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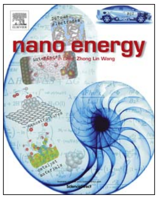

Full paper

Nano-tailoring of infiltrated catalysts for high-temperature solid oxide regenerative fuel cells

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ABSTRACT

Solid oxide regenerative fuel cells (SORFCs), which perform the dual functions of power generation and energy storage at high temperatures, could offer one of the most efficient and environmentally friendly options for future energy management systems. Although the functionality of SORFC electrodes could be significantly improved by reducing the feature size to the nanoscale, the practical use of nanomaterials has been limited in this area due to losses in stability and controllability with increasing temperature. Here, we demonstrate an advanced infiltration technique that allows nanoscale control of highly active and stable catalysts at elevated temperatures. Homogeneous precipitation in chemical solution, which is induced by urea decomposition, promotes crystallization behavior and regulates precursor redistribution, thus allowing the precise tailoring of the phase purity and geometric properties. Controlling the key characteristics of $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) nanocatalysts yields an electrode that is very close to the ideal electrode structure identified by our modeling study herein. Consequently, outstanding performance and durability are demonstrated in both fuel cell and electrolysis modes. This work highlights a simple, cost-effective and reproducible way to implement thermally stable nanocomponents in SORFCs, and furthermore, it expands opportunities to effectively exploit nanotechnology in a wide range of high-temperature energy devices.

1. Introduction

High-temperature solid-state electrochemical devices based on ceramic membranes, such as solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs), represent next-generation energy technologies for clean power generation and large-scale energy storage [1–4]. Due to the inherent reversibility of SOFC and SOEC reactions [5], it is technically feasible to construct “solid oxide regenerative fuel cells (SORFCs)” by integrating dual functions into a single cell and stack. SORFCs are expected to have a strong impact on the future energy infrastructure by offering efficient, cost-competitive and scalable energy management services [6–8]. For its widespread market penetration, however, innovation is still required to further improve its round-trip efficiency, lengthen its life span and reduce its costs. Based on technical issues identified by previous research, a general consensus has been reached that the air electrode is the key component determining the performance and reliability of the cell [9,10]. Because state-of-the-art air electrode materials suffer from sluggish oxygen exchange kinetics and high activation energy [11–13], extensive research efforts have been devoted to exploring new materials and structures. Although there have been considerable achievements in promoting electrode functionality using alternative materials [14–20] or nanostructures [21–25], implementing novel electrodes in practical cells has been mostly unsuccessful because high functionality inevitably comes at the expense of chemical and structural stability, especially at elevated temperatures [26].

One of the most promising approaches to overcome these technical barriers is nanoscale engineering based on solution infiltration [27–38]. In the infiltration process, a precursor solution of the active component is injected into a pre-fabricated porous scaffold, and the desired phase is formed by a subsequent thermal treatment. This unique procedure offers several advantages over conventional electrode fabrication processes. Specifically, calcination for phase formation is generally performed at a lower temperature than that of the typical electrode sintering process, wherein strong bonding must be developed at the interface, and reduced processing temperatures alleviate chemical compatibility issues such as detrimental chemical reactions and interdiffusion. Thermomechanical compatibility issues caused by a

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thermal expansion mismatch could also be mitigated because the infiltrated components are formed as discrete nanoparticles supported by the standard electrode. Therefore, the infiltration technique could potentially allow the implementation of a wide range of nanocomponents in standard cells with minimal compatibility problems, and the positive impact of infiltrating electrodes with various active materials has been empirically demonstrated by many researchers [27,28,30,37]. Now, the remaining task for its practical application is considered to be controlling the geometry of the infiltrated nanomaterials. Numerous modeling studies have proposed general guidelines for the rational design of infiltrated electrodes [39–44], but thus far, the physical construction of the intended nanoscale geometry has been extremely difficult at high temperatures. Large variations in the profile and performance of the infiltrated electrodes are readily found in the literature [45,46], and the cause of such wide discrepancies has been called a “mystery [45].” Therefore, an advanced technology to secure the controllability and reproducibility of the nanocomponent is eminently desirable to successfully implement the infiltration process.

To address this issue, we report herein a methodology to control the key characteristics of the highly active $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) nanocatalysts using urea decomposition in the infiltration process. The SSC, which has not been widely used as a stand-alone electrode because of its high chemical reactivity and large thermal expansion [47,48], was successfully incorporated as an active nanocomponent into the standard air electrode. We identified the major parameters controlling the thermal evolution of the nanoparticles and carefully tailored their size, morphology and spatial distribution based on fundamental understanding of nucleation and growth kinetics. Consequently, exceptional performance and long-term stability were achieved in both fuel cell and electrolysis modes. The effect of the solution chemistry and processing parameters on the final profile of the nanocatalysts is discussed in detail, and a strategy for realizing the ideal electrode structure is provided based on experimental and modeling studies.

2. Experimental

2.1. Preparation of chemical solutions

The SSC precursor solution was prepared by mixing stoichiometric amounts of $Sm(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$ and urea in a solvent composed of 55 vol% deionized water and 45 vol% ethanol. The concentration of the solution was fixed at 1 mol L^{-1}, and the [urea]/[cation] (U/C) ratio was varied to be either 6, 8, or 10.

2.2. Characterization of nanoparticles

For high-temperature X-ray diffraction (XRD) analysis, powder samples were prepared by thermally treating the precursor solutions at 80 °C for 1 h and then 500 °C for 2 h. The XRD patterns were collected between 600 and 800 °C at an interval of 50 °C. To investigate the morphology of powder samples using transmission electron microscopy (TEM), powders were derived from the precursor solutions by a thermal treatment at 80 °C for 1 h followed by calcination at 800 °C for 1 h.

2.3. Fabrication and characterization of symmetric cells

Symmetric cells were prepared using 2 mm thick 8 mol% yttria-stabilized zirconia (YSZ) discs as substrates. The slurries for the gadolinia-doped ceria (GDC) diffusion barrier layer, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)-GDC air electrode functional layer and LSCF air electrode current collecting layer were prepared by mixing ceramic powders with a dispersant, binder and plasticizer in α-terpineol using a planetary mill. The GDC diffusion barrier layer was screen printed on both sides of the disc and sintered at 1250 °C for 2 h in air. Then, LSCF-GDC air electrode functional layer and LSCF air electrode current collecting layer were sequentially applied on top of the GDC diffusion barrier layer on both sides, followed by sintering at 1050 °C for 2 h in air. The precursor solutions were infiltrated into the sintered air electrodes using a micro-syringe (1 μL), followed by a thermal treatment at 80 °C for 1 h. Then, the samples were calcined *in operando* at 800 °C for 1 h during the initial stage of the cell test. The electrochemical measurements were performed in a quartz tube reactor at 700–800 °C using a Solartron 1260/1287 potentiostat and frequency response analyzer, and the obtained impedance spectra were fit with an equivalent circuit model using Z-View 3.1 C software. The morphology of the infiltrated nanoparticles was examined using scanning electron microscopy (SEM) and TEM.

2.4. Fabrication and characterization of full cells

To fabricate full cells with fuel electrode-supported design, NiO, 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. The NiO/YSZ/PMMA volume ratio was 0.37:0.33:0.3. The fuel electrode substrates (2 cm×2 cm) were fabricated by uniaxially pressing the granules at 60 MPa. The slurries for the NiO-YSZ fuel electrode functional layer, YSZ electrolyte, GDC diffusion barrier layer, LSCF-GDC air electrode functional layer and LSCF air electrode current collecting layer were prepared by mixing ceramic powders with a dispersant, binder and plasticizer in α-terpineol using a planetary mill. The fuel electrode functional layer and electrolyte were screen printed sequentially on the substrate, followed by co-sintering at 1370 °C in air for 3 h. The GDC diffusion barrier layer was applied on top of the YSZ electrolyte by screen printing and fired at 1250 °C in air for 2 h. The fabrication of the full cell was completed by sequentially screen-printing the LSCF-GDC air electrode functional layer and LSCF current-collecting layer and sintering at 1050 °C in air for 2 h. The effective electrode area was 1 cm×1 cm. For infiltration, the precursor solution was injected into the air electrode using a micro-syringe (1 μL), followed by thermal treatment at 80 °C for 1 h. Then, calcination was performed *in operando* at 800 °C for 1 h during the initial stage of cell operation. The cells were tested in both fuel cell and electrolysis modes at 700–800 °C. The electrochemical performance was characterized using the Solartron 1260/1287 frequency response analyzer and potentiostat. For fuel cell mode operation, 97% H_2–3% H_2O and air were supplied to the fuel and air electrodes, respectively, and the electrolysis mode was tested with 50% H_2–50% H_2O on the fuel electrode and air on the air electrode. The gas flow rates were fixed at 200 sccm for both electrodes. The long-term stability was evaluated in fuel cell mode at a constant current of 0.5 A cm^{-2} and then in electrolysis mode at a constant current of 1.8 A cm^{-2} at 750 °C. After testing, cross-sections of the cells were examined using SEM, TEM and the energy-dispersive X-ray spectroscopy (EDS).

3. Results and discussion

In this article, we present an advanced infiltration technique with high controllability based on urea decomposition, and the procedure is schematically illustrated in Fig. 1. The processing steps involve preparing the scaffold (Fig. 1(a)), injecting the chemical solution (Fig. 1(b)), precipitating the precursors (Fig. 1(c)), solvent removal (Fig. 1(d)) and calcination (Fig. 1(e)). The key novelty of this approach is to separate the precipitation process (Fig. 1(c)) from solvent drying (Fig. 1(d)) using urea as a precipitation agent. For other infiltration processes, various organic additives have been used to improve the quality of the nanoparticles. For instance, adding a surfactant promotes cation intermixing through surfactant-cation complexing [27,49], improves wetting characteristics [50] and/or leads to the formation of templates for nanoparticle synthesis by self-assembly, such as normal and reverse micelles [51–55]. On the other hand, chelating agents,