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Fabrication and characterization of all-ceramic solid oxide fuel cells based on composite oxide anode

Jeonghee Kim [a,b], Dongwook Shin [c], Ji-Won Son [a], Jong-Ho Lee [a], Byung-Kook Kim [a], Hae-June Je [a], Hae-Weon Lee [a], Kyung Joong Yoon [a,*]

[a] *High-Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea*
[b] *Department of Fuel Cells and Hydrogen Technology, Hanyang University, Seoul, Republic of Korea*
[c] *Division of Materials Science and Engineering, Hanyang University, Seoul, Republic of Korea*

HIGHLIGHTS

- High performance all-ceramic anode is fabricated and electrochemically evaluated.
- Impedance characteristics are analyzed using half cell measurements.
- Rate limiting processes for individual electrodes are clarified.
- Chemical capacitance causes the major impedance for ceramic anode.

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ABSTRACT

All-ceramic solid oxide fuel cells (SOFCs), which offer advantages in carbon tolerance, sulfur resistance and redox stability, are fabricated and evaluated. The electrolyte-supported cells are composed of a $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM)–$Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ (GDC) anode, an Y_2O_3-stabilized ZrO_2 (YSZ) electrolyte, a GDC interdiffusion barrier layer, and a $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)–GDC cathode. A particle-dispersed glycine-nitrate process is developed to synthesize extremely fine and homogeneous LSCM–GDC ceramic composite powders. The electrochemical performance of the LSCM–GDC anode is comparable to that of conventional Ni-based anodes. The impedance spectra of the all-ceramic SOFCs are successfully interpreted by the independent characterization of the individual electrodes via half-cell measurements. The impedance of the LSCM–GDC anode is dominated by a low-frequency arc originating from the “chemical capacitance”, which is associated with the variation of the oxygen non-stoichiometry in the mixed conducting ceramic electrode. In addition, the impedance arc associated with the electrode–gas interaction is observed in the LSCM–GDC anode. The rate-limiting processes for the LSCF–GDC cathode are observed to be solid-state oxygen diffusion and surface chemical exchange. Herein, the reaction mechanisms and rate-limiting processes of the all-ceramic SOFCs are discussed in detail and compared with those of conventional Ni-based SOFCs.

1. Introduction

The solid oxide fuel cell (SOFC) is a solid-state device that directly converts the chemical energy of gaseous fuel to electricity through electrochemical reactions and offers numerous advantages over conventional power generation systems, such as high efficiency, low environmental impact, multi-fuel capability, and modularity [1–5]. Recently, SOFCs with all-ceramic anodes have become an exciting research area because they possess attractive features such as reduction–oxidation (redox) stability, coking resistance, and sulfur tolerance [6–9]. The metallic components of the anode such as Ni induces performance degradation and catastrophic failure during redox cycles, which may result from seal leakage, the interruption of the fuel supply, or system shut down due to large and irreversible volume changes accompanied by metal-oxide transitions [10–16]. In addition, Ni promotes coke deposition in the presence of

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[*] Corresponding author. Tel.: +82 2 958 5515; fax: +82 2 958 5529.
E-mail addresses: kjyoon@kist.re.kr, kyungjoong.yoon@gmail.com (K.J. Yoon).

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hydrocarbons, especially when the steam-to-carbon ratio is low, and is readily poisoned by trace amounts of sulfur [17–24]. Therefore, it is highly desirable to develop an alternative ceramic-based anode material with improved redox, coking, and sulfur tolerance, which would substantially simplify the SOFC systems operating on fuels derived from natural gas, coal and biomass and hence reduce SOFC packaging and costs. The ideal solution would be a single phase mixed conducting ceramic electrode in which the entire electrode surface would be active for electrochemical reaction [25]. However, in practice, it is extremely difficult to develop a single phase oxide material that fulfills the rigorous requirements for anodes, such as high electronic conductivity, ionic conductivity, chemical stability, mechanical strength, thermal expansion match, chemical compatibility, etc. [26]; thus, the need for a composite approach has been stressed [27,28]. Although some composite anodes have exhibited acceptable properties, their electrochemical performance has been substantially lower than that of the conventional Ni-based anode in most cases. To improve the performance of all-ceramic SOFCs, it is essential to understand the reaction mechanisms and rate-limiting processes involved because detailed knowledge of the pertinent electrode reactions allows for the identification of current limitations and the determination of future research directions.

In this work, all-ceramic SOFCs were fabricated and electrochemically evaluated. The electrolyte-supported cells were composed of a $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM)–$Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ (GDC) anode, an Y_2O_3-stabilized ZrO_2 (YSZ) electrolyte, a GDC interdiffusion barrier layer, and a $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)–GDC cathode. The performance of the all-ceramic SOFC was compared with that of the conventional Ni-based SOFC, and a comprehensive understanding of the electrode reaction kinetics was obtained by the independent characterization of the individual electrodes.

2. Experimental

A composite LSCM–GDC powder was prepared by the particle-dispersed glycine-nitrate process [29]. Commercially purchased GDC powder was dispersed in distilled water using a dispersant. The nitrate precursors of lanthanum, strontium, chromium, and manganese were added to the mixture and mixed according to the targeted stoichiometry with glycine. The glycine/nitrate/powder mixture was combusted, and the raw powder was calcined at 1200 °C in air for 2 h. After calcination, the phase purity was verified by X-ray diffraction (XRD) analysis, and the particle morphology was examined using transmission electron microscopy (TEM).

Electrolyte-supported button cells were fabricated using ~300 μm-thick 8 mol % YSZ substrates. Pastes were prepared by mixing the powders with desired amounts of solvent, dispersant, binder, and plasticizer. An LSCM–GDC anode with the active area of 1 cm^2 was screen printed on one side of the electrolyte substrate, and a GDC interdiffusion barrier layer was screen printed on the other side, followed by sintering at 1200 °C for 2 h in air. Then, an LSCF–GDC cathode was screen printed over the GDC interdiffusion barrier layer, and cell fabrication was completed by firing the cathode at 1050 °C in air for 2 h. The fabricated cells were tested at 750–850 °C with humidified hydrogen (97% H_2–3% H_2O) as the fuel and air as the oxidant using a ceramic-glass composite sealant and an Inconel-based interconnect. Electrochemical measurements were performed using a Solartron 1260/1287 potentiostat and a frequency response analyzer. After testing, the cross sections of the cells were examined by scanning electron microscopy (SEM), and the microstructural features were investigated using the image analysis software program ImageJ.

Anode symmetrical half cells were fabricated using 2–3 mm-thick YSZ discs as the electrolyte substrates. Anode paste was screen printed onto both sides of the discs and fired at 1200 °C in air for 2 h. To fabricate cathode half cells, a GDC interdiffusion barrier layer was screen printed on both sides of the 2–3 mm-thick YSZ discs and fired at 1200 °C in air for 2 h. Then, an LSCF–GDC cathode was screen printed on GDC, and the entire structure was fired at 1050 °C in air for 2 h. The fabricated half cells were tested in a quartz tube reactor at 750–850 °C under various gas compositions, and the obtained impedance spectra were analyzed by fitting to an equivalent circuit model using the Z-view 3.1C software program.

3. Results and discussion

LSCM–GDC composite powder was synthesized using the novel powder-dispersed glycine-nitrate method. The glycine-nitrate method is a self-sustaining combustion technique for synthesizing high-quality ceramic powders from aqueous solution of metal nitrate and glycine [29]. Because the glycine-nitrate method produces excellent powder properties for various ceramic processing applications, it has been widely used in many areas through diverse modifications [30,31]. In particular, the synthesis of yttrium chromite-ceria composite powder through the single step combustion of the glycine-nitrate process has been reported for SOFC ceramic anode applications [32]. In the present work, nano-scale LSCM–GDC composite powder was synthesized by the powder-dispersed glycine-nitrate method. In this process, commercially purchased GDC powder was dispersed in a solution of glycine and nitrate precursors of LSCM, and the LSCM–GDC composite powder was formed *in-situ* through self-combustion. Fig. 1 shows a TEM image of the composite powder synthesized by particle-dispersed glycine-nitrate process after calcination at 1200 °C in air. The surface of GDC inclusion particles were coated with extremely fine LSCM particles, which were formed from the nitrate precursors through combustion. The particle size of the GDC powder was 200–300 nm, while that of the LSCM primary powder was 20–30 nm. Such a composite powder is expected to provide excellent phase connectivity, homogeneity, thermo-mechanical strength, and triple phase boundary length in the form of a porous electrode.

In-situ phase analysis was performed from room temperature to 1200 °C using high-temperature XRD, the results of which are shown in Fig. 2(a). All of the peaks were indexed to the LSCM orthorhombic perovskite structure and GDC cubic fluorite structure, and no indication of secondary phase formation or major peak shift was detected within the sensitivity of the instrument. Fig. 2(b) compares the aforementioned XRD patterns with those of the LSCM–GDC composite powder measured at 25 °C after calcination at 1200 °C in air and after exposure to a reducing atmosphere ($pO_2 = 4 \times 10^{-23}$ MPa) at 800 °C for 12 h. No decomposition product was detected after reduction. Therefore, LSCM–GDC was confirmed to be chemically stable under both the processing and operating conditions of the SOFC anode.

To evaluate the electrochemical performance of the ceramic anode, the electrolyte-supported SOFC employing an LSCM–GDC anode was fabricated. The cell was composed of a ~15 μm-thick LSCM–GDC anode, ~300 μm-thick YSZ electrolyte, ~10 μm-thick GDC barrier layer, and ~15 μm-thick LSCF–GDC cathode. A GDC interdiffusion barrier layer was placed between the YSZ electrolyte and LSCF–GDC cathode to prevent unfavorable solid-state reactions [33–35]. The microstructure of the LSCM–GDC anode is illustrated in Fig. 3. The cross-sectional image in Fig. 3(a) reveals a highly porous structure with a uniform thickness of ~15 μm. The porosity of the anode was measured to be ~30% by image analysis. The SEM image in Fig. 3(b), obtained in the BSE mode, shows the particle size distribution of the composite powder. The LSCM