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Study on electrochemical re-oxidation of anode-supported solid oxide fuel cells using oxide ion current

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Abstract

The effect of the re-oxidation of anodes in anode-supported planar solid oxide fuel cells was investigated. Scanning electron microscopy (SEM) was used to observe the microstructure of the anode cross section. X-ray diffraction was used to measure the residual stress in the electrolyte.

The re-oxidation of the anode by ionic current was conducted at 800 °C by applying the current to a cell by supplying air for the cathode and pure N_2 for the anode.

From the cross-sectional SEM images of the anodes, it was confirmed that the morphology of Ni particles in a particular area of the anode—an active area for electrochemical reactions—was modified to a sponge-like structure. It was reported that the spongy microstructure was generated when Ni was re-oxidized by O_2 in air. On the other hand, the morphology change in the Ni particles outside of the active area was not observed. This suggests that this change in the microstructure resulting from re-oxidation was caused not by O_2 in air but by the oxide ion current. The larger degree of morphology change in the Ni particles was observed in close proximity of the electrolyte, which also suggests that the re-oxidation was caused by the ionic current. These results indicate that the effect of the anode structure on the electrolyte re-oxidized by ionic current was successfully investigated without the influence of the gas phase.

Then, the influence of anode expansion caused by the re-oxidation on the electrolyte is studied by measuring the residual stress in the electrolyte.

A large compressive stress in the electrolyte was observed as that before the re-oxidation. The residual stress in the electrolyte under the cathode was found to be relaxed after passing the ionic current. On the other hand, the relaxation of the residual stress in the electrolyte outside the area of cathode was not measured. This result is consistent with the microstructure observation results.

Keywords: SOFC; Re-oxidation; Ion current; Anode; Residual stress

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted considerable attention as highly efficient power generation systems. However, SOFCs suffer from the problem of mechanical degradation because SOFCs comprise laminated structures.

Mechanical degradation can occur because of the re-oxidation of the anodes of SOFCs when the fuel gas is not supplied to the SOFCs at the start or during emergencies, for example, during earthquakes particularly when city gas is used as the fuel under actual operation conditions. In anode-supported SOFCs (which have been actively investigated), the electrolyte is thin as compared to the anode substrate. Therefore, it has been suggested that the electrolyte can be seriously damaged because of the structure change of the anode. From this viewpoint, the tolerance of the anode-supported SOFCs on the re-oxidation of the anode is very important.

The re-oxidation of anodes occurs according to the following two mechanisms: (1) the oxidation of Ni by O_2 in air, which leaks from the cathode to the anode, and (2) the oxidation of Ni by oxide ions generated at the cathode and conducted through the electrolyte. The former mechanism occurs when the fuel supply to the SOFCs stops under high temperatures or when

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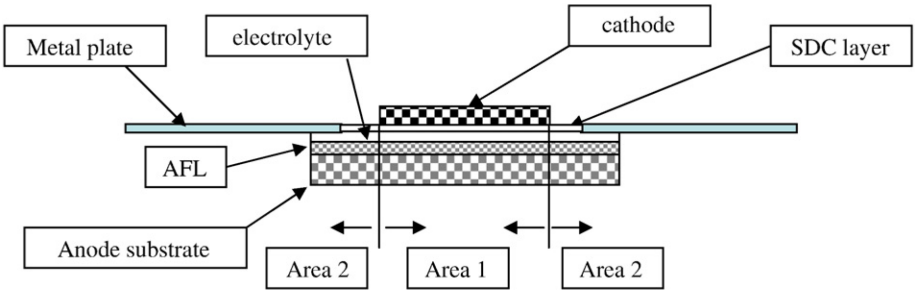

Fig. 1. Setup of a single cell.

cracks are caused at the electrolyte and/or the separator. The latter mechanism occurs when the quantity of the fuel supply is lesser than the fuel consumption required for power generation (i.e., a so-called fuel shortage).

Studies on the re-oxidation or re-oxidation and reduction (redox cycle) of anodes have been reported [1–7]. However, in these studies, Ni in the anode was re-oxidized by O_2 in air. According to this re-oxidation process, it was reported that cracks were generated in the electrolyte because of anode expansion due to the re-oxidation of the entire anode [1–4]. During re-oxidation, it was observed that Ni particles expanded as a result of the morphology change from dense Ni particles to porous NiO particles (i.e., a so-called sponge-like characteristic) [1–3,5,6].

On the other hand, there are a few studies on the re-oxidation of anodes by ionic currents during fuel shortages. For re-oxidation, this effect gets concentrated at the anode in close proximity to an electrolyte, which significantly contributes toward electrode reactions. Further, it is considered that re-oxidation has a considerable effect on performance and can easily cause mechanical degradation such as peeling or cracking of the electrolyte. However, it is difficult to evaluate, in detail, the effect of re-oxidation on tested and mechanically damaged cells since re-oxidation by O_2 in air occurs again when the re-oxidation by the ionic current causes mechanical degradation. We attempted to evaluate the effect of re-oxidation by ionic currents on anodes and electrolytes without the influence of the gas phase: we have reported the results.

2. Experimental

2.1. Sample preparation

The tests were conducted using the single cells of anode-supported planar SOFCs. A single cell comprised an anode substrate of Ni-8 mol%Y_2O_3-stabilized ZrO_2 (8YSZ) (wt.% of 50:50), an anode functional layer (AFL) of Ni-8YSZ (wt.% of 50:50), an 8 mol%Y_2O_3-stabilized ZrO_2 (8YSZ) electrolyte, and a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) cathode. A mixed powder of 8YSZ and NiO was pressed to form an anode substrate (5 cm × 5 cm × 0.2 cm). The AFL layer was fabricated by dipping the substrate into an AFL solution and calcinated at 1000 °C. Then, the electrolyte was prepared by dipping the substrate with the AFL layer into the 8YSZ solution, followed by calcination at 1500 °C. The thickness of the electrolyte was about 40 μm. A 20 mol% Sm_2O_3-doped CeO_2 (SDC) layer was prepared by using the method similar to that used to prepare the AFL layer and electrolyte, and calcination was performed at 1250 °C. Except for one side of the 5 × 5 plane, the SDC layer and electrolyte and the AFL layer were removed by polishing. The LSCF cathode was grown on the SDC layer at the other side of the polished surface and calcinated at 1100 °C. The cathode area was 2 cm × 2 cm. The NiO in the anode was reduced before performing an I–V test.

2.2. I–V tests

Fig. 1 shows an illustration of the setup of a single cell for the I–V test. Gas sealing was conducted by using a thin metal plate that was attached to the electrolyte outside the cathode. A Pt mesh was used as the current collector. The single cell was placed on the manifold with fuel paths and heated with 4% H_2+N_2 gas supplied to the anode side. When the sample reached 800 °C, the gas changed to H_2. The I–V characteristics were measured using a current pulse generator (Hokuto Denko Co. Ltd., HC-114) after reduction for 24 h.

The difference in Area 1 and Area 2 is that the cathode is on the electrolyte in the former and not in the latter. This indicates that only the cell in Area 1 exhibits the activity for electrode reactions.

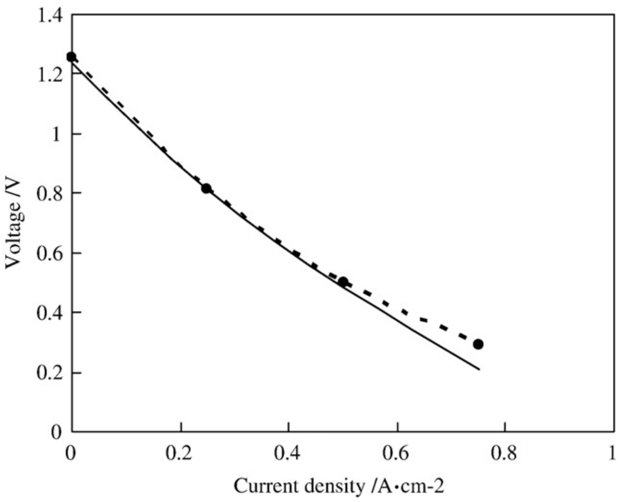

Fig. 2. I–V characteristics of the samples. Sample (A): dotted line, Sample (B): solid line.