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Chemical bulk diffusion coefficient of $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ cathode for solid oxide fuel cells

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HIGHLIGHTS

- The oxygen reduction activity is related to the oxygen bulk diffusion properties.
- SDC-infiltrated SSC cathode revealed a decrease in polarization resistance.
- Infiltration method creates extra triple-phase boundaries in cathode backbone.
- D_{chem} was measured by an electrical conductivity relaxation technique.

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ABSTRACT

This work reports the characteristics of $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) cathode including its chemical bulk diffusion coefficient (D_{chem}), current density (i_0), and single cell performance. In this study, the value of D_{chem} is measured by an electrical conductivity relaxation (ECR) technique. The equation of D_{chem} as a function of temperature in the range of 500–700 °C exhibits as follows:

$$D_{chem} = 4.65 \times 10^{-5} \exp\left(-\frac{91.33\,(\mathrm{kJ\ mol^{-1}})}{RT}\right)\left(\mathrm{m^2\ s^{-1}}\right)$$

To improve the cathode performance, the active ionic-conductive $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) nanoparticles deposit on a porous SSC cathode surface by infiltration method. The enhancement in electrochemical performances is ascribed to the creation of electrolyte/cathode phase boundaries, which considerably increases the electrochemical sites for oxygen reduction reaction. In this work, the 0.2 M SDC-infiltrated SSC reveals the maximum peak power density of 489 mW cm^{-2} at operating temperature of 700 °C with a thin film SDC electrolyte (30 μm), a Ni + SDC anode (1 mm) and a SDC-infiltrated SSC cathode (20 μm).

1. Introduction

Recently, solid oxide fuel cells (SOFCs) have attracted a great deal of attention due to the advantages of high electrical efficiency, fuel versatility, low-pollutant emission, etc [1–4]. However, their high operating temperatures limit the application of SOFCs, a lower operating temperature is required in the future applications [5]. Cathodes are important components of SOFCs, and developing new cathodes which perform well at the intermediate temperatures (600–800 °C) is a key step in reducing operating temperatures. Potential cathode candidates have normally been based on mixed oxygen ionic and electronic conducting oxides, which have both high ionic and electronic conductivities. The mixed conductivity extends the active oxygen reduction sites from the typical electrolyte–electrode–gas triple-phase boundaries (TPBs) to the entire cathode surface, therefore greatly reducing the cathode polarization at low operating temperatures [6]. The development of cathode materials with high electrocatalytic activity for oxygen reduction reaction (ORR) at intermediate temperature is great importance and it has received considerable attention during the past decade [7,8]. The cathodic reaction involves the reduction of molecule oxygen to oxygen ion by means of a series of intermediate steps, including gas diffusion, surface adsorption, dissociation, charge transfer and so on [9,10]. Consequently, evaluation of the

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electrocatalytic activity of the cathode toward oxygen reduction at reduced temperature is very important for SOFCs. The ORR activity of an SOFC cathode is closely related to the surface exchange and oxygen bulk diffusion properties. The detailed information about the surface exchange and oxygen bulk diffusion properties will be helpful in understanding the electrochemical properties to perform as a cathode, as well as in providing further guidance on performance optimization [11]. There are several techniques that can be applied to determine the surface exchange and bulk diffusion coefficients of a mixed conductor, such as oxygen permeation measurements, coulometric titrations, electrochemical impedance spectroscopy, oxygen isotope exchange depth profiling (IEDP) using secondary ion mass spectrometry (SIMS), oxygen isotope exchange using mass spectrometry, and relaxation techniques. The electrical conductivity relaxation (ECR) method has turned out to be a facile way to measure the chemical bulk diffusion coefficient (D_{chem}) and chemical surface exchange coefficient (k_{chem}) of a mixed conductor due to the high sensitivity of electrical conductivity to changes in oxygen concentration or oxygen partial pressure [12–17].

Recently, rare earth-doped cobaltite has attracted much attention due to its mixed-conduction characteristics and its relatively high ionic conductivity. Strontium-doped-samarium-cobalite materials ($Sm_{0.5}Sr_{0.5}CoO_3$, SSC) show high conductivity, up to 10^3 S cm^{-1} [18]. Therefore, SSC was selected as the cathode for investigating their ORR activity. In the present study, the D_{chem} of SSC-based materials at various temperatures and oxygen partial pressures was examined by an ECR method. The chemical diffusion coefficient of SSC was calculated from the Arrhenius plots of D_{chem} vs. 1000/T in the temperature range of 500–700 °C.

To improve the cathode performance of SSC, one commonly used method is mixture of a high ionic-conductive second phase like $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) within the cathode. Such a composite cathode can extent the electrochemically active TPBs, where the ORR occurs, and thus improve the electrochemical property [19]. In this study, the active ionic-conductive SDC nanoparticles deposited on a porous SSC cathode surface by infiltration or impregnation could provide a larger number of ORR sites and improving the electrochemical performance leading relatively low area specific resistances [20–23]. The microstructure and electrochemical performance of $Sm_{0.5}Sr_{0.5}Co_0O_{3-\delta}$ cathode with different infiltration parameters were also investigated systematically.

2. Experimental

2.1. Cathode and electrolyte materials preparation

$Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) cathode powders were synthesized by a conventional solid-state reaction synthesis method with high purity Sm_2O_3, $SrCO_3$, and CoO, powders (>99%) as starting materials. These powders were mixed under ethanol and milled for 12 h using zirconia balls. The ball-milled mixture was dried and ground into a powder with mortar and pestle and then calcined in air at 1000 °C for 4 h. The cathode powders were pelletized with a small amount of PVA as binder with an applied uniaxial pressure of 1000 kgf cm^{-2}. SSC was sintered in air at 1300 °C for 4 h with a programmed heating rate of 5 °C min^{-1}. The sintered samples were made up over 95% of the theoretical density in all the specimens for electrical conductivity measuring with different oxygen atmosphere. The $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) powder was synthesized by coprecipitation using $Ce(NO_3)_3 \cdot 6H_2O$ and $Sm(NO_3)_3 \cdot 6H_2O$ as the starting materials. These starting materials with stoichiometric ratio were dissolved in distilled water and then added to a solution of ammonia. The mixture solution was adjusted to a pH value in the range of 9.5–10. The resultant precipitate was filtered in a vacuum, and washed three times with water and ethanol, respectively. Then, the coprecipitation powder was calcined in air at 600 °C for 2 h. The SDC powder samples were pelletized with a small amount of PVA as binder with an applied unaxial pressure of 1000 kgf cm^{-2} and the dimensions of 15 mm in diameter and 1 mm in thickness. The disc samples were then finally sintered at 1500 °C for 5 h with a programmed heating rate of 5 °C min^{-1} [24].

Aqueous nitrate solution of SDC precursors with different concentration (0.1, 0.2, 0.3 M) were prepared by dissolving proper amount of $Ce(NO_3)_3 \cdot 6H_2O$ and $Sm(NO_3)_3 \cdot 6H_2O$ in water. Ethyl glycol (EG) was also added to the solution as a complex agent to form the correct phase. Ethanol was added into the aqueous solution with a ration of 1:1 to improve the wetting ability on the SSC backbone. Three microliters of this solution were infiltrated into each side of the porous SSC cathode using a micro-liter syringe in order to control the amount of loading. After allowing the solution to dry in air, the infiltrated cell was fired at 900 °C for 2 h to obtain the desired SDC nanoparticles within the SSC skeleton.

2.2. Electrical conductivity relaxation

The time dependence of the conductivity was measured using the four-probe DC technique, and was recorded by a Keithley 2420 source meter. Measurements were performed on a specimen with a rectangle geometry, having typical size of $5 \times 5 \times 10$ mm^3 and above 95% of the theoretical density over the temperature range of 500–700 °C at an interval of 50 °C. After each temperature change, the bar was stabilized for at least 30 min. A sudden change in the oxygen partial pressure (P_{O_2}), from 0.05 to 0.21 atm was caused by introducing standard gas mixtures of Ar and O_2. Small oxidation and reduction steps were alternatively applied to study the D_{chem}. Typically, a sequence of several reduction/oxidation cycles was performed at each temperature. The electrical conductivity relaxation curve was plotted as $g(t)$ versus t, which was fit by a least square method to an analytical solution of Eq. (1). Either D_{chem} or k_{chem} was the variable fitting parameters [25].

2.3. Symmetrical cell and the single cell fabrication

The working electrode (WE) was prepared by infiltration of nanosized SDC into SSC. The cathode paste consisted of cathode powder, solvent, binder, and plasticizer. The cathode paste was applied on both sides of SDC electrolyte discs with circle patterns using the screen-printing method with a diameter of 13 mm and a thickness of 1 mm. On one side, the cathode paste was painted as the WE with a surface area of 0.385 cm^2. The Pt reference electrode (RE) was located about 0.3–0.4 cm away from the WE. Such a distance was chosen to avoid measurement errors due to the misalignment of the working and counter electrodes. The Pt counter electrode (CE) was arranged on the other side of the SDC disk. After the cathode material was painted on the electrolyte, it was then sintered at 1000 °C for 4 h in air.

In order to evaluate the effect of the concentration of SDC infiltration on the cathode performance in a single cell, the anode-supported fuel cells were prepared. Anode substrates consisting of 58 wt% NiO, 38 wt% SDC and 4 wt% graphite were prepared by a die-pressing process. SDC nanopowders were then added onto the pre-pressed green NiO–SDC substrate. And then, the SDC powders and NiO–SDC substrate were co-pressed to form a green bilayer and subsequently co-sintered at 1400 °C for 4 h to form dense SDC electrolyte. The cathode paste consisted of SSC cathode powder, solvent, binder, and plasticizer was screen-printed onto the SDC electrolyte film supported by NiO–SDC anode and sintered at 1000 °C for 4 h. In order to obtain SDC-infiltrated single cell, nanostructured SDC was infiltrated into SSC cathode backbones. Finally,