Available online at www.sciencedirect.com
ScienceDirect
Solid State Ionics 179 (2008) 1553 – 1556
SOLID STATE IONICS
www.elsevier.com/locate/ssi

Effect of firing temperature on the performance of LSM–SDC cathodes prepared with an ion-impregnation method

Lei Zhang, Fei Zhao, Ranran Peng, Changrong Xia *

Laboratory for Renewable Clean Energy, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, 230026 Anhui, China

Received 19 June 2007; received in revised form 27 November 2007; accepted 7 December 2007

Abstract

LSM ($La_{0.85}Sr_{0.15}MnO_{3-\delta}$)–SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) composites, which are based on LSM matrices embedded with SDC particles, were fabricated with an ion-impregnation technique as cathodes for intermediate and low temperature solid oxide fuel cells(SOFCs). Effect of heat-treatment temperatures for both LSM matrices and SDC particles was investigated on cathodic interfacial polarization resistances. When the matrix was fired in the range of 800–1000 °C, low temperature resulted in high specific surface area, and therefore low resistance. On the contrary, high temperature enhanced the bonding between the particles and matrices, and consequently caused increased electrochemical performance when the impregnated SDC was heated at temperature from 700 °C to 800 °C. With the impregnated LSM–SDC composite as the cathode, a single cell generated 138 mW/cm^2 at 600 °C when humidified H_2 was used as the fuel, suggesting that it is possible to use LSM as the cathodes for SOFCs that operated at low temperature when the microstructure is further optimized.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Solid oxide fuel cells; Doped ceria; LSM; Ion-impregnation; Composite cathode

1. Introduction

Strontium-doped lanthanum manganate (LSM) is the classical material as cathodes for SOFCs. But its low ionic conductivity and high activation energy for oxygen disassociation limit its application in SOFCs, especially at intermediate and low temperatures. To increase the ionic conductivity in the cathode, second phase electrolytes such as yttria-stabilized zirconia (YSZ) and doped ceria are mixed with LSM to form a composite cathode with various techniques [1–3]. Among these techniques, ion impregnation technique is a very effective method to add the second phase. In addition, this method can optimize the microstructure that would increase the length of triple-phase boundary (TPB) between the electrolyte, electrode, and oxygen gas phase [4,5]. It consists of a series of steps including LSM matrix formation and second-phase ion impregnation, which are both close associated with heat-treatment temperature. The matrix must be fired to strengthen the electrode–electrolyte bonding; moreover heating of the impregnated ions is necessary to form the second phase with desired structure. For example, SP Jiang et al. reported LSM–GDC (Gd doped CeO_2) electrodes with the ion-impregnation process. The LSM matrix was fired at 1150 °C for 2 h while GDC was heated at 850 °C for 1 h [2]. In our previous report, LSM–SDC (Sm doped CeO_2) electrodes were fabricated on SDC electrolytes. The matrix was fired at 1000 °C for 2 h and SDC was heated at 850 °C for 1 h [3].

The performance of a composite electrode is known to be greatly affected by its microstructure, which depends upon sintering temperature and starting materials. For example, LSM–YSZ cathodes have shown less dense microstructure and smaller grains as the sintering temperature was decreased to the range of 1300–1150 °C [6]. This increased the active TPB amount, leading to a decrease in interfacial polarization resistance with decreasing sintering temperature. Similarly, the performance of an ion-impregnated composite cathode should be also sensitive to heat-treatment temperature, since the temperature usually has

* Corresponding author.
E-mail address: xiacr@ustc.edu.cn (C.R. Xia).

0167-2738/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ssi.2007.12.013

significant influence on its microstructure, on adhesion of the electrode to the electrolyte, and on reactivity between the two phases.

However, reports are seldom available upon the heat-treatment conditions for impregnated electrodes. In this work, correlation between the heat-treatment temperature, morphology and performance has been investigated on symmetrical cells with composite LSM–SDC electrodes prepared with the ion-impregnation process. In addition, single cells with impregnated cathodes were characterized at 600 °C with humidified hydrogen as the fuel.

2. Experimental

$La_{0.85}Sr_{0.15}MnO_{3-\delta}$ (LSM) and $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) oxide powders, were prepared using a glycine–nitrate combustion method [7]. The substrates were prepared by pressing SDC powders to disks 15-mm in diameter and sintering at 1400 °C for 5 h. LSM–SDC electrodes were fabricated by an ion-impregnation method, including screen-printed LSM matrix and ion-impregnated SDC particles. Slurry of grinding LSM powders mixed with an organic binder was screen-printed to both sides of the SDC substrates to form symmetrical layers. The printed layers were then dried and fired at 800, 900, and 1000 °C for 2 h to produce porous matrices. The LSM matrix thickness and area were about 60 μm and 1.0 cm^2, respectively on each side. To conduct the impregnating process, an SDC solution of 0.3 mol/L was dropped to the LSM matrix, dried and heated at 600 °C. The process was repeated until the weight of SDC was equal to that of LSM [3]. The impregnated SDC was finally heated at 700, 750, 800 and 850 °C for 2 h. Anode supported single cells with NiO–SDC as the anodes and SDC as electrolytes were prepared using a dry-pressing technique [8]. LSM–SDC cathodes were fabricated onto the SDC films with the impregnation method as mentioned above.

The specific surface areas of LSM powders fired at 800, 900, and 1000 °C was measured using Brunauer–Emmett–Teller method (BET, Deckman Coulter, SA3100). Microstructure was revealed by scanning electron microscope (SEM, FEI XL30). Crystalline size of the impregnated SDC was also estimated with X-ray diffraction (XRD, Philips X'pert PROS). Area specific resistance (ASR) was measured with the symmetrical cells using a two-probe model. Symmetrical cells consisted of SDC substrates and LSM–SDC electrodes were used for the measurement of interfacial polarization resistances. Single cell performance was characterized at 600 °C, using humidified (3% H_2O) hydrogen as the fuel and stationary air as the oxidant. Zahner IM6e electrochemical workstation was used for electrochemical characterizations.

3. Results and discussion

3.1. Microstructure characterization

Shown in Fig. 1a is the cross-sectional view of an LSM matrix which was fired at 900 °C and supported on an SDC substrate. It can be seen that the matrix was porous and consisted of particles with average size of 2~3 μm. A porous characteristic was further observed on the LSM particles. Shown in Fig. 1b is the enlarged image of an LSM particle. Although LSM was fired at 900 °C, the particles themselves were porous with micropores that were possibly caused by gas emission during the combustion reaction occurred in the glycine nitrate procedure [7]. The highly porous character might result in high electrode performance since oxygen reduction is believed to take place at the surface of LSM particle. In addition,

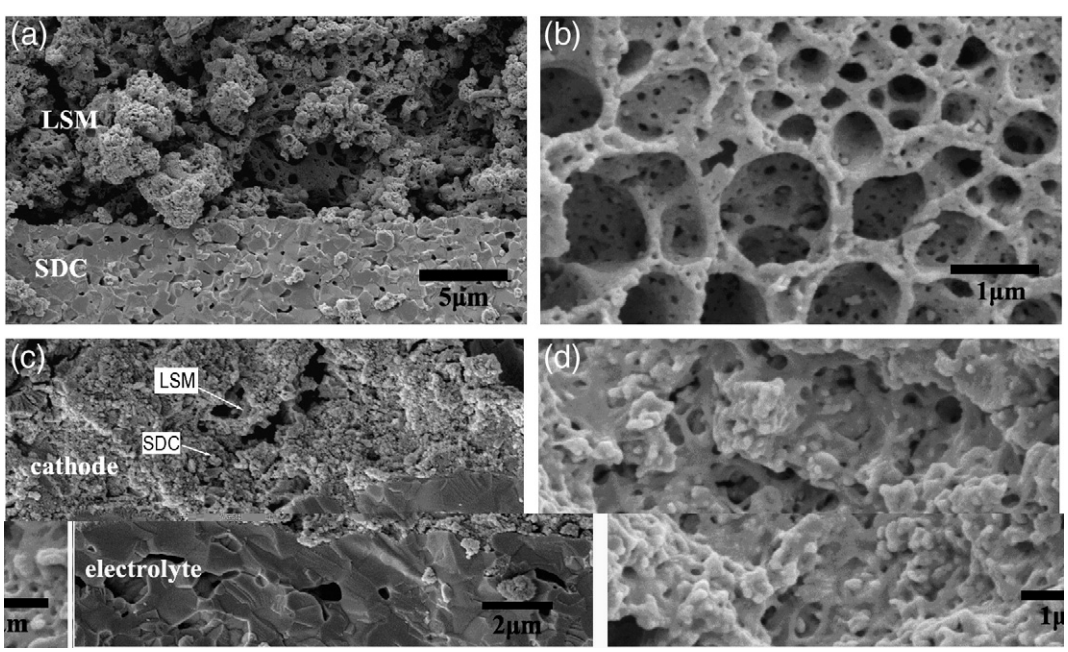

Fig. 1. SEM micrographs a) cross-sectional view of LSM matrix; b) LSM particle; c) cross-sectional view of impregnated LSM–SDC electrode; and d) SDC grains covered on LSM.