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Quantitative analysis of solid oxide fuel cell anode microstructure change during redox cycles

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HIGHLIGHTS

- Performance was enhanced and TPB density increased after redox treatment.
- Performance degraded and TPB density decreased after discharge process.
- As redox cycles are repeated, gradual degradation was observed.
- TPB density increased as the redox cycles are repeated.
- Performance degradation cannot be explained from microstructure change.

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ABSTRACT

In the present study, correlation between solid oxide fuel cell anode microstructure and electrochemical performance during redox cycles was investigated. Electrolyte-support cell with nickel/yttria stabilized zirconia composite anode was prepared and tested under discharge process with redox cycles. Redox treatment was basically conducted every 20 h during discharge process. Polarization resistance decreased just after redox treatment and increased during discharge process. Enhancement of cell performance after every redox cycles and faster degradation in the following discharge process were observed. Polarization resistance gradually increased as redox cycles were repeated. Focused ion beam-scanning electron microscopy (FIB-SEM) observation was conducted for reconstructing the three dimensional microstructures of the tested samples. From the three dimensional microstructure reconstruction, it is found that the shape of nickel particle got thinner and complicated after redox cycles. Triple phase boundary (TPB) length increased after redox treatment and decreased after discharge process. This TPB change was highly associated with Ni connectivity and Ni specific surface area. These microstructure changes are consistent with the change of cell performance enhancement after redox treatment and degradation after discharge process. However, TPB length density kept on increasing as redox cycles are repeated, which is inconsistent with the gradual degradation of anode performance.

1. Introduction

Nickel/yttria stabilized zirconia (Ni-YSZ) cermet is the most common material for the solid oxide fuel cell (SOFC) anode. To ensure high performance of SOFC for a long operation time, cell and system designs which have sufficient durability against cyclic reduction and oxidation (redox) of anode are essential. Redox is caused when chemical potential of oxygen increases in the anode side in cases such as high fuel utilization, gas leakage from the cathode side and fuel interruption [1–9]. The decrease of volume during reduction from NiO to Ni is as about 40%, and the increase of volume is about 70% during oxidation [3–5]. This Ni volume change leads to irreversible microstructure change and bulk deformation of Ni-YSZ anode and causes cracks inside the electrolyte in the most severe situation [1–9]. Sumi et al. [10] reported increase of polarization impedance after redox cycles with the decrease of TPB length and increase of Ni specific surface area. Increase of polarization resistance was also reported by Laurencin et al. [8]. Jeangros et al. [11] carried out in-situ observation during redox states of Ni-YSZ sample using ETEM and confirmed how Ni particle became

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porous and dense through re-oxidation and re-reduction processes. From the in-situ observation, they proposed a schematic mechanism of redox microstructure change, i.e. Ni diffusion becomes dominant during oxidation process which creates inner pore, whereas surface reaction is dominant during reduction process accompanying spongy-like Ni structure [7]. Regarding chemical reaction mechanism, Tikekar et al. [12] investigated on rate-determining kinetics of Ni oxidation and NiO reduction in various conditions. Rate determining process during redox atmosphere is also examined and high dependency on temperature and gas composition is reported [13,14]. Redox durability is strongly related with initial microstructure of anode. To prevent microstructure change during redox cycles, composite anodes with various dopants are examined [15]. In addition, redox dependency on temperature is also investigated by the same authors [16]. Nevertheless, precise mechanism of redox cycle has not been fully understood due to its high dependency on cell design, experimental conditions, etc.

Understanding the details of relationship between microstructure change and cell performance during redox cycles is necessary to reveal redox kinetics. In this work, discharge tests were conducted with and without redox treatment to clearly identify the effects of redox cycles. The three-dimensional microstructures of the samples were analyzed using FIB-SEM observation technique.

2. Experimental procedure

2.1. Electrolyte support cell fabrication

8YSZ disc (Tosoh Japan) of 24 mm in diameter was used as an electrolyte. Slurries for Ni-8YSZ composite anode, Ni anode current collecting layer, LSM-8YSZ composite cathode, LSM cathode current collecting layer (AGC Seimi Chemical, Japan), were each mixed with terpineol solvent and 3 wt% ethylcellulose binder. Then, they were screen printed onto the YSZ disc to form ϕ 10 mm electrode. Electrodes were sintered in the electric oven in air atmosphere. Sintering temperature was 1450 °C for the anode and 1200 °C for the cathode.

2.2. SOFC operation test

Fabricated cell was set inside the test rig. Pt reference electrode was fixed around the side of the electrolyte disk. Temperature was kept at 800 °C during cell operation test. Initially, anode was reduced with nitrogen diluted hydrogen. Then 5% humidified hydrogen and pure oxygen were supplied to anode and cathode sides, respectively. Current–Voltage and impedance measurements were conducted using Solatron 1287 and Solatron 1255B. Impedance measurement was conducted for every 20 h. Between the impedance measurements, cell was discharged under constant current of 0.2 A cm^{-2}. For the tests with-redox cycles, impedance measurements were also conducted before and after each redox treatment.

Pure oxygen is introduced for 2 h during the oxidation process, and pure hydrogen is introduced for 1 h during the reduction process. Nitrogen was flushed when switching gas supply from oxygen to hydrogen. Electrochemical measurements were conducted before and after 20 h discharge process. Oxidation time was set to achieve full Ni oxidation, and we confirmed that Ni is fully oxidized after 2 h oxidation from the EDX analysis. Operation was conducted with several different sequences to evaluate the influences of redox cycles. Cell operation conditions are shown in Table 1. First test consists of 5 sets of 20 h discharge without redox treatment (100 h discharge test, hereafter), as a reference case. Second one was carried out with 5 sets of 20 h discharge processes with 4 redox treatments held every 20 h between the discharge processes (4 redox test). Third test was conducted to confirm degradation ratio after single redox treatment, in which continuous 80 h discharge was conducted after initial 20 h discharge and following single redox treatment (1 redox test). Total discharge time is 100 h for these three tests.

Table 1
Cell operation condition.

Test name	Operation sequence
100 h discharge test	5 × 20 h discharge
4 redox test	20 h discharge + 4× (redox + 20 h discharge)
1 redox test	20 h discharge + redox + 4 × 20 h discharge
10 redox test	20 h discharge + 10× (redox + 20 h discharge[a])

[a] Discharge time for 2nd and 5th redox cycles are 19 h.

In addition, to confirm the accumulated redox treatment influence on cell performance, longer operation was conducted with 10 redox cycles (10 redox test). Basic experimental condition is the same with the "4 redox test", except that oxidation was 3 h for the initial redox, and the discharge time after 2nd and 5th redox cycles were 19 h

2.3. Microstructure analysis

After the experiment, each anode sample was filled with epoxy resin (Struers Epofix), and polished with sand paper and cross section polisher (JEOL SM-09020CP). Then, series of cross sectional images were taken by FIB-SEM (NVision 40, SII Nanotechnology) [17]. Each image data was converted to ternarized images and merged to 3D voxel structures to calculate microstructural parameters. Calculated parameters are porosity, connectivity from the electrolyte to the current collector, total and active TPB densities, interception lengths, specific surface area and tortuosity factor. Calculation methods of each parameter are described in Refs. [17–21].

3. Results and discussion

3.1. Electrochemical performance change

Temporal changes of anode-reference voltage are shown in Fig. 1. Interruptions of each line correspond to the periods of

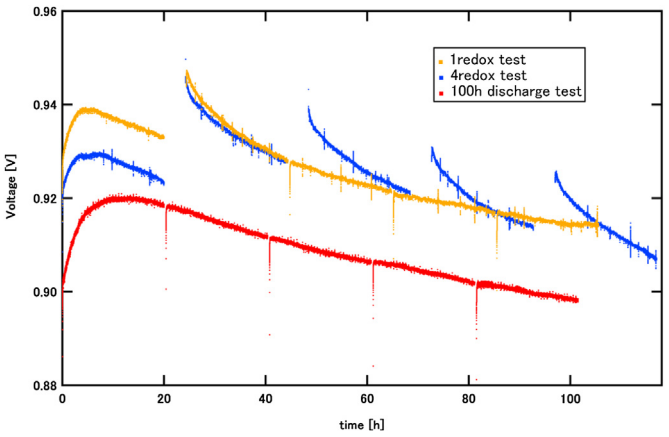

Fig. 1. Anode-reference voltage change during Redox tests. "100 h discharge test" (red), "4 redox test" (blue) and "1 redox test" (orange). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).