species at high temperatures and low partial pressures of water. By the vehicle mechanism, on the other hand, H_3O^+ diffuses in liquid-like water at low temperatures and high partial pressures of water [15]. It is noteworthy that various applications to a concentration cell exist for power generation at room temperature [20]. Heterogeneous catalysis at low temperatures [21–23] can be anticipated by virtue of the high protonic conductivity at low temperatures.

Results presented in our earlier report show that the steam partial pressure plays an important role in surface protonics [21]. Recently, detailed mechanisms of protonic surface transport in porous YSZ ceramic have been investigated with equivalent circuits representing the ionic transport in internal grains and over the oxide surface [24]. Use of a pellet having low density of approximately 50% to extract the surface protonic conduction revealed that humidity induces surface protonics

onto the porous YSZ below 150 °C. Free protons are regarded as migrating in the chemisorbed water layer by the Grotthuss mechanism. The transport mechanism changes to a vehicle mechanism in the physisorbed layer at around 60% relative humidity quite independent of temperature [24].

This study specifically examines the surface transport property of bare CeO_2 under wet conditions. We evaluated surface proton conduction as a function of temperature and as a function of partial pressure of water at 400 °C, using pellets with low relative density of around 60%.

2. Experimental

2.1. Preparation of CeO_2 pellets

For this study, CeO_2 (JRC-CEO-1) was used to prepare the pellets. First, CeO_2 powders were suspended in *iso*-propanol and were crushed into fine particles using a planetary mill (Fritsch GmbH), with rotation at 300 rpm for 15 min, followed by pausing for 10 min, and rotation again at 300 rpm for 15 min. After evacuation of the *iso*-propanol, powders of CeO_2 were pressed at 2 tons for several min and calcined at 1000 °C for 2 h under air. The pellet diameter was 10 mm. The thickness was 1.0 mm. The relative density of the pellets was around 60%, calculated from the weight and the geometric factor of pellets. Then circular Pt electrodes were painted on both sides with Pt ink (Pt ink number 6926; Metalor Technologies UK Ltd.) and were calcined at 900 °C for 1 h under air.

2.2. Characterization and measurements

X-ray diffractometry (XRD, MiniFlex600 with Cu-K_α radiation sources: $\lambda = 1.5418$ Å; Rigaku Corp.) and scanning electron microcopy (SEM, 15 kV, S4500S; Hitachi Ltd.) were used to observe the structure and morphology of the prepared CeO_2 pellets. Electrochemical impedance spectroscopy (EIS) measurements were conducted in a measurement cell

(ProboStat; NorECs AS, Norway) with a 2-electrode 4-wire set up connected to a Novocontrol alpha-A impedance spectrometer with a ZG4 interface. All AC impedance spectra were recorded within the frequency range of 10^7–10^{-3} Hz with amplitude of 0.1 V RMS. Temperature dependence of electrical conductivity was investigated in dry Ar at 150–500 °C or wet Ar flow ($P_{H2O} = 0.026$ atm) at 125–400 °C. Partial pressure of water (P_{H2O}) dependence of electrical conductivity was investigated at 400 °C for P_{H2O} of 0.026–0.2 atm by bubbling Ar through thermostatted water followed by a heated gas line to the measurement cell, which had heated base unit. The obtained data were analyzed using an equivalent circuit fitting software (ZView ver. 3.5a; Scribner Associates Inc.). A model of the equivalent circuit is presented in Fig. 1. Details are discussed in an earlier report [24]. First, data recorded under dry conditions were analyzed without elements for components of surface career transport: "intra" and "inter". Then data recorded under wet conditions were analyzed with the full equivalent circuit keeping parameters R and C fixed at the values obtained under the corresponding dry condition. In case R_b and R_{gb} were too large compared with the surface protonic resistances, especially in case of high P_{H2O} (>0.05 atm), we used the simple equivalent circuit without elements for these components of internal grain carrier transport. Therefore, we obtained at most 6 or 4 (without parameters for electrode: R_{el} and C_{el}) parameters when one-time fitting was conducted. Finally, each conductivity (σ_{intra}, σ_{inter}, σ_b, and σ_{gb}) was calculated with equation (1), where S denotes the area calculated from the diameter of pellet, and L signifies the thickness of the pellet.

$$\sigma = \frac{1}{R}\frac{L}{S} \tag{1}$$

3. Results and discussion

Before elucidating surface conductivity, the physicochemical properties of CeO_2 were confirmed using XRD and SEM. Results are presented
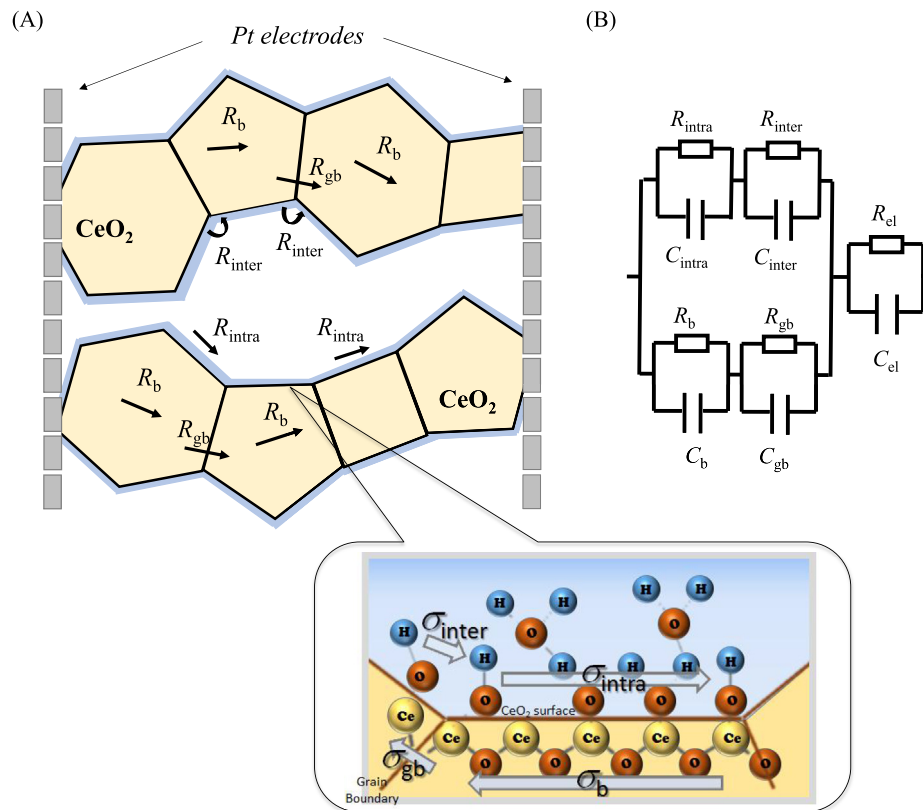

Fig. 1. (A) Schematic illustration of surface and grain resistance for CeO_2 and (B) equivalent circuit describing career transport in grain bulk (b), across grain boundary (gb), over the grain surface (intra), and over the grain boundary surface (inter).