Prediction of overpotential and effective thickness of Ni/YSZ anode for solid oxide fuel cell by improved species territory adsorption model

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HIGHLIGHTS

- SOFC anode overpotential is studied by improved species territory adsorption model.
- The model is combined with DFT-database to improve the reliability.
- Reduction of unknown parameters enables to estimate effective anode thickness.
- Effective anode thickness tends to increase with temperature in six Ni/YSZ anodes.
- The model describes anode over-potential dependency on steam partial pressure well.

GRAPHICAL ABSTRACT
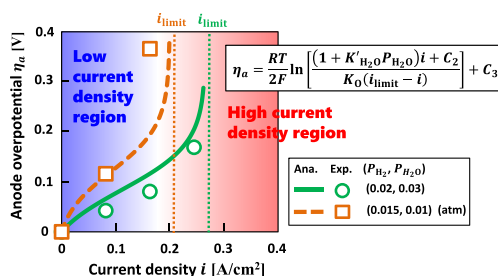
$$\eta_a = \frac{RT}{2F} \ln\left[\frac{(1 + K'_{H_2O} P_{H_2O})i + C_2}{K_0(i_{limit} - i)}\right] + C_3$$

ABSTRACT

The reliability of analytical model for hydrogen oxidation at Ni/YSZ anode in solid oxide fuel cell named as species territory adsorption model has been improved by introducing referenced thermodynamic and kinetic parameters predicted by density function theory calculations. The model can explicitly predict anode overpotential using unknown values of quantities of state for oxygen migration process in YSZ near a triple phase boundary (TPB), frequency factor for hydrogen oxidation, and effective anode thickness. The former two are determined through careful fitting process between the predicted and experimental results of Ni/YSZ cermet and Ni-patterned anodes. This makes it possible to estimate effective anode thickness, which tends to increase with temperature in six kinds of Ni/YSZ anodes in references. In addition, the comparison between the proposed model and a published numerical simulation indicates that the model can predict more precise dependence of anode overpotential on steam partial pressure than that by Butler-Volmer equation with empirical exchange current density. The introduction of present model into numerical simulation instead of Butler-Volmer equation can give more accurate prediction of anode polarization.

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1. Introduction

Solid oxide fuel cells (SOFCs) have been identified as one of the next-generation energy conversion devices, which can convert chemical energy of various fuels such as hydrogen, carbon

monoxide, and hydrocarbon to electrical energy directly. The oxidation reaction of these fuels on anode is one of the key processes in SOFC operation. As an anode material for SOFCs, a cermet electrode consisting of Ni and yttria-stabilized zirconia (YSZ) is widely used because of its high catalytic activity for hydrogen oxidation and of high chemical stability at elevated temperature [1]. Hydrogen oxidation is considered to occur at the triple phase boundary (TPB) consisting of Ni, YSZ and gas phases because the hydrogen should be reacted with the oxide ion accompanied with release of electrons [2,3].

The performance of Ni/YSZ anode is dominated by following two phenomena; electrochemical reaction at the TPB and transport of gases, oxide ion, and electron in a porous structure. Recently, numerical simulations of SOFC anode have been conducted based on actual microstructure obtained by focused ion beam-scanning electron microscopy (FIB-SEM). In those simulations, gases, ions and electron transport are solved by lattice Boltzmann method (LBM) [4,5], volume of fluid (VOF) method [6], or sub-grid scale (SGS) method [7]. The development of those analysis and simulations can provide accurate description of transport phenomena in SOFC anode. On the other hand, electrochemical reaction at the TPB has been mainly described by Butler-Volmer equation and exchange current density, which has been originally developed for reactions at interface between metal electrode and liquid electrolyte [8]. In this scheme, all detailed reaction kinetics are lumped together into exchange current density, which is not established via phenomenological description but treated as fitting parameters [6] or given by empirical expressions [4,5,7,9]. This description is sometimes followed by inaccurate prediction for the dependence of anode overpotential on temperature or steam partial pressure [4,5,7,9]. For accurate prediction and physically-based interpretation of anode polarization, development of reliable electrochemical reaction model at the TPB based on elementary chemical reactions, such as H_2 adsorption, O migration, or surface reactions, are required [7].

Detailed electrochemical reaction models based on elementary chemical reactions have been developed by Vogler et al. [10] or Goodwin et al. [11] to explain the experimental results of Ni-patterned anode [12–14], which has well-defined TPB geometry. These models include adsorption/desorption of the gas-phase species, surface reactions and diffusions of adsorbed species, and charge transfer processes at the TPB. Although such multi-step elementary kinetic approaches are useful to investigate detailed reaction mechanism, it is difficult to combine with numerical simulations at anode microstructure because it requires high computational power and many unknown parameters. The number of needed parameters such as quantities of state, activation energy, or frequency factor increases with the number of assumed elementary reactions. Some of those are roughly estimated, taken from different studies, or obtained from fitting to a limited data set. Therefore, generality and reliability of reaction model and parameters are still questionable [15,16].

In contrast, we have developed analytical model of hydrogen oxidation at the TPB on SOFC anode [17]. The model has been constructed from elementary chemical reactions at the TPB, and gives simple explicit expression of anode overpotential as a function of current density. This simple model enables to predict current density or anode overpotential with a small number of parameters compared to multi-step reaction models reported previously [10,11]. The trends of anode overpotentials with respect to hydrogen partial pressure, water vapor partial pressure, or temperature predicted by the model were qualitatively consistent with experimental ones [17], while quantitative investigation is still ongoing because all reaction parameter, such as equilibrium constant and reaction rate constant was determined by fitting to experimental results.

In this paper, the reliability of our model is improved through the introduction of referenced thermodynamic and kinetic parameters predicted by density function theory (DFT) calculations [16,18]. The model can predict anode overpotential using unknown values of quantities of state for oxygen migration process in YSZ near a TPB, frequency factor for hydrogen oxidation, and effective anode thickness. The former two are determined through careful fitting process between the predicted and experimental results of Ni/YSZ cermet and Ni-patterned anodes. This makes it possible to estimate effective anode thickness based on the model. The analytical results are compared with six experimental results using Ni/YSZ cermet [4,5,7,9,17,19,20], and the quantitative validation of the model or estimated effective anode thickness are discussed.

2. Species territory adsorption model

The details of the species territory adsorption model proposed by the authors were shown in our previous work [17]. Therefore, only overview of the model is shown here. Fig. 1 shows a schematic of the TPB consisting of metal (Ni), oxide ion conductor (YSZ), and gas phases. In this model, some finite areas, which contribute to species adsorption, are assumed around TPB, and these areas on Ni and YSZ are defined as Area 1 and 2, respectively. All chemical reactions considered in this model are listed in Table 1. In this model, hydrogen and oxygen are assumed to be adsorbed mainly on the surface areas of Area 1 and 2, respectively. Dissociative adsorption of hydrogen molecule on Ni surface is well-known phenomena, however, oxygen migration from YSZ bulk to its surface is not well understood [21]. As shown in Fig. 1, an oxygen atom supplied from YSZ bulk has a possibility to be adsorbed on (i) YSZ surface or (ii) interface between Ni and YSZ. In the case (i), oxygen atom forms chemical bond to only YSZ surface while it forms to both YSZ and Ni surface in the case (ii). The favored adsorption site for oxygen atom is discussed based on the comparison between the model and experiments later.

In this model, current density i [A cm^{-2}] is described as a function of oxygen activity a_O in the YSZ bulk near the TPB, as follows.

$$i = \frac{(k_{aI} + k_{aII})K_H P_{H_2} K_O a_O - \left(k_{cI} K_{H_2O} P_{H_2O} + k_{cII} K'_{H_2O} P_{H_2O}\right)}{\left(1 + \sqrt{K_H P_{H_2}} + K_{H_2O} P_{H_2O}\right)^2 \left(1 + K_O a_O + K'_{H_2O} P_{H_2O}\right)} \quad (1)$$

In addition to this, the analytical expression of anode overpotential η_a [V] could be obtained explicitly as a function of current density i as follows.
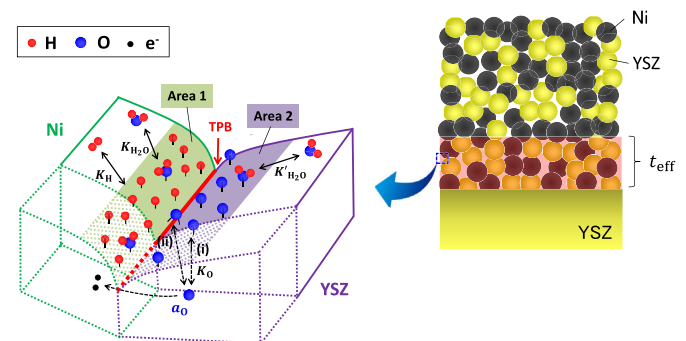

Fig. 1. Schematics of the TPB consisting of Ni, YSZ and gas phases and of the concept of an effective anode thickness t_{eff}. Area 1 and 2 are assumed finite area on Ni and YSZ which contribute to species adsorption. Two possible paths for oxygen migration (i) and (ii) are shown.