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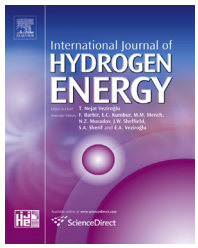

Effect of various sintering inhibitors on the long term performance of Ni-YSZ anodes used for SOFCs

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ABSTRACT

Sintering of Ni in solid oxide fuel cell (SOFC) anodes (Ni-YSZ) is a major cause of anode degradation. To reduce this growth rate, several sintering inhibitors (SiC, SiN, Al_2O_3, AlN, CeO_2 and GDC) were added into Ni-YSZ anode using powder methods. The modified anodes were screen printed on YSZ electrolyte to prepare symmetric half-cells and their performance was investigated by long term stability test at high temperature. X-ray diffraction (XRD) analysis showed that the most sintering inhibitors were chemically compatible with anode materials except Al_2O_3 and AlN. During the long term test, area specific resistance (ASR) was measured at 1000 °C in 25vol% H_2 and 75vol% N_2 environment. Triple phase boundary (TPB) density was calculated by image analysis techniques before and after operation. A clear relation was found between ASR change rate determined from electrochemical measurements and TPB density change rate calculated from image analysis. Moreover, among the various sintering inhibitors, CeO_2 and GDC exhibited the best performance by showing the lowest ASR and TPB density change rates. ASR change rate has been discussed in view of loss in TPB density during operation.

Introduction

Solid Oxide Fuel Cells (SOFCs) are promising electrochemical devices for efficient conversion of chemical energy of fuels (usually H_2) directly into electrical energy. For commercialization, the SOFCs must operate for at least 40,000 h for stationary while 20,000 h for mobile applications [1]. The components of SOFCs (anode, cathode, electrolyte and interconnects etc) undergo various types of degradations during the operation. Hence, accessing the fundamental degradation mechanism is one of basic and essential tools to increase the durability of the cell.

The anodes most frequently used for SOFCs are the composites of NiO and YSZ. These are suggested to be designed with a dual-layer microstructure for superior performance [2–4]. The top layer comprising coarser particles which acts as

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the conduction layer while the second layer near the electrolyte consists of a fine particles and known as Anode Functional Layer (AFL). The AFL must have high Triple Phase Boundary (TPB) density which results in high electro–catalytic activity and decreased activation polarization. TPB can be defined as an active area where oxygen ion oxidizes fuel gas and results electron. Higher TPB density or length (expressed in μm^{-2} or $\mu m/\mu m^3$) determines the faster kinetics of the charge transfer reaction and hence higher cell performance. Several studies have reported different ways to increase TPB density of an anode [5–7]. However when an SOFC system operates for several thousand hours, the TPB density declines due to several microstructural changes.

On-going approach in the anode development is the enhancement of long-term performance stability to acquire the expected goals (i.e. 40,000 h) with very small performance degradation. In Ni-YSZ anode system, it is quite renowned to carry out quantitative image analysis of the microstructure in order to investigate the correlation between the electrochemical properties and microstructure. Utilizing the image processing technique, Simwonis et al. [8] successfully investigated that the nickel particle size in an anode increased with operating time of 1000–4000 h in 3% H_2O at 1000 °C. Moreover, L. Holzer and his coworkers [9] presented the methodology with phase size distribution (PSD) measurement for quantification of nickel grain growth in porous SOFC anode under dry and humid condition. So far, the Ni-YSZ anode studies focus on the quantification of nickel particle growth with qualitative observations. Nevertheless, there is another parameter i.e TPB density, which must be considered to have a more direct influence on the electrochemical performance of an anode.

The aim of this study was to investigate the long-term stability of AFL at 1000 °C under dry and humid atmosphere. The addition of the so-called sintering inhibitors was proposed in order to increase the life time of AFL, because they can hinder the Ni grain growth by providing sufficient resistance in the growth path. It was expected that the sintering inhibitor would be able to prevent nickel coarsening which in turn would improve the TPB density. X-Ray Diffraction (XRD) was carried out to determine whether any new phases were formed by sintering inhibitors addition. The Area-specific Resistance (ASR) was measured for the conventional and sintering inhibitors modified anodes during the exposure at 1000 °C. A reducing environment containing 25% H_2 and 75% N_2 was maintained during the long term test. The TPB density was calculated using imaging software. A distinct relationship between the two parameters i.e ASR change rate and TPB density change rate was obtained. Hence by describing the rate of TPB density change as well as the rate of ASR change, the life time of an anode can be successfully predicted.

Materials and methods

Cell preparation

A powder mixture consisting of 60wt% NiO and 40wt% YSZ (Fuel Cells Materials, USA) was used to produce reference AFL. To investigate the effects of sintering inhibitors on the AFL's long-term stability, 1–10 wt % of desired powders (alumina/Al_2O_3; aluminum nitride/AlN; silicon carbide/SiC; cerium oxide/CeO_2; and gadolinium-doped ceria/GDC – Sigma Aldrich, USA) were added to Reference AFL powder (mixture of NiO and YSZ powder). The powders were then ball milled with ethanol for 48 h. After drying and sieving, the powders were mixed with a solvent (α-terpinol) and binder (mixture of α-terpinol and ethyl cellulose) to produce AFL pastes (58% solid loading). These pastes were then symmetrically screen printed on YSZ substrate (Fuel Cells Materials, USA) and subsequently pre-heated and sintered, respectively, at 350 °C for 3 h and 1350 °C for 5 h in air. The schematic of the symmetric cell produced is shown in Fig. 1. The effective area of sintered AFL was 1 cm^2 and 40–50 μm thick.

Characterization

The chemical compatibility between NiO-YSZ and sintering inhibitor was investigated with X-ray diffractometer (Rigaku, Japan) before and after the long term test. The voltage and current values for the Cu target used in the diffractometer were 40 kV and 100 mA, respectively. The crystal structure was examined at 2θ diffraction angle with continuous scanning from 20° to 80° using a step size 0.04°. The crystal system of the phases was analyzed using the Joint Committee on Powder Diffraction Standard (JCPDS) database.

To obtain the microstructures of AFL before and after the long term test, samples were mounted cross-sectionally in polymer resin. Samples were grinded with SiC paper and polished with diamond suspension in order to obtain a mirror-like surface for microstructure observation. The microstructures were observed with a high resolution Secondary Electron Microscope (Magellan 400, USA) equipped with back scattered electron detector. The characteristics of generated SEM images were then quantitatively analyzed with image processing software (Image-Pro Plus 6).

In order to investigate the electrochemical performance of AFL during the long-term exposure, ASR of the cells was measured with four-wire resistance measurement method. Platinum (Pt) mesh and nickel (Ni) wire were used as current collectors and attached to the active area with adhesive ceramic sealant (Aremco Products, USA). The contact resistance between current collector and electrode was minimized by applying non-fluxed Pt paste. Insulating mica paper was attached on the Pt mesh, so that a good contact between current collector and active electrode could be maintained during the long term experiment. The measurement was then carried out at 1000 °C in dry and humid

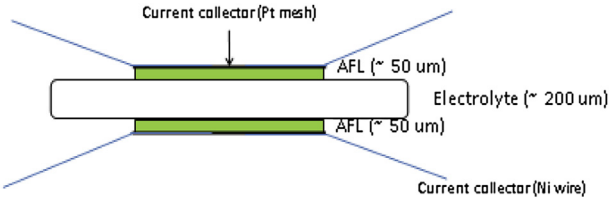

Fig. 1 – Schematic of symmetrical AFL screen printed on YSZ electrolyte along with current collectors.

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