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A novel high performance composite anode with in situ growth of Fe-Ni alloy nanoparticles for intermediate solid oxide fuel cells

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ABSTRACT

A redox reversible composite anode with Fe-Ni alloy nanoparticles in situ growth on $SrLaFeO_4$-type and $LaFeO_3$-type oxide substrates has been prepared for intermediate temperature solid oxide fuel cell (IT-SOFC) by reducing perovskite precursor $La_{0.4}Sr_{0.6}Fe_{0.75}Ni_{0.1}Nb_{0.15}O_{3-\delta}$ (LSFNNb) in wet H_2 at 900 °C for 1 h. The anode has shown an excellent electrochemical catalytic activity for oxidation of hydrogen with much smaller E_a ($25.1 \sim 68.9\,kJ\,mol^{-1}$) than the value ($>160\,kJ\,mol^{-1}$) at Ni-YSZ anode. A scandium stabilized zirconia (ScSZ) electrolyte supported SOFC with the anode achieves maximum power densities of 0.71, 0.52, 0.35, and 0.21 $W\,cm^{-2}$ at 800, 750, 700 and 650 °C, respectively in wet H_2 (3% H_2O), and the corresponding R_p of 0.16, 0.21, 0.35, and 0.60 $\Omega\,cm^2$ under OCV. Moreover, the single cell shows stable power output during ~105 h operation at 800 °C under 0.7 V in wet H_2 after a initial degradation, indicating that R-LSFNNb is an excellent candidate as anode of IT-SOFC.

1. Introduction

Solid oxide fuel cells (SOFC) are able to convert various fuels into electricity with high efficiency and low emission [1]. Some of the main limitations of SOFCs for long-term utilization are the problems faced by the state-of-the-art nickel-based anodes such as redox–cycling instability in the start-up/shut down processes or with seal leakage occurrence [2], the agglomeration of Ni particles occurring at high temperature, a rapid deposition of carbon and trace sulfur (>1 ppm) poisoning coming from hydrocarbon fuels [3,4]. Tremendous efforts have been devoted to explore alternative ceramic anodes to overcome the problems of Ni-based anodes. Perovskite $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM) [5] and double perovskite $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) [6] have been proved to be promising anode materials with redox stability and improved coking and sulfur resistance under SOFC anodic operating conditions. However, the availability of redox stable perovskite oxides is very limit, and many of them still suffer from low electrical conductivity and/or poor electrochemical activity for oxidation of fuels, especially at intermediate temperature range (600–800 °C) [7].

In order to increase the electrical conductivity and electrochemical activity of ceramic anodes, metallic nanoparticles have been incorporated into the porous ceramic substrates by infiltration [8–10], nevertheless, the size, distribution, and anchoring of the extraneous nanoparticles are difficult to be controlled [11] in addition to the time consuming preparing process and agglomeration of the nanoparticles upon long term operation. Recently, the exsolution of endogenous metallic nanoparticles from perovskite precursors through in situ reduction is attracting much attention in producing new anode materials because of the unique properties and high performance of the anodes as well as one step preparing procedure [12–16]. The anodes normally demonstrate a reversible structure transition between perovskite phase in air and a reduced form composed of metallic nanoparticles and oxide matrix in reducing atmosphere. The reversibility of the nanoparticle generation endows the catalyst redox-cycling stability and free from agglomeration through re-oxidation. The in situ growth of nanoparticles directly from the porous backbone provides more control over the size, distribution and anchorage of the nanoparticle species [11,14]. The exsolved metallic nanoparticles uniformly dispersed on the oxide substrate not only increase the electrical conductivity of the anodes in reducing atmosphere, but also enhance the catalytic activity for anodic reactions. Moreover, the strong interaction between the metallic nanoparticles and the oxide substrate further suppresses the agglomeration and enhances the coking and sulfur tolerance [11,12,16], thus greatly increasing the performance, lifetime and reliability of the anodes.

In this work, a novel anode material has been prepared by in situ reducing the perovskite precursor $La_{0.4}Sr_{0.60}Fe_{0.75}Ni_{0.1}Nb_{0.15}O_{3-\delta}$

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(LSFNNb) in wet H_2 for 1 hour to generate Fe-Ni alloy nanoparticles, and the microstructure, electrochemical activity and stability of the anode were investigated in wet H_2 fuel at intermediate temperature range (600–800 °C).

2. Experimental

$La_{0.4}Sr_{0.6}Fe_{0.75}Ni_{0.1}Nb_{0.15}O_{3-\delta}$ (LSFNNb) precursor was synthesized using a solid-state reaction method as we previously described [15,16]. Initially, stoichiometric amounts of La_2O_3, $SrCO_3$, Fe_2O_3, NiO and Nb_2O_5 powders were mixed by ball milling for 24 h, and then calcined in air at 1300 °C for 10 h to obtain the LSFNNb precursor. The $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.15}Nb_{0.05}O_{3-\delta}$ (LSFCN) cathode powders were also synthesized by a solid-state reaction method [17], and the $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) powders were prepared by a sol-gel process as described previously [18,19].

The crystal structures of the powders in various atmospheres were characterized by X-ray diffraction (XRD) measurements performed on an X-ray diffractometer (Rigaku D/max-2200/PC) with a Cu Ka radiation, $\lambda = 0.15415$ nm. The chemical compatibility between LSFNNb and commonly used electrolytes, such as $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) and scandia stabilized zirconia (ScSZ:10Sc1CeSZ), was also examined by XRD measurements on the mixtures of LSFNNb powders and the electrolyte powders with the ratio of 1:1 wt% calcined at 1000 °C for 3 h. The microstructures of the cross section of porous LSFNNb pellets or powders after reduction in wet H_2 (3%H_2O) at 900 °C for 1 h were examined using field emission scanning electron microscope (FE-SEM, Nova NanoSEM 450, FEI Company, USA) and a high-resolution transmission electron microscopy (HRTEM, JEM-2100, JEOL Ltd, Japan). The conductivity of LSFNNb in wet 5% H_2-Ar (3%H_2O, 4.85%H_2 and 92.15%Ar) with was measured via four-terminal DC technique using a digital sourcemeter (Keithley 2420) on rectangular bars with a dimension of 4 mm × 4 mm × 15 mm. The bars with the relative density of 95% were fabricated by uniaxial pressing LSFNNb powders at a pressure of 200 MPa, annealed in air at 1300 °C for 10 h before the conductivity measurements in air. The bars were then heated in wet 5% H_2-Ar at 900 °C for 10 h before the conductivity measurements in reducing atmosphere.

Symmetric half cells LSFNNb/SDC/YSZ/SDC/LSFNNb (YSZ: yttria stabilized zirconia, 10Y1CeSZ) were prepared by firstly screen-printing SDC ink onto the YSZ electrolyte pellets and sintered at 1250 °C for 2 h to form a protection interlayer with the thickness of ~10 μm, then the LSFNNb ink was screen-printed onto both sides of the SDC layer and sintered at 900 °C for 2 h [20,21].

Single cells with configuration of LSFNNb|SDC|ScSZ|SDC|LSFCN configuration (LSFCN: $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.15}Nb_{0.05}O_{3-\delta}$) were fabricated based on the commercial electrolyte ScSZ membrane (250 μm) purchased from Ningbo SOFCMAN Energy Technology Co., Ltd, China. The SDC interlayer were prepared the same as in half cells, then the LSFNNb and LSFCN inks were successively screen-printed on the SDC interlayer and sintered at 900 °C for 2 h in air. The thickness and active area of the electrodes are ~30 μm and ~0.28 cm^2, respectively.

Electrochemical impedance spectra (EIS) of the R-LSFNNb composite anode in the symmetric half-cell were collected via AC impedance method using Autolab PGSTAT 302 N electrochemical workstation in temperature range of 600–800 °C. An AC signal with 10 mV amplitude and a frequency range from 10^{-2} Hz to 10^6 Hz was applied as stimuli. The half-cell was reduced at 900C in wet 5%H_2-Ar for 10 h before data collection. The values of impedance were normalized by multiplying by the area of the symmetrical cell and divided by 2.

The current density-voltage (I–V) curves of the single cells were tested by four-probe configuration. The anode side is fed by wet H_2 at the flow rate of 60 ml min^{-1}, while the cathode is exposed to stationary air as oxidants. The cell was heated at 900 °C for 1 h, then the I-V(P) data between 800–600 °C were collected in cooling process. Detailed test processes and instruments setup can be found in our previous reports [17–19].

3. Results and discussion

3.1. Crystal structure, microstructure and chemical compatibility

In order to examine the redox reversibility of LSFNNb powders, the as-prepared LSFNNb precursor in air was reduced in wet H_2 at 900 °C for 1 h to obtain R-LSFNNb composite, then the R-LSFNNb was re-oxidized in air for 2 h. The crystal structures of the three samples have been examined respectively by Powder X-ray diffractometer (PXRD), and the results are shown in Fig. 1. The XRD pattern of the LSFNNb precursor is indexed well in orthorhombic phase with $(La_{0.8}Sr_{0.2})FeO_3$-type structure (JCPDS 35-1480) as shown in Fig. 1a pattern (1). After exposure in wet H_2 at 900 °C for 1 h, the sample partially decomposed to a mixture of $LaFeO_3$-type (JCPDS 37-1493) perovskite main phase, $SrLaFeO_4$ -type (JCPDS 29-1305) layered perovskite minor phase, and metallic Fe-Ni alloy with $Fe\text{-}Ni_3$ structure (JCPDS 65-3244) as observed in Fig. 1a pattern (2) and Fig. 1b. The reduced sample can be re-oxidized to the original perovskite phase as shown in Fig. 1a pattern (3), which is an indication of good redox reversibility of LSFNNb.

The microstructures of porous LSFNNb pellets after reduction in wet H_2 at 900 °C for 1 h are exhibited in Fig. 1c, it can be clearly seen that the surface of connected oxide grains (0.1–1 μm) is homogenously coated with nano-sized (20 ~ 40 nm) Fe-Ni alloy nanoparticles.

To further characterize the exact nature of the nanoparticles and the matrix, the particles, interfacial boundary between the nanoparticles and substrate zones of the reduced LSFNNb were studied by high resolution transmission electron-microscopy (HRTEM) (as shown in Fig. 1d). HRTEM analysis of sphere shaped nanoparticles in the reduced powder sample has revealed a lattice space of 0.205 nm, consistent with (111) planes of Fe-Ni alloy structure (JCPDS 65-3244) determined by the XRD analysis (Fig. 1b). For the substrate of the reduced sample, two types of lattice fringe can be observed, one lattice space between planes is measured as 0.393 nm, corresponding to the lattice constant of (101) planes of $LaFeO_3$-type structure (JCPDS 37-1493); and another is 0.286 nm, attributing to layered perovskite $SrLaFeO_4$ structure (JCPDS 71-1745) as determined by the XRD analysis in Fig. 1a.

The chemical compatibility between LSFNNb and commonly used electrolytes (SDC and ScSZ) is also investigated by PXRD. Fig. 1e demonstrates the XRD patterns of LSFNNb, SDC, ScSZ and their mixtures at a ratio of 1:1 wt % co-heated at 1000 °C for 3 h in air. Second phases of $SrZrO_3$ and $LaScO_3$ can be observed for the mixture of LSFNNb and ScSZ, whereas no new phase can be found for the mixture of LSFNNb and SDC, indicating that the LSFNNb powders react with ScSZ, but not with SDC under the testing condition. Therefore, a SDC interlayer needs to be added between R-LSFNNb anode and ScSZ electrolyte in cell fabrication to prevent the reactions and cation diffusion between them at elevated temperatures.

3.2. Electrical conductivity

Sufficient electronic conductivity is necessary for anode of SOFC to ensure efficient current collection and to decrease ohmic resistance in cell operation. Fig. 2 shows reciprocal temperature dependence of total conductivity (σ) of LSFNNb in air and in wet 5% H_2-Ar. A maximum conductivity of 160 Scm^{-1} was obtained at