Sensors and Actuators B 203 (2014) 670–676

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Development of nanosized lanthanum strontium aluminum manganite as electrodes for potentiometric oxygen sensor

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ARTICLE INFO

Article history:
Received 13 May 2014
Received in revised form 4 July 2014
Accepted 8 July 2014
Available online 18 July 2014

Keywords:
Electrochemical sensor
Oxygen
Potentiometric
YSZ
LSM
High temperature

ABSTRACT

Nanocrystalline $La_{0.8}Sr_{0.2}Al_{0.9}Mn_{0.1}O_3$ (LSAM) was synthesized by a microwave-assisted citrate method, and characterized by electron microscopy and X-ray diffraction. Electrical behavior of LSAM was investigated by impedance spectroscopy and activation energy of conduction was obtained. Joining of sintered bodies of LSAM and yttria-stabilized tetragonal zirconia polycrystals (YTZP), an extensively studied oxygen ion conducting electrolyte, was examined by isostatic hot pressing methods. Characteristics of the joining region were evaluated with microprobe Raman spectroscopy, and products formed at the interface, primarily strontium zirconate, was confirmed by examination of high temperature chemical reaction between LSAM and YTZP powders. The electrical properties of the LSAM were exploited for development of a high temperature oxygen sensor in which LSAM functioned as the electrode and YTZP as electrolyte.

1. Introduction

Yttria-stabilized zirconia (YSZ), because of its oxygen-ion conducting property is used as an electrolyte for oxygen sensors and solid oxide fuel cell (SOFC) applications. Platinum is typically used as an electrode material for oxygen sensors. However, for SOFC, there are a variety of electrodes that are being studied. Amongst these, lanthanum strontium manganite $La_{1-x}Sr_xMnO_3$ (LSM, $x = 0.1$–0.3 most commonly), an ABO_3 perovskite, is frequently used as a cathode because of its oxygen reduction characteristics and high electronic conductivity at fuel cell operating temperatures (600–1000 °C) [1,2]. The triple point boundaries (TPB) between YSZ, LSM and oxygen are active sites for oxygen reduction, much like Pt, YSZ, and oxygen TPB for oxygen sensors. A significant hurdle with the use of LSM is its reaction with YSZ to form insulating pyrochlores lanthanum zirconate ($La_2Zr_2O_7$) and strontium zirconate ($SrZrO_3$). In order to reduce formation of an insulating interlayer between LSM and YSZ [3–7], previous studies have doped out varying amounts of the B site Mn in LSM for Al, $La_xSr_{1-x}Al_yMn_{1-y}O_{3-\delta}$ [6–8].

Another potential use of electroceramic materials is in the area of oxygen sensors [9]. We have reported earlier on use of lanthanum strontium iron cobalt oxide as an electrode for an oxygen sensor [10]. Use of composite lanthanum strontium manganite and YSZ as an oxygen sensor electrode resulted in internally reference sensors stable over a period of 6600 h [11]. Other internally referenced sensors have also been fabricated, by Kaneko [12], van Setten [13] and Zhuiykov [14]. We have also reported on an oxygen sensor, in which the reference cavity was formed by joining of two YSZ pieces by grain boundary sliding [15]. In all of these designs, some sort of a glass frit is used to seal the cavity, e.g. in our design the internal reference electrode (typically Pt) breached the YSZ joints, and this cavity was sealed with a glass seal. Such glass seals soften at around 800 °C, and limit the use of such devices to temperatures below this limit. An electroceramic material that can act as an internal reference electrode and at the same time form a hermetic seal with an electrolyte like YSZ will make possible design of air-reference free oxygen sensors that can operate at temperatures >800 °C.

In this study, we focus on synthesis of nanometer-sized aluminum-doped $La_{0.8}Sr_{0.2}Al_{0.9}Mn_{0.1}O_3$ (LSAM) using a microwave-assisted hydrothermal method. Prado-Gonjal [16] used this method to produce nanoparticles of several lanthanum based perovskites, including $LaAlO_3$, $LaMnO_3$, and $La_{0.8}Sr_{0.2}FeO_3$. Lanthanum manganites incorporating Sr and Gd were also synthesized by microwave methods [17,18]. These methods are very

Abbreviations: LSAM, $La_{0.8}Sr_{0.2}Al_{0.9}Mn_{0.1}O_3$.

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http://dx.doi.org/10.1016/j.snb.2014.07.027
0925-4005/

similar to the Pechini synthesis, also used to make lanthanum based perovskite nanoparticles for sensing applications [19], however the hydrothermal step occurs in a microwave. We examine the electrical and mechanical properties of nanoparticulate LSAM. The nanosize of LSAM should influence its joining with other electroceramics and is examined. There have been two previous studies on high pressure joining of micron-sized LSAM to yttria stabilized tetragonal zirconia polycrystals (YTZP), a form of YSZ. Spirig et al. reported that the joint was produced by grain boundary sliding, and found no spectroscopic evidence for any product at the joint surface. Pappacena et al. examined a different LSAM composition ($La_{0.8}Sr_{0.2}Al_{0.5}Mn_{0.5}O_3$), but still micron-sized, and reported a strong joint with YTZP, but noted that an intermediate Sr containing layer was cementing the joint. We follow the high pressure and temperature bonding between nanoparticulate LSAM and YTZP by microprobe Raman spectroscopy. LSAM was bonded to YTZP by isostatic hot pressing methods and its properties as an electrode for an oxygen sensor is examined, a concept previously proposed but not yet reduced to practice [6,7].

2. Materials and methods

2.1. Synthesis, physical, and electrical characterization

$La_{0.8}Sr_{0.2}Al_{0.9}Mn_{0.1}O_3$ was prepared by a microwave-assisted hydrothermal method. Nitrate salts of lanthanum $La(NO_3)_3{\cdot}6H_2O$ (Alfa Aesar), strontium $Sr(NO_3)_2$ (Alfa Aesar), aluminum $Al(NO_3)_3{\cdot}9H_2O$ (Aldrich), and manganese $Mn(NO_3)_2{\cdot}xH_2O$, x = approximately 4 (Alfa Aesar) were combined in the stoichiometric ratio 0.8:0.2:0.9:0.1 respectively. To an aqueous solution of these salts was added citric acid monohydrate (Fischer Scientific) in equimolar ratio to the sum of all metal salts. The pH of the solution was then buffered at pH 9.0–9.1 using ammonium hydroxide (Certified A.C.S. Plus, Fischer Scientific).

The synthesis was carried out in a CEM Mars 5 microwave reactor with HP500 Plus reaction chambers. The microwave was set to 200 °C and then dwelled for 6 h. The slurry was then heated in air (95 °C) then under vacuum (100 °C) to remove excess water. The resultant hard brittle solid was ground in a mortar and pestle, ball milled, and calcined in air at 650 °C for 2 h. The resultant low density solid was then ground in a mortar and pestle to a fine powder and pressed into pellets.

SEM micrographs were obtained on a Philips XL-30 ESEM. Samples were prepared by cutting a cross section, grinding with 240, 320, 480, and 600 grit, and then polishing down to 1 μm polish. The cross section was then thermally etched in air at 1200 °C for 3 h to reveal the grains. TEM micrographs were obtained on a Tecnai F20 transmission electron microscope on a lacy carbon grid. XRD was performed on a Rigaku Geigerflex diffractometer using monochromated Cu Kα (λ = 1.5405 Å) radiation and 2 mm, 1 mm, 3 mm slits.

Impedance experiments were performed on a Solartron 1260 impedance/gain-phase analyzer impedance measurement system inside a Lindburg Blue tube furnace. Experiments were performed between 100 and 300 mV AC under varying temperatures (500–800 °C) in air and nitrogen. The applied frequency was 0.1–10^7 Hz. No DC voltage was applied. Samples were prepared in a pellet press using a bar mold. Samples were sintered at 1500 °C for 50 h.

The Arrhenius equation (1) was used to determine activation energy of a process where A is an exponential factor, T is the temperature, R is the ideal gas constant, and E_a is the activation energy.

$$\ln(\sigma_e T) = A + \frac{-E_a}{RT} \quad (1)$$

2.2. Chemical reactivity of $La_{0.8}Sr_{0.2}Al_{0.9}Mn_{0.1}O_3$ and YSZ

YSZ powder (TOSOH) was thermally treated for 14 h at 1300 °C. Equimolar quantities of YTZP and LSAM powder were combined and ball milled. The resultant powder was formed into a pellet in a 1.3 cm die and pressed under 3000 kg for 20 min. The pellet was sintered at 1300 °C for 3 h in Ar using the same heating profile used during joint fabrication. The pellet was then crushed and ball milled. The final sintered powder was examined by XRD.

2.3. Joining of $La_{0.8}Sr_{0.2}Al_{0.9}Mn_{0.1}O_3$ and YTZP

The YTZP for the joint was made with pellets made from nanoparticles of YTZP 3% from Tosoh (Japan). The LSAM was pellet pressed and then densified for 50 h at 1500 °C in air. Both sides of each pellet were coarse ground to a 600 grit polishing paper. One side of each was then polished down to a 1 μm polish. The two pellets were loaded into an Instron Universal Testing Machine with the mirror polished sides facing and protected above and below by graphite foil. The chamber was evacuated and flushed with argon gas three times and then maintained in an Ar atmosphere. A load of 50 N was applied while the chamber was heated to temperature (1250–1350 °C) to ensure maintained load on the sample. After dwelling at temperature for at least 45 min a steady state strain rate of 1.5–4.5 × 10^{-5} mm/mm was applied to the samples. For sensor fabrication, samples were also joined by a steady state stress method, where stress was ramped linearly (0.5 MPa/h) to a final stress and then relieved.

2.4. Raman spectroscopy

Raman spectroscopy was performed with a Renishaw Raman Microprobe using a 514 nm laser wavelength. Reference spectra were obtained on powders and mapping experiments were performed on a polished cross section of a joined sample. Mapping experiments were performed with a 100× objective over a 30 μm × 6 μm area using 1 μm steps in both the "x" and "y" directions. The long edge of the Raman mapping ran perpendicular to the sample interface.

2.5. Sensor fabrication and sensing experiments

A pellet of LSAM sintered at 1500 °C for 50 h was joined to a pellet of sintered commercial YTZP by the methods described above. Porous platinum electrodes were then attached with platinum ink and wires to the center of the top and bottom of the joined samples. The joined sample was then mounted onto the end of a quartz tube with Ceramabond 552 alumina paste (Aremco). The pores of the alumina paste were filled with Ceramabond 617 glass sealant paint (Aremco). Pt lead wires were run along the inside of the quartz tube to the platinum electrode and a lead wire was connected to the LSAM electrode on the outside of the tube. Oxygen sensing experiments were performed in a Lindburg Blue tube furnace Type TF55035A with an Agilent LXI data acquisition/switch unit and in house LabVIEW software and Sierra mass flow controllers for mixing gases. Sample gas mixtures (1–21% O_2 breathing air mixed with 4.8 N_2) were flowed at 100 sccm outside of the quartz tube in the tube furnace chamber. The interior of the quartz tube was left open to lab air as a reference.

3. Results

3.1. Synthesis of nanoparticulate LSAM

Nitrates of lanthanum, strontium, aluminum, and manganese were dissolved in distilled water with molar ratio of