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Short communication

Hydrogen oxidation at metal–ceria boundary by electrical conductivity relaxation method

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ABSTRACT

Electrical conductivity relaxation (ECR) method is utilized to determine H_2 oxidation process on $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) with scattered Pt or Au particles by increasing the H_2 partial pressure in the gas stream. For SDC with Au particles, the reaction occurs only at the SDC–gas interface. When Pt is introduced, the surface exchange kinetics can be remarkably improved whereas the contribution from the ceria–gas interface can be as small as 4.3%. The improvement increases linearly with the Pt–SDC boundary length, demonstrating that H_2 oxidation pathway is dominated by the Pt–SDC–gas three-phase boundaries.

1. Introduction

The metal–ceramic mixtures are widely used as the anodes for solid oxide fuel cells (SOFCs) [1]. The metal works mainly as an electronic current path while the ceramic performs as the oxygen ionic way. When the ceramic is yttria-stabilized zirconia (YSZ), the anode reaction distinctly takes place at the three-phase boundary (TPB) sites, where the metal, ceramic, and gas phase meet [2]. However, the reaction sites cannot be easily ascertained when it comes to the ceramic material of doped ceria (DCO), since DCO has mixed ionic and electronic conductivities under the reducing atmosphere [3]. Haile and coworkers [4,5] have demonstrated that the near-equilibrium H_2 oxidation pathway is dominated by the ceria–gas interface with minimal contributions from the TPBs by analysis of electrochemical impedance data for ceria–metal (Pt, Ni) structures. Gorte and coworkers [6–8] have reported that the cell power density does not significantly change when metal such as Cu, Au, or conductive carbon is introduced, which suggests the reaction pathway is confined to the ceria–gas interface. An interesting result contrary to the previous one has also been reported [9]. It is found that the addition of 1 wt.% Pd could significantly improve the cell performance. To be specific, the peak power density practically doubles compared with the cell without Pd, proving that the anode reaction is not limited to the ceria–gas interface. Our previous work [10] showed that the peak power density was not affected by the area of the DCO–gas interface of the Ni–ceria anode but increased with the TPB length, suggesting that the anode reaction takes place dominantly at the TPBs.

Therefore, the reaction site is of considerable debate. To design and fabricate optimized metal–ceria anodes, it is essential to know where the electrode reaction takes place. Whatever, the general anode reaction for electro-oxidation when H_2 is used as the fuel is given by Kroger–Vink notation [4]

$$H_2(g) + O_O^{\times} \rightarrow H_2O(g) + V_O^{\bullet\bullet} + 2e' \quad (1)$$

Where $V_O^{\bullet\bullet}$ represents a doubly ionized oxygen vacancy. The reaction can be characterized by interfacial polarization resistance and/or overpotential, which are determined with electrochemical impedance spectroscopy [2,4,5]. In addition, it may be characterized using the power density of a single cell, where both the anode and cathode reactions take place [6–10]. Obviously, the reaction rates can be obtained from the concentration changes in either the gas phase (H_2 and H_2O) or the solid phase ($V_O^{\bullet\bullet}$ and electron). In this work, electrical conductivity relaxation (ECR) method is chosen to determine the concentration change in the solid phase. Assuming linear interface kinetics, [11] the reaction rate, R (mol s^{-1}), can be expressed as

$$R = -Sk[c(t) - c(\infty)] \quad (2)$$

Where k is the oxygen surface exchange coefficient that can be obtained from ECR measurement. By reducing the oxygen partial pressure (pO_2) in the reducing gas, oxygen ions ($O_O^{\times}$) are released from DCO and subsequently react with H_2 to form H_2O. S is the surface area, $c(t)$ instantaneous oxygen concentration at time t, and $c(\infty)$ the concentration for the reduced pO_2. To demonstrate this method, samaria-doped ceria (SDC) is selected as the ceramic electrolyte and Pt or Au as the metal. Scattered metal particles are

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Table 1
Characteristics for Pt or Au particles on SDC surfaces.

Sample code	Metal weight (10^{-5} g cm^{-2})	Evaporation time (s)	Heating temperature (°C)	θ_{metal} (−)	L_{TPB} (μm^{-1})	k (10^{-5} cm s^{-1})	k_{metal} (10^{-5} cm s^{-1})
SDC	0	0	–	0	0	2.185	0
20Au700	4.919	20	700	0.142 ± 0.003	2.483 ± 0.069	1.820	−0.005
10Pt900	2.574	10	900	0.026 ± 0.001	0.923 ± 0.011	4.060	1.931
15Pt900	3.539	15	900	0.102 ± 0.002	4.305 ± 0.117	9.352	7.390
20Pt700	4.826	20	700	0.157 ± 0.002	6.004 ± 0.080	16.63	14.79
15Pt700	3.861	15	700	0.178 ± 0.005	8.736 ± 0.329	23.16	21.36
10Pt700	2.252	10	700	0.219 ± 0.001	17.67 ± 0.18	40.00	38.29

deposited onto the SDC surface by vacuum evaporation and heating. The reaction rate is linked to the surface microstructures so that the effects of the TPB and SDC–gas interface can be quantitatively discussed.

2. Experimental

SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) was prepared using oxalate co-precipitation method [12]. The SDC powders were uniaxially pressed into rectangular bars at 320 MPa and sintered at 1500 °C for 5 h. The bar samples were about 30.0 mm long, 5.18 mm wide and 0.56 mm thick. Au and Pt were deposited onto the SDC surface with vacuum evaporation (JFC-1600, JEOL) followed by heating to form metal particles. Details are summarized in Table 1. The surface microstructures were revealed using scanning electron microscopy (SEM, JSM-6700F, JEOL). Details of ECR measurement were reported previously [13]. The electrical conductivity was measured at 700 °C using the four-point technique with a digital multimeter (2001-785D, Keithley). The gas was changed from flowing wet H_2/Ar (4:96) (humidified using a moisture bottle, 3% H_2O) to flowing wet H_2/Ar (20:80) in 1 s and fixed at flowing wet H_2/Ar (20:80) so that the gradient of atmosphere can be neglected in the relaxation process. The pO_2 at 700 °C is changed from 3.17×10^{-22} to 1.27×10^{-23} atm as calculated with the thermodynamic data.

3. Results and discussion

Fig. 1 shows the surface microstructures. The density of bare SDC bar (Fig. 1a) is 98.2% as determined with the Archimedes method in distilled water, which is higher than the requirement for the ECR measurement, ~95% [14]. Fig. 1b is the typical microview for Au particles on SDC surfaces. The average size is about 220 nm, bigger than Pt's (Fig. 1c–g). The average size of Pt particles is about 100 nm for the samples heated at 900 °C. It decreases when the heating temperature is reduced to 700 °C. Fig. 1g shows that the average size is about 50 nm. Obviously, the particles are disconnected, and the dispersion is relatively uniform. So, the scattered particles do not affect the substrate conductivity though the metal conductivity is usually much high. The SEM pictures

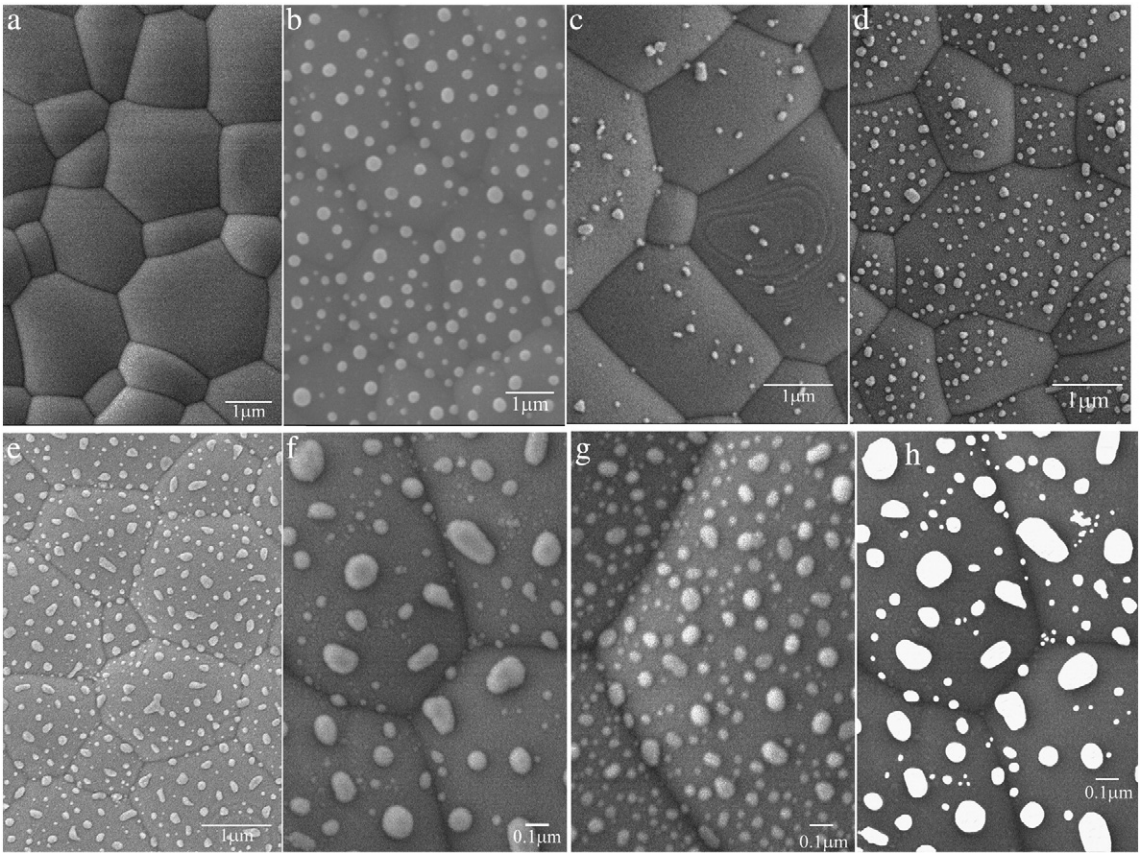

Fig. 1. SEM micrographs for (a) bare SDC, (b) 20Au700, (c) 10Pt900, (d) 15Pt900, (e) 20Pt700, (f) 15Pt700, (g) 10Pt700, and (h) an example (15Pt700) for the micrograph treatment to obtain θ_{metal} and L_{TPB}.