



Evaluation of nickel-yttria stabilized zirconia anode degradation during discharge operation and redox cycles operation by electrochemical calculation



Takaaki Shimura ^{a,*}, Zhenjun Jiao ^{a,b}, Naoki Shikazono ^{a,b}

^a Institute of Industrial Science, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan

^b CREST, JST, Gobancho 7, Chiyoda-ku, Tokyo 102-0076, Japan

HIGHLIGHTS

- Changes in exchange current density and YSZ ionic conductivity were evaluated.
- Three dimensional electrochemical simulations were conducted.
- These parameters decreased during discharge and increased after redox treatment.
- Changes in these parameters were consistent with experimental results.

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ABSTRACT

Degradation of Solid Oxide Fuel Cell (SOFC) anode during discharge operation and redox cycles operation were evaluated by three-dimensional electrochemical calculations using a Lattice Boltzmann method (LBM). Three dimensional microstructures were obtained by Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) reconstruction. In the electrochemical calculations, changes in exchange current density and ionic conductivity of Yttria stabilized Zirconia (YSZ) during the operations were assumed and their values were calculated by fitting the calculated overpotential values to the experimental ones. Changes in triple phase boundary density calculated from the reconstructed microstructures were inconsistent with the gradual degradation observed during repeated redox-discharge cycles. Changes of the fitted exchange current density and YSZ ionic conductivity values in both discharge operation and redox cycle operation showed same tendency as the experimental results. Change in exchange current density or YSZ ionic conductivity should be considered as an essential factor which governs the cell performance change regardless of the redox treatment.

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1. Introduction

Tolerance against redox cycles is one of the most important issues to achieve stable operation of solid oxide fuel cells (SOFCs). In cases of system shutdown for maintenance or by accidental power loss etc., undesirable increase of oxygen partial pressure in the anode side will take place. Nickel, which is the most common electron conductor in the anode, will be oxidized and this results in volume expansion of the anode. When the oxygen partial pressure in the anode side decreases again, nickel is reduced accompanied

by the volume shrinkage. Due to the large volume expansion from Ni to NiO (about 70% [1,2]) and volume shrinkage from NiO to Ni (about 42% [2]), irreversible microstructure changes after the redox cycles lead to degradation of the cell performance [1–5].

Recently, quantitative analysis of anode microstructure using dual beam focused ion beam and scanning electron microscopy (FIB-SEM) has been conducted [6–8]. In our previous work, FIB-SEM was applied to evaluate the microstructure change during redox cycles, and the relationship between the microstructure parameters and the cell performance was investigated [9]. Redox followed by 20 h discharge was repeated using YSZ electrolyte-supported cell with Ni-YSZ anode. Performance degradation was observed during the discharge process. From impedance measurement, both ohmic and polarization resistances increased

* Corresponding author.

E-mail address: tshimura@iis.u-tokyo.ac.jp (T. Shimura).

during the discharge process. On the other hand, decrease in polarization resistance was observed just after every redox treatment, whereas ohmic resistance remained nearly unchanged just after the redox process. During the subsequent discharge process, both polarization and ohmic resistances increased again. Showing performance enhancement just after each redox process and degradation after subsequent discharge process, cell performance showed gradual degradation as the redox-discharge cycles are repeated. From the microstructure analysis, active triple phase boundary (TPB) density increased just after the redox process and decreased during the discharge process. This TPB change was consistent with the polarization resistance change mentioned above. However, active TPB density showed gradual increase as the redox-discharge cycles are repeated. This is inconsistent with the gradual increase of polarization resistance during repeated redox-discharge cycles. Therefore, it becomes unclear that the degradation during discharge is solely attributed to the decrease of TPB density. It is implied that cell performance is dominated not only by the microstructure change, but also by the other factors.

As for the factors which affect the cell performance, two parameters were considered in this study. First is the local exchange current density at TPB, which represents the electrochemical reaction rate at the reaction site. There are several studies on the local exchange current density values at TPB using Ni-YSZ patterned electrodes. However, reported values show large variations [10–12]. In addition, it is not fully understood whether the exchange current density values from the patterned anodes can be applied to the porous ones. Furthermore, it is reported that segregation of impurities at TPB will increase the overpotential, which means that local exchange current density might deteriorate during the operation [13–15]. Therefore, the change in exchange current density can be considered as one of the factors which leads to the change in electrode performance during the operation.

Second possible factor is the YSZ ionic conductivity deterioration [17,18]. Several researchers reports that the existence of Ni accelerates the phase transition of YSZ from cubic to tetragonal phases under reduced atmosphere, which results in faster degradation of YSZ ionic conductivity [16,19,20]. Formation of tetragonal YSZ at Ni/YSZ grain boundaries is observed [21,22]. Nickel can dissolve into YSZ during the co-sintering of NiO and YSZ [20], which implies that the phase transition of YSZ is enhanced in the composite Ni-YSZ anode. Therefore, decrease in YSZ ionic conductivity can be another factor of cell performance deterioration.

In this study, exchange current density and YSZ ionic conductivity were considered as the degradation factors, and their changes during discharge operation and redox cycles operation were evaluated. In order to evaluate the electrode performance, three dimensional lattice-Boltzmann method (LBM) calculations were conducted [23,24] using the anode microstructure reconstructed by FIB-SEM. Values of exchange current density and YSZ ionic conductivity were estimated by fitting the calculated overpotential values to the experimental ones.

2. Methods

2.1. Experiments

Fabrication process of electrolyte supported cell is described in Ref. [9]. NiO-8YSZ composite powder was used as anode material. The ratio of NiO to YSZ is 60: 40 vol %. Redox cycles test was conducted as described in Ref. [9]. Redox treatment was conducted between every 20 h discharge operation and repeated for ten times (“10 redox test”). In this study, “220 h discharge test” was additionally carried out. In the same way as the “10 redox test”, current density was set at 0.2 A/cm². Humidified hydrogen (5% H₂O) was

supplied, and all tests were carried out at 800 °C. Fuel utilization is calculated as 9.53% based on the applied current density. Terminal voltage and electrochemical impedance between the anode and the reference electrode were measured. The reference electrode is a platinum wire wound around the rim of the YSZ electrolyte. Collected impedance data were fitted with the equivalent circuit to calculate the ohmic and polarization resistances [9]. The electrochemical impedance measurements were conducted at open circuit voltage (OCV) after every 20 h discharge. Then, the microstructures were reconstructed using FIB-SEM. The operation sequences are summarized in Table 1. Microstructure parameters are calculated as described in Ref. [9].

For the LBM calculations, reconstructed microstructures were all rescaled from voxel size of 30 nm to 120 nm due to the computational cost. The number of voxels used in the LBM simulations are shown in Table 1. It is reported that voxel size of at least 124 nm is required for the overpotential calculation of the anode [23].

2.2. Numerical simulation

Assuming that Ni and YSZ are perfect electronic or ionic conductors, the diffusion equations of gas, electron and ion are written as follows:

$$\nabla(D_1 \nabla C_{H_2}) + \nabla(D'_1 \nabla p_t) = \frac{i_{\text{react}}}{2F} \quad [1]$$

$$\nabla(D_2 \nabla C_{H_2O}) + \nabla(D'_2 \nabla p_t) = -\frac{i_{\text{react}}}{2F} \quad [2]$$

$$\nabla\left(\frac{\sigma_e}{F} \nabla \tilde{\mu}_e\right) = -i_{\text{react}} \quad [3]$$

$$\nabla\left(\frac{\sigma_{O^{2-}}}{F} \nabla \tilde{\mu}_{O^{2-}}\right) = i_{\text{react}} \quad [4]$$

where C_i stands for the molar fraction of each gas species, and p_t is the total gas pressure. D_i is a diffusion coefficient for each species, and D'_i is a coefficient for total gas pressure gradient. $i_{\tilde{\mu}_i}$ stand for the electrochemical potentials of electron and oxygen ion. σ_i stand for the conductivities of ion and electron. F is the Faraday constant. i_{react} is the reaction current at local TPB defined as follows:

$$i_{\text{react}} = i_0 L_{\text{TPB}} \left\{ \exp\left(\theta_a \frac{F}{RT} \eta\right) - \exp\left(-\theta_c \frac{F}{RT} \eta\right) \right\} \quad [5]$$

where i_0 is the local exchange current density, L_{TPB} is local active TPB density, and η is the local overpotential. θ_a and θ_c are the anodic charge transfer coefficient and cathodic charge transfer coefficient, respectively. Values of θ_a and θ_c are given as 2 and 1, respectively [25].

In this work, Cylindrical Pore Interpolation Model (CPIM) is used for the gas diffusion model [26]. D_i and D'_i are derived from the CPIM model as follows:

$$D_i = \left[\frac{y_i}{(D_A)_{ij}} \sqrt{\frac{M_i}{M_j}} + \frac{y_j}{(D_A)_{ij}} \right]^{-1} \quad [6]$$

$$D'_i = D_i \left[\frac{1}{(D_A)_{ij} A_A \sqrt{M_j}} - \frac{1}{RT} \right] \quad [7]$$

where M_i is the mass of molecules. $(D_A)_{ij}$ and A_A are interpolated diffusion coefficient and pressure gradient coefficient, respectively

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