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Effect of sintering temperature on surface morphology and electrical properties of samarium-doped ceria carbonate for solid oxide fuel cells

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Abstract

The effects of sintering temperature on the surface morphology, roughness, and electrical properties of samarium-doped ceria (SDC)–carbonate (SDCC) composite electrolyte were examined. SDCC composite pellets were fabricated and sintered at various temperatures ranging from 500 °C to 650 °C. Brunauer–Emmett–Teller technique and atomic force microscopy were used to investigate the surface area and surface roughness of the composite materials, respectively. Conductivity measurements using impedance spectroscopy were conducted from 350 °C to 550 °C. The specific surface area of the pure SDC powder decreased from 8.85 m^2/g to 4.24 m^2/g after the carbonate phase was incorporated into the SDC phase with increasing particle size. The composite pellet sintering temperature affected the continuity between the two phases [SDC and (Li/Na) carbonate], roughness, mean particle size, and conductivity of the composite electrolyte. A fully dense SDCC composite electrolyte pellet sintered at 550 °C exhibited a maximum ionic conductivity of 0.077 S/cm at 550 °C. In addition, 550 °C was the minimum sintering temperature to achieve good wetting between the two phases, moderate particle size, low surface roughness, and high ionic conductivity.

Keywords: A. Sintering; B. Composites; C. Ionic conductivity

1. Introduction

Solid oxide fuel cells (SOFC) are among the most efficient fuel cells that operate at high temperatures to convert chemical energy into electrical energy [1–4]. Zirconia-based electrolytes, such as yttria-stabilized zirconia (YSZ), are commonly used because of their high ionic conductivity ($>10^{-1}$ S/cm), high efficiency, and excellent chemical and thermal stabilities in both oxidizing and reducing environments. YSZ-based SOFCs are usually operated at temperatures reaching 800 °C to 1000 °C [5,6]. Han et al. [7] reported the maximum power density of 0.95 W/cm^2 at 800 °C for YSZ electrolyte-based anode-supported SOFCs using hydrogen as fuel and air as oxidant. Reducing the operating temperature can increase the lifetime and can expand the choices for the constituent materials [8]. In recent studies, the operating temperature was reduced by the development of new electrolyte materials [9,10]. Ceria-based electrolyte materials, such as samarium-doped ceria (SDC) or gadolinium-doped ceria, offer the best ionic conductivity at operating temperatures between 400 °C and 800 °C [11,12]. However, ceria-doped electrolytes tend to easily reduce at low oxygen partial pressure, thereby exhibiting high electronic conductivity in an anodic background [13]. This electronic conduction results in a great loss in cell performance and exhibits poor mechanical strength.

Increased ionic conductivity and electronic conduction suppression of ceria-doped electrolytes can be achieved by introducing a small amount of alkaline salts [14–16]. Ceria–carbonate

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composite electrolytes exhibit higher ionic conductivity (10^{-2} S/cm to 1.0 S/cm) and power density (400 mW/cm^2 to 1700 mW/cm^2) in the intermediate temperature range than pure SDC [14]. The ionic conductivity of ceria-based electrolytes can be influenced by various interrelated factors, such as grain boundary, grain size, particle shape, composition, and processing. The composition and processing conditions can significantly alter the electrolyte powder properties and overall performance of the cell. The effects of these factors on ceria-based electrolytes have been discussed in other studies [16–20].

Xia et al. [21] studied the influence of different surface properties of SDC powder prepared using the sol–gel (SG), glycine–nitrile (GN) and co-precipitation method on the performance of SDC–carbonate (SDCC) composite electrolyte. They found that the surface properties of SDC (powder structure, surface area and interface between SDC and carbonate phase) and electrolyte thickness significantly influence the performance of fuel cells. They also recognized that ionic transport and thermal behavior of SDCC composite electrolyte strongly depend on the surface property of SDC. Powders with rod-like SDC particles prepared by oxalate co-precipitation show the best performance because of the formation of the consecutive interface and dual-phase (SDC and carbonate phase) in ionic conduction. In addition, the performance of SDCC composites can be improved by increasing the interfacial area. SDC powders prepared by the GN and SG methods shows slightly poor performance because of poor interfacial conduction area formation. Powders prepared using the GN and SG methods exhibit foam-like (porous structure) and agglomerated (core-like structure) SDC, respectively, which may destroy the interfacial conduction path and limit the carbonate phase continuity.

Bodèn et al. [22] achieved high ionic conductivity and low activation energy for the composite electrolyte with 80% SDC and 20% (Li/Na) carbonate. They found that conductivity strongly depends on the carbonate content. Two phases of SDCC composite electrolyte powders were formed in a mixture of 10% (Li/Na) carbonate and 20% (Li/Na) carbonate. Meanwhile, large (Li/Na) carbonate crystals without a continuous phase with SDC particles were formed in a mixture with 50% (Li/Na) carbonate. They also recognized that different gas environments do not strongly influence the conductivity of SDCC composites. According to Zhu et al. [20], conductivity can be enhanced several times compared with pure SDC when the carbonate content is less than 30%.

The processing condition is another important factor that influences the electrical conductivity of electrolytes. This factor includes the different sintering techniques to prepare ceramic pellets with controlled microstructures, such as grain size, density, and purity. In our recent work [23], we investigated the electrical conductivities of pellets sintered at different temperatures based on current–voltage characteristics in SDCC composite electrolyte. We have identified that the pellet sintered at 550 °C has the best microstructure with less porosity, better open circuit voltage (OCV) and higher power density than pellets sintered at higher temperatures. This phenomenon is noticeably different with those reported by Xia et al. [24], who observed that the samples sintered at 675 °C for 2 h produces a superior interfacial microstructure, 98.9% density, and better ionic conductivity than pellets sintered at 600 °C, 625 °C, 650 °C and 700 °C.

The aforementioned examples indicate that the factors such as composition, processing condition and micro-structure influence the performance of SDCC composite electrolytes. Surface roughness and physical treatment also influence the electrolyte properties, particularly the carbonate phase melting of (Li/Na) carbonate to form a continuous phase with SDC particles. Although numerous studies have reported on the performance of SDCC composite electrolyte, reports on the effect of sintering temperature on surface roughness and the consequent electrical properties are limited. Therefore, in this study we focused on the effects of sintering temperature on the surface roughness, and electrochemical properties of SDCC composite electrolytes. The surface roughness and surface morphology of SDCC composite electrolyte pellets sintered at various temperatures were examined using atomic force microscopy (AFM). The grain size growth of the pellets sintered at various temperatures ranging from 500 °C to 650 °C was observed by field-emission scanning electron microscopy (FESEM). Electrochemical impedance spectroscopy (EIS) was also applied to investigate the ionic conductivity of the SDCC composite electrolytes from 350 °C to 550 °C.

2. Experimental procedure

SDC with $Ce_{0.8}Sm_{0.2}O_{1.9}$ composition was prepared using citrate SG-based methods [25]. SDCC composite electrolyte powder was prepared by the solid-state reaction method [23]. The pure SDC and SDCC composite electrolyte powders were obtained after calcining at 850 °C for 5 h and at 680 °C for 1 h, respectively. A detailed description of the preparation procedure of the SDC and SDCC composite electrolyte powders is available in a previous publication [23]. X-ray diffraction (XRD) patterns were recorded at room temperature using an X-ray diffractometer (Shimadzu XRD-6000, Germany) with CuKα ($\lambda = 1.5418$ A°) radiation and 2θ ranging from 20° to 80° to identify the crystalline phase of the pure SDC and SDCC composite powders. The specific surface areas of the pure SDC and SDCC calcined powders were measured using a surface area analyzer (Micrometritics, ASAP 2010, USA) and the Brunauer–Emmett–Teller technique. Pore size and volume were calculated using the Barrett–Joyner–Halenda cumulative adsorption and desorption methods.

The SDCC composite electrolyte powders were cold-pressed at 80 MPa into 25 mm-wide and 1 mm-thick cylindrical pellets using a uniaxial die-press. The as-prepared green pellets were sintered at 500, 550, 600, and 650 °C for 5 h in air and then designated as 500SDCC, 550SDCC, 600SDCC, and 650SDCC, respectively. FESEM (Zeiss Supra-55VP) was used to examine the microstructure, particle size, shape, and morphology of the SDCC composite pellets. AFM was used to investigate the roughness and surface morphology of the sintered pellets before electrochemical impedance measurement. AFM raw data were processed and analyzed using NOVA (Version: 3.5.0.2069) software.

The conductivities of the SDCC composite electrolytes were measured at temperatures from 350 °C to 550 °C using impedance