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Short communication

High performance air electrode for solid oxide regenerative fuel cells fabricated by infiltration of nano-catalysts

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HIGHLIGHTS

- High performance air electrode is fabricated by nano-catalyst infiltration.
- Homogeneous nano-catalysts are formed by urea decomposition.
- Surface chemical exchange is accelerated by nano-catalysts.
- Performance is improved for power generation and hydrogen production.
- Nano-catalysts are stable against coarsening at high temperatures.

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ABSTRACT

A high performance air electrode fabricated by infiltration of highly active nano-catalysts into a porous scaffold is demonstrated for high-temperature solid oxide regenerative fuel cells (SORFCs). The nitrate precursor solution for $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) catalyst is impregnated into a porous $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)–gadolinia-doped ceria (GDC) composite backbone, and extremely fine SSC nano-particles are uniformly synthesized by *in-situ* crystallization at the initial stage of SORFC operation via homogeneous nucleation induced by urea decomposition. The SSC nano-catalysts are in the size range of 40–80 nm and stable against coarsening upon the SORFC operation at 750 °C. The electrochemical performance is significantly improved by incorporation of SSC nano-catalysts in both power generation and hydrogen production modes. Systematic analysis on the impedance spectra reveals that the surface modification of the air electrode with nano-catalysts remarkably accelerates the chemical surface exchange reactions for both O_2 reduction and O^{2-} oxidation, which are the major limiting processes for SORFC performance.

1. Introduction

In recent years, solid oxide regenerative fuel cell (SORFC) technology has attracted increasing attention for development of a highly-efficient energy conversion and storage system because a single SORFC unit can perform the dual functions of a solid oxide fuel cell (SOFC) and solid oxide electrolysis cell (SOEC) [1,2]. Although the overall SOEC reaction for hydrogen production is simply the reverse of the SOFC reaction for power generation, there are fundamental differences in two operating modes, such as the mass flux, heat flow, electric potential and gas environments, which strongly influence the performance and system efficiency. It is generally accepted that the performance of an SOEC is inferior to that of an SOFC [3], and in particular, the polarization loss occurring at the air electrode dominates the overall performance [4]. It was reported that the surface chemical exchange is the major rate limiting process for the conventional mixed ionic-electronic conducting (MIEC) air electrodes [5], which emphasizes the need of improved electrode materials and/or structures with enhanced electrocatalytic activity toward O_2 reduction and O^{2-} oxidation for a successful development of SORFC technology. Although extensive research efforts have been devoted to reduction of the polarization loss of the air electrode, satisfactory materials and structures for SORFC still remain elusive.

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Among the number of advanced electrode materials proposed to date, $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) exhibits an excellent surface oxygen exchange rate, electrical conductivity and bulk oxygen ion diffusion coefficient [6–8]. However, its practical application as a porous electrode has been limited due to the lack of the thermal compatibility and high cost; i.e., the large thermal expansion coefficient of SSC (20×10^{-6} K^{-1}) makes it extremely difficult to secure a stable interface with other cell components in a multi-layer structure during fabrication, operation, and thermal cycles [9,10], and the use of samarium in large scale is undesirable due to its high cost [11]. These technical challenges can be overcome and the merits of SSC can be efficiently utilized by incorporating a small amount of SSC catalyst into the stable porous scaffold in the form of nano-particles. As it is extremely difficult to infiltrate and uniformly distribute the pre-synthesized nano-particles inside the porous scaffold with submicron-scale pores, it is preferable to inject a precursor solution into the pores and then thermally treat to form the desired phase through precipitation and decomposition of metal salts. In typical solution impregnation techniques, the concentration of nano-particles is higher near the exposed surface because the precipitation of metal salts is induced by drying process [12]. Such segregation may disrupt the effectiveness of nano-catalyst incorporation because the electrochemical reaction predominantly occurs near the electrode-electrolyte interface. In this work, advanced infiltration and *in-situ* crystallization technique, where precipitation occurs via homogeneous nucleation induced by urea decomposition, was developed to obtain uniform distribution of SSC nano-catalysts throughout the porous $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)–gadolinia-doped ceria (GDC) composite air electrode. The phase formation, morphology and distribution of nano-catalysts were investigated in the urea decomposition technique. The electrochemical performance and stability were evaluated in SORFC operation, and the effect of nano-catalyst incorporation on the electrode reaction kinetics and overall performance of SORFC was discussed in detail.

2. Experimental

For fabrication of hydrogen electrode substrate, NiO, yttria-stabilized zirconia (YSZ), and a poly(methyl methacrylate) (PMMA) pore-forming agent were mixed via ball-milling for 24 h in ethanol with a dispersant, binder and plasticizer, and granules were obtained by spray drying. A NiO, YSZ, and PMMA volume ratio was 0.37:0.33:0.3. The substrates (2 cm × 2 cm) were fabricated by the uni-axial pressing of the granules at 60 MPa. The slurries for the hydrogen electrode functional layer (NiO/YSZ), electrolyte (YSZ), interdiffusion barrier layer (GDC), air electrode functional layer (LSCF + GDC), and air electrode current-collecting layer (LSCF) were prepared by mixing ceramic powders with a dispersant, binder, and plasticizer in α-terpineol using a planetary mill for the subsequent screen-printing. The hydrogen electrode functional layer and electrolyte were screen printed sequentially, followed by co-sintering at 1370 °C. The GDC interdiffusion barrier layer was screen-printed on top of the co-sintered YSZ electrolyte and fired at 1250 °C. Next, the LSCF–GDC air electrode functional layer and LSCF current-collecting layer were screen-printed and sintered at 1050 °C in air. The effective electrode area was 1 cm × 1 cm. Details on the cell fabrication procedure is described in our previous publication [13].

A 1 mol L^{-1} SSC precursor solution was prepared by mixing $Sm(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$ and urea in a solvent composed of water and ethanol. The [urea]/[cation] ratio was 10, and the [water]/[ethanol] volume ratio of the solvent was 1.7. Infiltration was performed using a micro-syringe, followed by thermal treatment at 80 °C for 2 h. The infiltration and thermal treatment steps were repeated 3 times before *in-situ* crystallization at 800 °C in cell operation. In a separate experiment, the crystallization behavior of SSC and its chemical compatibility with LSCF was investigated by dispersing LSCF powder in the SSC precursor solution, thermally treating it at 80 °C for 2 h and 800 °C for 72 h, and examining the crystal structure of the resulting powder using X-ray diffraction (XRD).

The cells were tested with humidified H_2 containing 3–50% H_2O on the hydrogen electrode and air on the air electrode between 700 and 800 °C for both power generation and hydrogen production modes. The gas flow rates were fixed at 200 sccm for both electrodes. Electrochemical characterization was performed using a Solartron 1260/1287 frequency response analyzer and potentiostat. Current collection was made using Pt mesh on the air electrode and Ni foam on the fuel electrode. No current collection paste was used. After testing, the cells were sectioned and parts of the cells were impregnated with epoxy in a vacuum. After the epoxy had hardened, the samples were polished down to 0.25 μm. The cross-sections of the fractured and polished surfaces were examined using scanning electron microscopy (SEM).

3. Results and discussion

In infiltration process for synthesizing the ceramic nano-catalysts, the processing temperature required for formation of the desired crystal structure plays a critical role in the size and morphology of the nano-particles. In SORFC applications, it is desirable to crystallize the nano-catalysts at the temperatures not substantially higher than the operating temperature because it enables the simple *in-situ* crystallization process during operation and prevents the excessive particle growth and unwanted chemical interactions. In Fig. 1, the phase formation of SSC nano-catalysts and their chemical compatibility with LSCF backbone are examined at 800 °C via XRD analysis. In this experiment, pre-synthesized LSCF powder was dispersed in the chemical solution containing SSC nitrate precursors and urea, with a [urea]/[cation] ratio of 10. Then, urea decomposition was performed at 80 °C, followed by calcination at 800 °C in air. The phase purity of the resulting SSC-LSCF composite powder was examined by XRD. All of the major peaks in the XRD pattern in Fig. 1 are identified as the SSC and LSCF perovskite structures, and secondary phase formation is not detected within the instrument sensitivity. In the urea

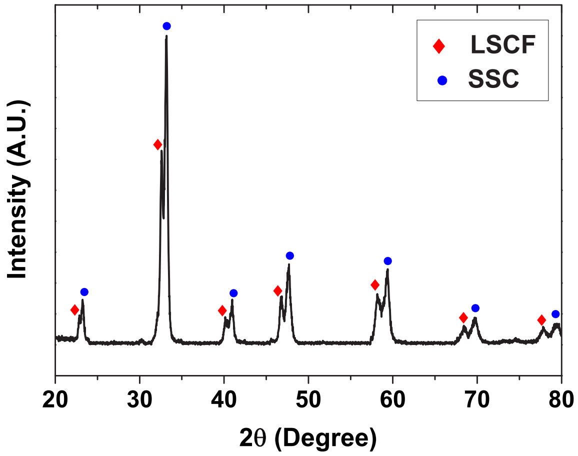

Fig. 1. XRD pattern of the SSC–LSCF powder mixture, showing the crystallization behavior of SSC derived from the precursor solution and its chemical compatibility with LSCF at 800 °C. The powder mixture was prepared by dispersing LSCF powder in the SSC precursor solution and thermally treating it at 80 °C for 2 h and 800 °C for 72 h in air.