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Compaction pressure effect on microstructure and electrochemical performance of $GdBaCo_2O_{5+\delta}$ cathode for IT-SOFCs

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Abstract

In order to optimize the morphology of starting powder, raw GBCO powder synthesized via solid state reaction was repeatedly compacted by uniaxial die pressing at two apparent compaction pressures of 500 and 1000 MPa. The particle size distribution curves and SEM images indicated that, with increasing compaction pressure and number of compaction times, the larger particles in the powder were gradually broken apart and the particle size became small and uniform. Then the effect of pressing treatment for the starting GBCO particles on the microstructure and performance of sintered cathode was studied. The results demonstrated that, after being sintered under the same conditions, the cathode prepared from the treated GBCO particles showed a finer microstructure compared with that prepared from the raw GBCO particles. In addition, optimizing the morphology of the starting GBCO powder by pressing treatment could improved the cathode performance and made the polarization resistance of final cathode reduce from 1.33 $\Omega\ cm^2$ to 0.40 $\Omega\ cm^2$ at 600 °C.

Keywords: A. Pressing; E. Fuel cells; Cathode; Microstructure

1. Introduction

Recently, much attention has been focused on intermediate-temperature solid oxide fuel cells (IT-SOFCs) operating at ≤800 °C, because the reduced temperature operation can extend the range of material selection, reduce the costs of fabrication and application and improve the stability and reliability for the SOFC systems [1–4]. With the decreasing of operation temperature, however, due to the high activation energy for cathodic reaction, the contribution of the cathode polarization resistance to the total resistance of the cell becomes the dominant contribution in an anode-supported SOFC using membrane electrolyte with low ohmic resistance [5,6]. Hence, great efforts have been paid to reduce the cathode polarization and enhance the electro-catalytic activity of cathode for oxygen reduction reactions (ORRs), so as to improve the performance of IT-SOFC.

Currently, there is considerable number of research activities on the potential of mixed ionic and electronic conductors as cathode materials of IT-SOFCs [7–9]. The mixed conductivity of such materials greatly extends the active oxygen reduction sites from the typical triple phase boundary (TPB) to the entire cathode surface (cathode–gas phase interface), and thereby these materials exhibit high electrochemical activity for oxygen reduction at reduced temperatures [10,11]. Layered Perovskite oxides with general formula of $LnBaCo_2O_{5+\delta}$ (Ln = rare earth, $0 > \delta > 1$) have received tremendous attention as potential alternative MIEC oxides in recent years [12–22]. These compounds exhibit high electronic conductivity and excellent oxygen transport properties (i.e. high oxygen surface exchange coefficient and rapid oxygen–ion diffusion), which are very beneficial for cathodes [19,20,22–24]. According to Kim et al. [19], the oxygen ion diffusivity and surface exchange coefficient of $PrBaCo_2O_{5+\delta}$ were $10^{-5}\ cm^2/s$ and 10^{-3} cm/s at 623 K, respectively, which are higher than typical Perovskite MIECs such as $La_{0.5}Sr_{0.5}CoO_3$, $Sm_{0.5}Sr_{0.5}CoO_3$. In addition, these oxides also demonstrate attractive electrochemical activity. On doped ceria electrolyte and at ~600 °C, the cathodic polarization resistances of $GdBaCo_2O_{5+\delta}$ and $PrBaCo_2O_{5+\delta}$ were reported as 0.58 $\Omega\ cm^2$ and 0.4 $\Omega\ cm^2$, respectively [13,25].

Many studies show that the cathode performance is also heavily dependent on its microstructure in addition to the

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intrinsic properties of cathode materials [26–28]. Therefore, the improvement of cathode performance may be realized through optimizing the microstructure of cathode for a given cathode material. The microstructure of the resulting cathode is closely related to the morphological characteristics of the starting powder [29,30], and the morphology of powder could be affected by the synthesis techniques and subsequent treatment processes.

Many different syntheses methods have been developed for production of ceramic powders used as cathode materials in SOFC, such as solid-state reaction, sol–gel technique, co-precipitation, and combustion [31–34]. The solid-state reaction is a conventional method of ceramic processing. Although the sample prepared by solid-state reaction presents larger particle size than the samples prepared by wet chemical methods, the wet chemical methods usually involve complicated process and environmental pollution caused by the emission of noxious gases, e.g. NO_2. Yet solid-state method is capable of circumventing these problems in preparation of ceramic powders. So, in this paper, cathode powder was synthesized by the solid-state reaction method.

The ball-milling and repeated grinding in a mortar are the common methods used to refine the raw powders prepared by solid-state reaction, but these methods are energy-intensive and time-consuming. Therefore, a simple, fast treatment method is needed in order to optimize the morphology of the raw powders.

Forming techniques such as uniaxial compaction pressing, cold isostatic pressing (CIP) have played an important role in production of ceramic materials. These forming processes cannot only press the loose ceramic powder into a mass of certain density and definite shape, but the applied stress during forming also have significant influence on the microstructure and properties of powder. For example, Gao et al. [35] found that the sintering behavior of Y-TZP ceramics compacted by a superhigh pressure can be largely improved because of the increase in contact points between the particles and the decrease in pore size as the applied pressure increased. Lee et al. [36] made Ni–YSZ anode substrate by liquid condensation process under the compaction pressure ranges of 2–7 MPa, and showed that the microstructure (like porosity and pore size) of Ni–YSZ anode substrate can be manipulated by the degree of compaction pressure during forming. In addition, the transition of microstructure with compaction pressure had profound effects on the performance of anode substrate. Kim et al. [37] fabricated the indium tin oxide (ITO) powder compacts by cold isostatic pressing (CIP). Results showed that the inhomogeneity in powder compact was controlled by changing the CIP pressure, and an increase in the forming pressure enhanced the homogeneity of the powder compact.

Uniaxial die pressing is a simple forming technology used to compact the ceramic powders. In the preparation of SOFCs, NiO/YSZ composite powder is usually compacted by this process to form anode substrate [38,39]. In addition, Chen et al. [38,39] found that the applied compaction pressure during forming had great influence on the particle size distributions of raw NiO and YSZ powders. However, up to now, there are few reports about the method of uniaxial pressing used designedly to control the morphology of starting powder as cathode for IT-SOFCs. Therefore, in this paper, the raw GBCO powder prepared by solid-state reaction method was treated by uniaxial die pressing, and then its morphology could be controlled by changing treatment conditions. Moreover, the effect of the morphology of starting powder on microstructure and electrochemical performance of final cathode were investigated.

2. Experimental

$GdBaCo_2O_{5+\delta}$ (GBCO) powder was synthesized by the conventional solid-state reaction method as reported in our previous paper [14]. The raw GBCO powder was repeatedly compacted by uniaxial die pressing at two compaction pressures of 500 and 1000 MPa, respectively. To distinguish these GBCO powders treated under different compaction conditions, they were denoted as various designations, for example, the GBCO powders compacted repeatedly at 1000 MPa pressure for 4 and 6 times were denoted as GBCO1000-4 and GBCO1000-6, respectively. The untreated raw GBCO powder was denoted as GBCO0. The particle size distributions of raw GBCO powder and treated GBCO powders were measured with a laser scattering technique Mastersizer 2000 (Malvern Instruments). The morphology and microstructure of powder and cathode layer were observed by a scanning electron microscope (SEM, Hitachi-S4800).

Symmetrical half cells with the configuration of electrode/electrolyte/electrode were fabricated for electrochemical measurements. In this study, $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) was used as electrolyte material. The SDC powders were uniaxially pressed into pellets under 300 MPa and then sintered at 1400 °C for 4 h in air to obtain dense electrolyte substrates with about 11.5 mm in diameter and 0.5 mm in thickness. In order to improve the adhesion of interface, the surface of SDC pellet was coarsened by spin coating a SDC layer before sintering. Each GBCO powder (raw and treated powders mentioned above) was mixed thoroughly with ethylcellulose–terpineol binder to obtain the corresponding cathode slurry, which was then symmetrically painted on both sides of dense SDC electrolyte pellet to form symmetrical half cell. After drying, these half cells were sintered at 950 °C for 4 h in air. The effective area of cathode was ~0.26 cm^2. Silver paste (DAD-87) was paint onto the electrode surfaces of the symmetrical half cells serving as the current collector and adhereing silver leads.

AC impedance spectroscopy of the symmetrical cells was measured to characterize the electrochemical performance of cathode using impedance response analyzer (Solartron SI 1260) and electrochemical interface (Solartron SI 1287). The impedance data were collected with ZPlot software under open circuit conditions with an AC signal amplitude of 10 mV in a frequency range from 91 kHz to 0.1 Hz, and fitted with ZView 2.3 software. Impedance measurements were taken over a temperature range of 500–700 °C in air.