Theoretical analysis of hydrogen oxidation reaction in solid oxide fuel cell anode based on species territory adsorption model

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H I G H L I G H T S

- New analytical reaction model for hydrogen oxidation at anode in SOFC was proposed.
- Analytical expression of anode overpotential with current density could be obtained.
- Overpotential at high and low current density could be combined to unique expression.
- Current density asymptotes limit value as oxygen coverage at TPB approaches unity.
- Analytical results based on the model were in good agreement with experiments.

A R T I C L E   I N F O

A B S T R A C T

A modified reaction model of hydrogen oxidation around a triple phase boundary (TPB) is proposed for solid oxide fuel cells (SOFCs) with a Ni/oxide ion conductor cermet anode containing proton conductor particles in order to describe the mechanism of anode overpotential reduction. In this model, three kinds of TPBs consisting of nickel metal, oxide ion conductors, proton conductors, and gas phases were considered. It was assumed that the chemical species could be adsorbed within a finite narrow area on each material around the TPB. The reaction rate in the anode was controlled by the surface reaction between the adsorbed hydrogen and adsorbed oxygen; all other reactions took place under chemical equilibrium. Based on the reaction model, analytical expressions of current density with oxygen activity and anode overpotential with current density could be obtained. The latter could combine the anode overpotential at low- and high-current-density regions, which were conventionally expressed independently. The analytical results were in good agreement with the experimental results for both the conventional anode and the new anode incorporating a proton conductor. Especially, the anode overpotential reduction could be explained by the additional supply of adsorbed hydrogen from the proton conductor to the TPB.

1. Introduction

Solid oxide fuel cells (SOFCs) have recently attracted considerable attention because of high conversion efficiencies (50–60%), flexibility of fuel type (hydrogen, natural gas, and others), and high-temperature exhaust gas (useful for thermal management) [1]. Recently, a 1–2 kW class SOFC with internal reforming achieved an AC electricity conversion efficiency of more than 60% (based on the low heating value) through rigorous thermal management, which enhances energy recirculation and reduces heat loss and energy consumption of the air supply [2]. However, research is still being conducted to further reduce electrical resistances, improve endurance, and enhance the reaction rate for applications in material science, thermal engineering, or system engineering.

SOFCs generally show two types of resistance: one is an ohmic resistance (caused by the conduction of ions and electrons in the electrolyte, the anode, and the cathode) and the other is an overpotential (which consists of an activation overpotential and a concentration overpotential). The activation overpotential is caused by electrochemical reactions at the triple phase boundary (TPB) on both the anode and the cathode sides, whereas the concentration overpotential is caused by a decrease in the partial pressure of the reactant gases at high current densities [3]. To increase the power density of SOFCs, both types of resistance should be reduced.

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In general, cermet electrodes made of Ni and oxide ion conductors, such as yttria-stabilized zirconia (YSZ) or gadolinium-doped ceria (GDC), are used for SOFC anodes. To produce SOFCs with a high power density, a new anode incorporating a proton conductor (barium−cerium/yttrium oxide (BCY): $BaCe_{0.8}Y_{0.2}O_{3-\delta}$) was previously proposed by the authors, and the anode over-potential was reduced by adding BCY particles to the Ni/GDC cermet anode [4]. Moreover, it was disclosed that a significant amount of hydrogen was adsorbed onto the surface of the BCY and Ni particles in an experiment using a thermal desorption spectroscopy (TDS) method [5]. From the results, it was concluded that in the Ni/GDC-BCY anode, the BCY particles helped supply the adsorbed hydrogen to the TPB in the anodic reaction; as a result, the output power of the Ni/GDC-BCY-anode SOFC was almost two times higher than that of a conventional Ni/GDC anode.

Various reaction mechanisms around the TPB in SOFC anodes have been proposed [6–13]. For example, Ihara's group assumed competitive adsorption equilibrium among the adsorbed species, i.e., H_{ad}, H_2O_{ad}, and O_{ad}, at the TPB of a Ni/YSZ cermet anode [8]. They assumed that the reaction rate was controlled by the surface reaction between H_{ad} and O_{ad} to produce H_2O_{ad} (Langmuir-type reaction). In the reaction model, the current density was expressed by a function of oxygen activity in the anode. A comparison was also made between the analytical and experimental results [8]. How-ever, the previous model cannot explain why the current density, i.e., the reaction rate, increased with the addition of a proton conductor to the conventional anode because in the conventional model, which assumes a complete competitive adsorption equi-librium condition, the adsorption sites on the TPB were occupied by the additional adsorbed hydrogen, resulting in a reduction of adsorbed oxygen, i.e., a decrease in reaction rate.

In a conventional cermet anode consisting of Ni and oxide ion conductors, hydrogen is mainly adsorbed onto the Ni surface, which has been verified by TDS measurement [5]. On the other hand, most of the oxygen would be adsorbed onto the surface of the oxide ion conductors around the TPB after the oxide ions released their electrons to the Ni particles. Then, the adsorbed hydrogen reacts with the adsorbed oxygen at the TPB. Consequently, these species are adsorbed in a finite area around the TPB and do not necessarily occupy the same adsorption sites.

In this paper, a new modified model is proposed for anodes with a proton conductor based on the Langmuir-type surface reaction between adsorbed hydrogen and oxygen and other reactions at chemical equilibrium by assuming that the chemical species are adsorbed in a finite surface area of Ni, oxide ion conductor, or proton conductor particles around the TPB. The analytical results were compared with those obtained from experiments [4,8,14–17].

2. Reaction model

2.1. Assumptions

Fig. 1 shows a schematic of the arrangement of Ni, oxide ion conductor, and proton conductor particles in the anode [5]. Oxide ions are transferred through a network structure made of oxide ion conductors from the electrolyte. Around the TPB, the oxide ions change to adsorbed oxygen by the release of electrons to the Ni particles. Hydrogen molecules are adsorbed on the surfaces of the Ni and proton conductor particles. From the previous research, it was disclosed that the addition of BCY proton conductor particles to Ni/GDC anode was effective although the volume ratio of BCY was less than 20% [5]. According to the percolation theory, to retain the network structure of each particle for conduction of ion or electron, the particle number concentration in the anode should be greater than 30% [18]. Therefore, it is considered that the BCY particle does
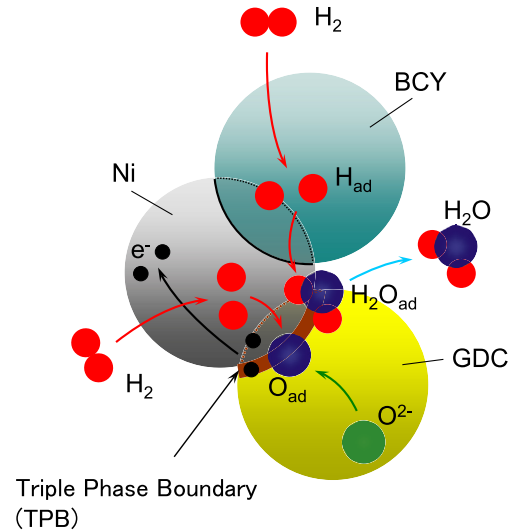

Fig. 1. Schematic of the reaction mechanism for overpotential reduction in the Ni/GDC-BCY anode [5].

not play a role as a proton conductor, but as a hydrogen adsorber. For simplicity, it is assumed that the particle size is uniform and the concentrations are the same. As a result, the unit structure consists of a single particle of Ni, an oxide ion conductor particle, and a proton conductor particle (Fig. 1).

Fig. 2(a) shows a schematic of an idealized arrangement of Ni, an oxide ion conductor, and a proton conductor for analysis. There are three kinds of triple phase boundaries consisting of Ni, an oxide ion
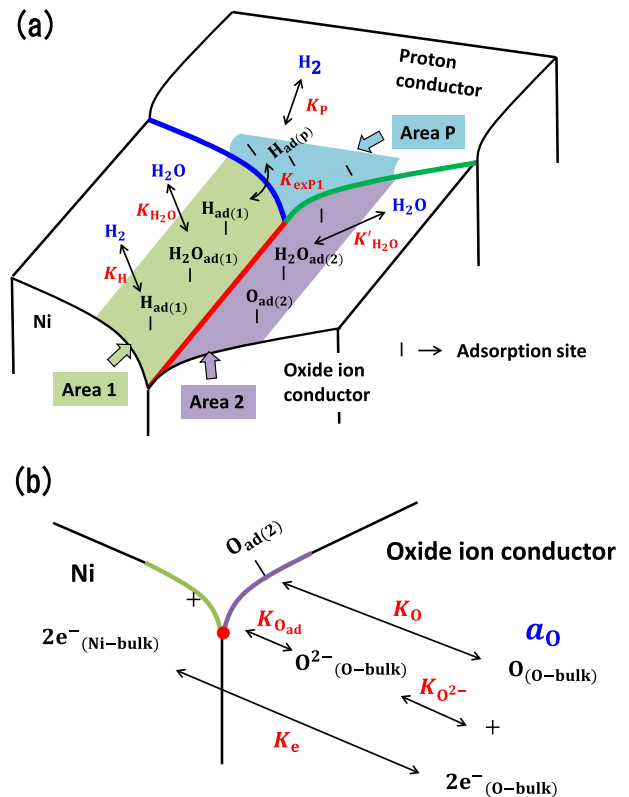

Fig. 2. (a) Schematic of three kinds of TPBs consisting of Ni, oxide ion conductor, and proton conductor materials. (b) Schematic of the cross section of the interface between Ni and oxide ion conductor.