Effect of microstructure on the electrochemical performance of Ni-ScSZ anodes

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ABSTRACT

The effects of NiO powder morphology and sintering temperature on the microstructure and the electrochemical performance of Nickel-scandia-stabilized zirconia (Ni-ScSZ) cermet anodes for solid oxide fuel cells (SOFCs) were investigated. The particle size and agglomeration of the starting powders were found to affect both the microstructure and electrochemical performance of the Ni-ScSZ cermet anodes. The lowest polarization resistance, $0.690\ \Omega\ cm^2$ at 700 °C, was measured for the Ni-ScSZ anode prepared with fine NiO powder ($\sim 0.5\ \mu m$ grain size). This was attributed to the increase in the number of reaction sites afforded by the small grains and well-dispersed Ni and ScSZ phases. The effect of the anode sintering temperature was also found to affect the anode microstructure, adhesion with the electrolyte, and consequently anode polarization resistance. The lowest polarization resistance was observed for the anode sintered at 1400 °C and this was 3–5 times lower than the corresponding values for anodes sintered at lower temperatures.

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1. Introduction

Nickel-yttria-stabilized zirconia (Ni-YSZ) has been commonly used as the anode material for solid oxide fuel cells (SOFCs) owing to its good electro-catalytic properties and chemical/mechanical compatibility with the YSZ electrolyte. Nickel serves as an electrocatalyst for the electrochemical oxidation of hydrogen and provides sufficient electronic conductivity to the anode. On the other hand, YSZ acts as a framework for the dispersion of Ni and prevents the coarsening of the Ni powder [1]. In addition, it effectively enlarges the triple-phase boundaries (TPBs) by offering sufficient ionic conductivity at high temperatures.

Currently, significant efforts are being devoted to the development of low-cost intermediate-temperature solid oxide fuel cells (600–800 °C; IT-SOFCs) with long-term stability [2]. However, the conventional YSZ electrolyte is not suitable for IT-SOFCs because of its relatively low ionic conductivity in the IT range [3]. To develop new solid oxide electrolytes with higher ionic conductivity for intermediate- or low-temperature SOFCs, a number of studies have been performed on fluorite-structured zirconia, ceria or bismuth oxide, and perovskite-structured $LaGaO_3$ [4–7]. Nevertheless, zirconia-based oxygen-ion conductor is still accepted as the best candidate electrolyte for SOFCs, owing to its stability under both reducing and oxidizing atmospheres. Scandia-stabilized zirconia (e.g., ZrO_2 doped with 11 mol% Sc_2O_3) is known to exhibit the highest ionic conductivity among doped ZrO_2 systems [8]. However, below 600 °C, the highly conductive cubic phase transforms to the rhombohedral β-phase with an abrupt reduction in the conductivity due to the ordering of oxygen vacancies [9,10]. This ordering phenomenon can also occur over time at higher temperatures leading to decreased ionic conductivity [11]. In contrast, ZrO_2 co-doped with 1 mol% CeO_2 and 10 mol% Sc_2O_3 (denoted as ScSZ, hereafter) exhibits good phase stability at low temperatures, as well as the highest ionic conductivity among zirconia-based electrolytes [12,13]. This material was, therefore, chosen as an ionic conductor for the Ni-zirconia cermet anodes investigated in this study.

The electrochemical performance of Ni-zirconia cermet anodes strongly depends on the catalytic activity of the anode material and on the length of the TPB where Ni, zirconia-based ionic conductor, and fuel gas meet. In order to maintain high performance at intermediate- or low-temperatures, the decrease in catalytic activity should be compensated by maximizing the

electrochemical reaction sites from the TPB [14]. Results have shown that the TPB lengths can be increased through precise control of Ni and zirconia grain sizes. Mogensen et al. [15] reported that Ni and YSZ grain sizes affect the performance of cermet anodes. In the case of Ni-YSZ anodes, several studies have shown that the characteristics of the NiO and YSZ starting powders affect the microstructure of the resulting anode and consequently determine its electrochemical properties [16,17]. Schneider et al. carried out analytical modeling using the discrete element method to estimate the TPB lengths in composite electrodes and showed that the TPB lengths are maximized when the composite anode contains 50 vol% ionic conducting phase [18]. This analysis has since been validated in a recent study of Ni-GDC (gadolinium-doped ceria) and Ni-SDC (samarium-doped ceria) electrodes [19,20]. However, Schneider's analytical model assumes monosized particles in the electron and ion conducting phases. The volume fraction of the solid at which the TPB length is maximized in each phase could, therefore, be different. In another study, Ni-YSZ anodes with a Ni solid volume fraction of 0.34 have been shown to exhibit minimal polarization resistance [21], with the ionic conductivity and particle size in the ion conducting phase being the crucial factors.

In the present study, we modified the microstructure of Ni-ScSZ cermets by controlling both the initial powder characteristics and the sintering temperature. NiO/ScSZ weight ratio of 60:40 was chosen for the experiments. In addition, we investigated the correlation between the microstructure and electrochemical properties in the Ni-ScSZ cermet anodes.

2. Experimental

2.1. Sample fabrication

Commercial NiO and ScSZ $((Sc_2O_3)_{0.10}(CeO_2)_{0.01}(ZrO_2)_{0.89})$ powders were used to prepare NiO-ScSZ composites and subsequently to prepare Ni-ScSZ cermets in reducing atmospheres for SOFC anodes. First, three different kinds of NiO powders were used with the same ScSZ powder purchased from Fuel Cell Materials (FCM, USA). Field emission scanning electron microscopy (FESEM; S-4700, Hitachi, Japan) images were used to classify each type of NiO and ScSZ powder according to its particle size distribution. The NiO powders were classified as either ultrafine (Alfa Aesar, d_{50}: 8–20 nm), fine (Sumitomo, d_{50}: ~0.5 μm), or coarse (Alfa Aesar, d_{50}: ~3 μm), while the ScSZ powder (FCM, d_{50}: 0.1–0.3 μm) was well dispersed. The NiO-ScSZ mixtures were wet ball-milled in ethyl alcohol with zirconia balls for 24 h and then dried. The NiO/ScSZ mixing weight ratio was 60:40 in all the cases. Assuming complete reduction of NiO to Ni under SOFC operating conditions, the Ni and ScSZ compositions were calculated in terms of the solid volume fraction (vol%), based on the initial NiO and ScSZ contents (wt%) and theoretical densities. Nickel and ScSZ were estimated to have solid volume fractions of 0.44 and 0.56, respectively.

An electrolyte supported Pt/ScSZ/Ni-ScSZ single cell was fabricated to measure the electrochemical performance of the Ni-ScSZ anodes. First, commercial ScSZ powder (FCM, USA) was pressed into a pellet and sintered at 1600 °C for 6 h in air. The anode paste was prepared by mixing the NiO-ScSZ powder and a terpineol-based ink vehicle (FCM, USA). The anode paste was then applied to the surface of ~1 mm thick ScSZ electrolyte by screen-printing and then fired in the temperature range of 1200–1400 °C for 2 h in air. The active area of the anode was 0.785 cm². Platinum paste was then applied to the ScSZ electrolyte to form a counter electrode and the sample was fired at 950 °C for 1 h. A reference electrode made of Pt wire was placed on the side of the ScSZ disk, and Pt mesh and wire were attached to the surface of both electrodes using Pt paste for current collecting. A three-electrode
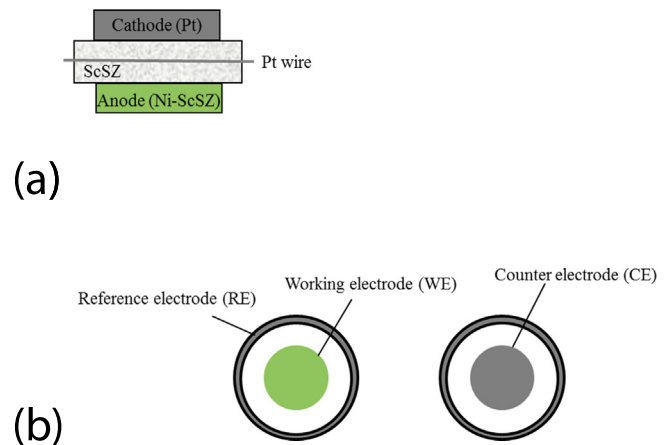

(a)

(b)

Fig. 1. Schematic diagrams of (a) Pt/ScSZ/Ni-ScSZ single cell setup used to measure the anodic polarization resistance, and (b) top (left) and bottom (right) views of the electrode position.

configuration was used to measure the anodic polarization resistance of each cell, as shown in Fig. 1. Each cell was sealed onto alumina tubes via Pyrex glass rings. The entire cell was placed inside a furnace and heated to 900 °C to soften the glass rings.

In addition, two electrolyte-supported fuel cells were constructed using either the fine or coarse NiO powders mentioned above for the anode layer. The cell configuration consisted of cathode (40 μm)|$Ce_{0.9}Gd_{0.1}O_{2−δ}$ (GDC, buffer layer, 10 μm)|ScSZ (solid electrolyte, 150 μm)|Ni-ScSZ (anode, 40 μm), with $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3−δ}$ (LSCF)-GDC composite oxide used for the cathode. After preparing the ScSZ electrolyte (~150 μm thick), the anode paste was screen-printed on the surface of the electrolyte before firing at 1400 °C for 2 h in air. A GDC buffer layer was then screen-printed on the opposite side of the anode before firing at 1250 °C for 2 h in air. Finally, the LSCF-GDC composite cathode was screen-printed on top of the GDC layer and the device was fired at 1000 °C for 2 h in air. The electrolyte-supported fuel cell was also sealed onto alumina tubes via Pyrex glass rings, and Pt meshes were spring-pressed against the anode and cathode to be used as current collectors.

2.2. Characterization

The microstructure of the electrodes was characterized by FESEM. The grain size distribution and the average grain size were calculated from the FESEM images using the software Image-Pro Plus (Media Cybernetics, Inc., USA) and Adobe Photoshop CS5 (Adobe systems Inc., USA). The images were initially treated graphically using Adobe Photoshop CS5, to identify the boundaries and nickel grains. At least 300 grains were measured for each sample. Feret mean diameter was obtained from the treated images with the software, Image-Pro Plus [22,23]. The feret diameter is a measure of the particle size along a specified direction, the so-called caliper diameter, which can be selected in the measurement mode of the software. The average grain size (Ave.) was obtained after dividing the calculated value by 0.76 to determine the 3D grain size [22,23]. After testing the cells, an environmental scanning electron microscope (ESEM; Quanta 650 FEG, FEI, USA) equipped with an energy-dispersive X-ray (EDX) attachment was used to characterize the Ni distribution in the Ni-ScSZ anode. Furthermore, the extent of anode/electrolyte adhesion was determined by calculating the fraction of junction segments between anode layer and electrolyte layer from SEM images of the cells. The samples were sectioned by low-speed diamond saw, ground, and polished to a 0.25 μm finish. The fraction can be calculated as