Electrochemistry Communications 51 (2015) 93–97

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

Barium carbonate nanoparticle as high temperature oxygen reduction catalyst for solid oxide fuel cell

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ARTICLE INFO

Article history:
Received 24 November 2014
Received in revised form 11 December 2014
Accepted 11 December 2014
Available online 17 December 2014

Keywords:
Barium carbonate
Oxygen reduction catalyst
Cathode
Solid oxide fuel cells

ABSTRACT

$BaCO_3$ nanoparticles are demonstrated as outstanding electrocatalysts to enhance the high temperature oxygen reduction reaction (ORR) in solid oxide fuel cells (SOFCs). $BaCO_3$ nanoparticles are formed from thermal decomposition of barium acetate, $Ba(Ac)_2$ infiltrated to porous cathode skeleton and shows good chemical compatibility with cathode materials. $BaCO_3$ nanoparticles can greatly reduce the area specific resistance (ASR) of typical SOFC cathode materials, including $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ (LSF), $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM). For example at 700 °C, ASR for LSF on yttria-stabilized zirconia (YSZ) electrolyte decreases from 2.95 Ω cm^2 to 0.77 Ω cm^2 when 12.9 wt.% $BaCO_3$ nanoparticles are deposited on the surface of the porous LSF electrode. Impedance spectra analysis shows that the decrease in ASR mainly comes from the reduction of the low frequency resistance. Furthermore, $BaCO_3$ nanoparticles are found to greatly enhance the oxygen chemical exchange coefficient. Most importantly, it has been found that the catalytic activity of $BaCO_3$ nanoparticles is even higher than those of the precious metals such as Pd, Rh, Pt and Ag, infiltrated into LSF, LSCF and LSM electrodes supported on YSZ electrolytes.

1. Introduction

Oxygen reduction reaction (ORR) is critical in various electrochemical applications such as sensors, catalytic converters, oxygen separation membranes, metal–air batteries, solid oxide fuel cells (SOFCs), and solid oxide electrolysis cells [1–3]. The ORR has long been an active research topic, particularly in material investigation to improve the catalytic activities. Historically, precious metals such as Ag [4], Pt [5], and Pd [6] have been extensively investigated as the catalytic materials, which have demonstrated very good catalytic properties for ORR. For example, oxygen reduction on yttria-stabilized zirconia (YSZ) has been accomplished for over 100 years using porous Ag and Pt [7]. However, cost has been a major concern for commercialization using the precious metal catalyst for ORR. In addition, the long-term stability of precious metal catalyst is also a significant concern in high temperature applications such as SOFCs. Therefore, transition-metal oxides have been developed as the ORR catalysts due to their good electronic/ionic conductivities and catalytic activity as a relatively low-cost alternative to Pt and Pd [8]. Typical oxides are perovskite materials, including $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) [9], $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ (LSF) [10], and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [11] which have been widely investigated to substitute the noble metals and have shown great potentials as the ORR catalysts in SOFC cathodes. Their catalytic activity still needs to be enhanced to lower the operational temperatures so that SOFC life could be extended and cost could be reduced [12]. Infiltrating noble metals to the perovskites is one effective way to enhance the ORR activity. The use of a small amount of Ag [13,14], Pt [15], Rh [16], and Pd [17–19] could greatly enhance the activity, i.e. reducing the cathodic interfacial polarization resistance. For example, at 850 °C, infiltrating only 0.08 mg cm^{-2} Pd to LSM electrode could result in an 8 fold decrease in the resistance [17].

$BaCO_3$ is a widely available and very cheap material that has not attracted any attention for ORR. Here we report the catalytic activity of $BaCO_3$ nanoparticles, which are formed from thermal decomposition of barium acetate, $Ba(Ac)_2$ infiltrated to the typical SOFC porous cathode. $BaCO_3$ is chemically compatible with typical SOFC cathode materials. $BaCO_3$ nanoparticles are found to greatly reduce the interfacial polarization resistance of LSM, LSF and LSCF electrodes which is mainly due to the reduction of low frequency resistance. $BaCO_3$ nanoparticles are also found to greatly enhance the oxygen chemical exchange coefficient of LSF and LSCF. Furthermore, $BaCO_3$ nanoparticles exhibit catalytic activity even higher than the precious metals.

2. Experimental section

2.1. Sample fabrication

$La_{0.8}Sr_{0.2}FeO_{3-\delta}$ (LSF), $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF), $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM), and $Zr_{0.85}Y_{0.15}O_{2-\delta}$ (YSZ) powders were synthesized by a glycine-nitrate process (GNP). Symmetrical cells were fabricated using

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http://dx.doi.org/10.1016/j.elecom.2014.12.017
1388-2481/

dense YSZ electrolyte substrates and porous LSF, LSCF, or LSM electrodes impregnated with different amount of barium acetate. YSZ substrates were prepared by uniaxially pressing YSZ powders followed by sintering at 1500 °C for 5 h to achieve a relative density of ~98%. LSF, LSCF, or LSM slurry was prepared by mixing the electrode powders with organics (α-terpineol as solvent and ethyl cellulose as the binder). The slurry was then printed onto both sides of the YSZ substrates. After drying under an infrared lamp, the sandwich fresh bodies were heated at 1000–1100 °C for 2 h to form symmetrical cells with porous electrodes. To obtain $BaCO_3$ nanoparticles on the surface of the electrode, $Ba(Ac)_2$ was dissolved in a mixture of water and ethanol (2:1 volume ratio) with Ba^{2+} concentration of 0.3 mol l^{-1}. The infiltration was carried out by placing a drop of the $Ba(Ac)_2$ solution on the top of the porous electrode, letting the solution soak into the porous structure, drying, and heating the sample at 800 °C in air for 1 h to form $BaCO_3$ particles by thermal decomposition of barium acetate. The sample mass before and after each infiltrating–drying–heating cycle was measured with an electronic balance (METTLER TOLEDO AB135-S) to determine $BaCO_3$ loading, which was expressed as the mass ratio of the impregnated material to the porous electrode. To conduct the electrical conductivity relaxation (ECR) measurement, the LSF and LSCF powders were ground, pressed into rectangular bars at 300 MPa, and sintered at 1450 °C for 5 h in air to form dense LSF and LSCF samples. The sintered LSF and LSCF bars had dimensions of $40.00 \times 5.42 \times 0.90$ mm^3. The sintered samples had a density in excess of 95% of the theoretical density and an average relative density of 97% as determined using the Archimedes method. Furthermore, $Ba(Ac)_2$ solution was dropped onto the sintered LSF and LSCF bar surfaces and then heated at 800 °C to form $BaCO_3$ nanoparticles on the surface.

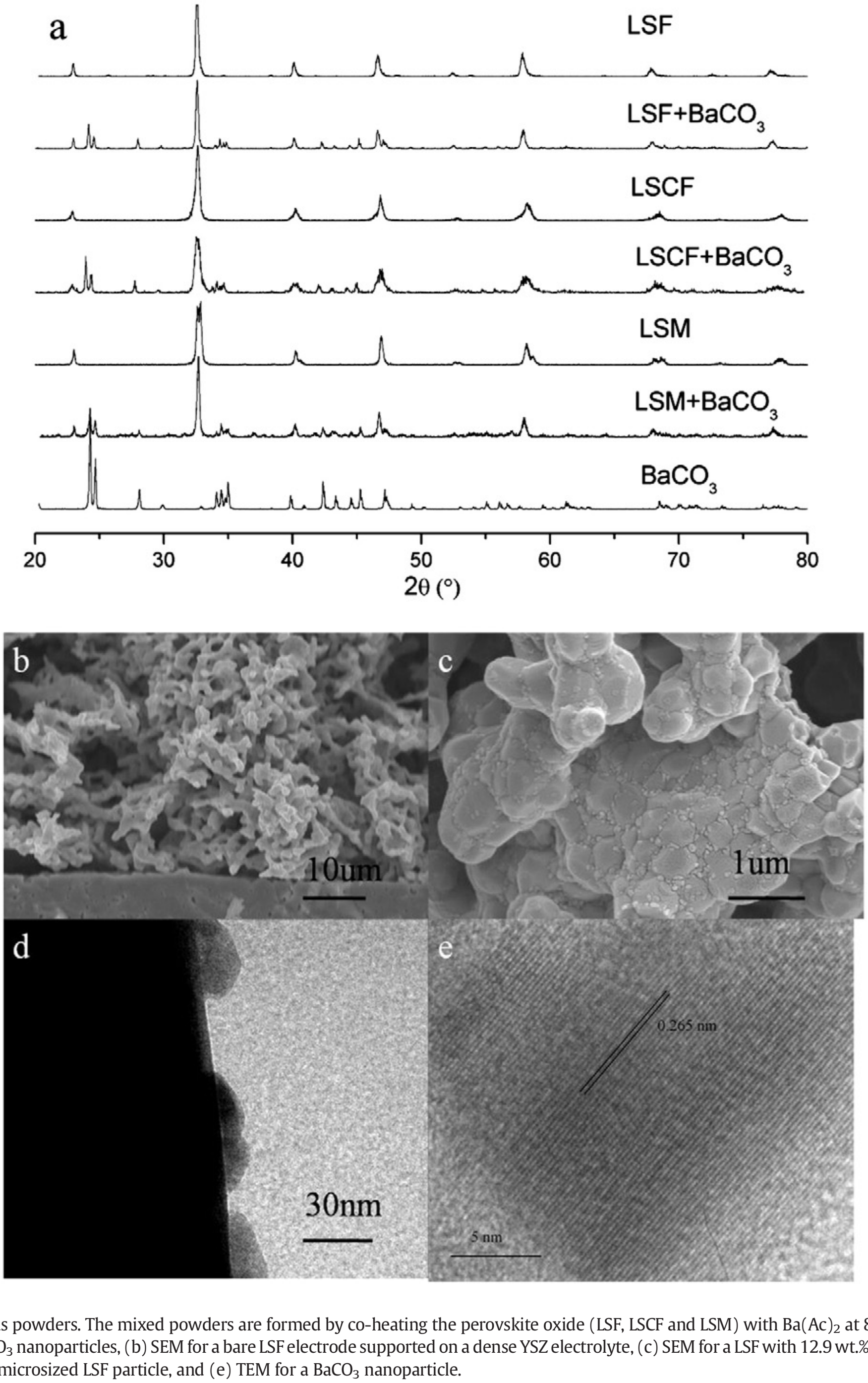

Fig. 1. (a) XRD patterns for various powders. The mixed powders are formed by co-heating the perovskite oxide (LSF, LSCF and LSM) with $Ba(Ac)_2$ at 800 °C for 1 h. And microstructure images for LSF electrodes and $BaCO_3$ nanoparticles, (b) SEM for a bare LSF electrode supported on a dense YSZ electrolyte, (c) SEM for a LSF with 12.9 wt.% $BaCO_3$ particles, (d) TEM showing 3 nanosized $BaCO_3$ particles on a microsized LSF particle, and (e) TEM for a $BaCO_3$ nanoparticle.