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Low-temperature co-sintering technique for the fabrication of multi-layer functional ceramics for solid oxide fuel cells

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ABSTRACT

The low-temperature co-sintering technique for the fabrication of the multi-layered electrolyte supported on a planar anode substrate is demonstrated for solid oxide fuel cells (SOFCs). A NiO/gadolinia-doped ceria (GDC) anode substrate is fabricated using tape casting and lamination processes, and yttria-stabilized zirconia (YSZ) bottom electrolyte and GDC top electrolyte layers are sequentially screen-printed, followed by co-sintering at 1230 °C. The electrolyte layers are successfully densified at an extremely low processing temperature by promoting the sinterability of the individual components, and a continuously graded electrolyte structure is constructed to suppress the delamination of the electrolyte films. Based on the camber analysis, the cell structure is optimized to minimize the structural distortion and eliminate the processing defects. The low-temperature co-sintering technique presented in this study is expected to widen the material selection and resolve the compatibility issues associated with high-temperature processing for the fabrication of SOFCs.

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1. Introduction

Solid oxide fuel cells (SOFCs) represent one of the most environmentally friendly and versatile technologies for the efficient generation of electrical power and heat from a variety of fuels. In recent years, the anode-supported planar configuration has been actively pursued because this configuration allows for improved performance at lower operating temperatures compared with other SOFC designs [1]. Anode-supported cells reportedly offer a power density that is approximately five times higher than that of electrolyte-supported cells, and recently, the current density as high as 1.2 A cm⁻² was demonstrated at 0.7 V and 700 °C in a stack level by Jülich [2–4]. One of the major challenges to the commercial development of anode-supported planar SOFCs has been the sophisticated fabrication process that is associated with the co-sintering procedure. In general, the anode substrate and thin electrolyte layer are co-sintered at high temperatures to eliminate open pores in the electrolyte because co-shrinking substrate is necessary for the sufficient densification of the elec-

trolyte film, and constrained sintering of the electrolyte layer on rigid anode substrate leads to inadequate film density [5,6]. The high-temperature co-sintering process often leads to compatibility issues that decrease the long-term stability and restrict the choice of materials. Although a number of novel materials have been identified as promising alternatives to conventional SOFC anodes and electrolytes, their practical applications have been limited by the chemical and mechanical complications occurring during the high-temperature co-sintering process. Therefore, the development of low-temperature processing techniques with reduced compatibility problems is highly desirable to further improve SOFC technologies.

Since the early stage of SOFC development, yttria-stabilized zirconia (YSZ) has been the most popular electrolyte material due to its adequate ionic conductivity, negligible electronic conductivity, chemical stability and thermal compatibility with other cell components. Recently, gadolinia-doped ceria (GDC) has received increasing attention as an alternative electrolyte material for reduced temperature operation due to its superior ionic conductivity and chemical compatibility with cobalt-containing cathode materials [7–9]. However, upon exposure to the reducing atmosphere on the anode side, the Ce⁴⁺ in the GDC is partially reduced to Ce³⁺, which induces *n*-type electronic conductivity and a leakage current through the electrolyte, resulting in oxygen permeation

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flux and loss of electrical efficiency [10,11]. In addition, a large change in the oxygen non-stoichiometry of the GDC electrolyte on the anode side causes defect-induced dilation, which is known as “chemical expansion” [12]. This effect is due to a loss of bridging lattice oxygen and/or increased ionic radius of Ce^{3+} with respect to Ce^{4+} , which leads to internal stresses, structural distortion and possibly, mechanical failure [13,14]. Therefore, the GDC electrolyte on the anode side should be blocked for practical applications, and approaches to construct a bi-layer electrolyte composed of the GDC on the cathode side and YSZ on the anode side have been proposed [15–17]. Considering the anode materials, a cermet of Ni and GDC is known to possess superior catalytic activity toward fuel oxidation [18,19] and resistance to carbon coking and sulfur poisoning [20,21] compared with the conventional Ni–YSZ cermet. Based on the material characteristics described above, a SOFC composed of a Ni–GDC cermet anode, YSZ electrolyte on the anode side and GDC electrolyte on the cathode side is considered to be the nearly ideal combination for both performance and stability. However, the realization of such a cell structure in the anode-supported planar configuration via conventional ceramic processing routes based on high-temperature co-sintering processes is extremely difficult due to the aforementioned compatibility challenges. In particular, the processing temperature should be lower than 1250 °C when the GDC and YSZ are co-sintered because the chemical interaction between the two phases at high temperatures leads to the formation of highly resistive reaction products enriched in Gd, exhibiting the ionic conductivity lower than that of YSZ by two orders of magnitude [22–24]. To address these issues, various vacuum deposition techniques, such as pulsed laser deposition [25], aerosol-assisted chemical vapor deposition [26], atomic layer deposition [17] and electron beam evaporation [27], have been used to fabricate multi-layered electrolytes supported on an anode substrate containing both YSZ and GDC, but their practical application remains questionable from the standpoint of manufacturing costs, scale-up and mass production. These challenges emphasize the importance of low-temperature fabrication techniques based on the cost-competitive ceramic powder processes.

In the present study, a low-temperature co-sintering technique was used to fabricate planar SOFCs consisting of a NiO–GDC anode substrate, a YSZ bottom electrolyte layer on the anode side and a GDC top electrolyte layer on the cathode side based on a conventional powder processing route. The anode substrate was fabricated by tape casting, and the electrolyte layers were sequentially screen-printed, followed by co-sintering at a sufficiently low temperature to prevent harmful interactions between GDC and YSZ. The electrolyte layers were successfully densified via a low-temperature process by controlling the sintering stresses and using a small amount of the nano-crystalline powder, and the thermal stresses were relieved by constructing a continuously graded electrolyte structure. The thermo-chemical and thermo-mechanical issues associated with the co-sintering of multi-layered ceramics are discussed in detail, and the strategy to suppress the generation of processing defects is presented.

2. Experimental

Commercially purchased NiO (Metal Tokyo, Japan) and GDC powders (Rhodia, U.S.) were used to tape cast the anode substrate. To prepare the slurry, the NiO and GDC powders were first mixed by ball milling for 24 h in ethanol and toluene containing a dispersant (Hypermer KD-1). The desired amounts of the binder (polyvinyl butyral (PVB)), plasticizer (dibutyl phthalate (DBP)) and pore former (poly(methyl methacrylate) (PMMA)) were added to the slurry, which was ball-milled for an additional 24 h. After aging the slurry for 24 h, the slurry was tape-cast on a carrier film at a

casting velocity of 0.5 cm/s. After casting, the tape was dried for 24 h at room temperature and machined into square pieces, followed by the lamination of multiple tapes using a warm uniaxial press at 40 MPa and 80 °C to complete the fabrication of the green anode substrates of desired thickness. The anode functional layer and electrolyte layers were applied to the top of the anode substrate by screen printing. In addition to the NiO and GDC powders mentioned above, commercially purchased YSZ (Tosoh, Japan) and nano-YSZ (Fuel Cell Materials, USA) powders were used to produce the pastes. To prepare the pastes, the dispersant was added to the solvent (α -terpineol) and planetary-milled for 30 min. The ceramic powders were then added and planetary-milled for 24 h. Finally, the binder (BH-3) and plasticizer (DBP) were added, and the slurry was planetary-milled for an additional 24 h to complete the paste production. The anode functional layer and electrolyte layers were sequentially applied by screen printing to achieve the desired structure and thickness, and the green samples consisting of the anode and electrolyte were co-sintered at 1230 °C in air. The sintering shrinkages of the individual components were measured using a dilatometer (DIL 402PC, Netzsch Instruments, Germany), and the microstructure was characterized by scanning electron microscopy (FEI XL-30 SEM, Philips, Netherlands).

3. Results and discussion

Basically, the cells in this study were fabricated by co-firing the NiO–GDC anode substrate, YSZ bottom electrolyte layer and GDC top electrolyte layer at a sufficiently low temperature to form a dense electrolyte while preventing harmful chemical interactions. Because one of the primary concerns when co-sintering dissimilar materials is the disparity of the sintering behaviors of the components [28], the sintering characteristics of the individual component materials were individually characterized using dilatometry prior to cell fabrication. Fig. 1(a) shows the effect of the forming process on the sintering behavior of the NiO–GDC anode substrate. The anode substrate could be fabricated via several ceramic-shaping techniques, such as tape casting/lamination or compaction of spray-dried granules [29–31]. Although the composition and powder characteristics of the ceramic components are identical for the tape-cast and compacted samples used in this study, substantially different sintering behaviors are evident in Fig. 1(a). The onset sintering temperature of the tape-cast sample is ~ 800 °C, which is significantly lower than that of the compacted sample (~ 950 °C). At 1230 °C, which is the target processing temperature for co-sintering, the NiO–GDC tape showed 13% sintering shrinkage, while the NiO–GDC compact shrank by only 9%. The results in Fig. 1(a) indicate that the packing structure, green density and amount of organic compounds differed between the two samples, which were made from identical starting powders; these differences resulted in different sintering characteristics [32]. The coordination number in a green body is a critical factor that determines the shrinkage behavior at the early stage of sintering because the mass diffusion mechanisms operate at the surface and grain boundaries [33–35]. Furthermore, the geometrical arrangement of particles heavily depends on the stresses applied during the forming process [36]. In slurry-based forming techniques, including tape casting, the powder is dispersed in a complex organic system and the inter-particle spacing is controlled by the polymer network. By contrast, the particle arrangement in a compaction process depends on the external pressure, which is generally higher than the capillary forces during a tape-casting process, resulting in a higher green density. Thus, tape casting has been suggested to provide an adequate porosity for particle rearrangement during the early stages of sintering, leading to a lower onset sintering temperature and improved densification behavior, whereas the highly

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