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New anode materials for IT-SOFC derived from the electrolyte $BaIn_{0.3}Ti_{0.7}O_{2.85}$ by lanthanum and manganese doping

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ABSTRACT

New perovskite oxides, Ba0.5La0.5Ti0.3Mn0.7O3 (BLTM) and Ba0.5La0.5In0.3Ti0.1Mn0.6O3 (BLITIM), were investigated as new anode materials that are compatible with BIT07 electrolyte. At 700 °C under air, BLTM and BLITIM exhibit a total conductivity of 13.4 and 11.7 $S \cdot cm^{-1}$ correspondingly. Under reducing atmosphere, total conductivity decreases to 0.3 and 0.6 $S \cdot cm^{-1}$ respectively. Anode-supported symmetrical cells Ni-BLTM/BIT07 and Ni-BLITIM/BIT07 were prepared by tape casting and co-sintering. An anode area specific resistance of 0.11 Ω cm2 at 700 °C was reached for an initial NiO content (40 wt.%) which is much lower than that used in Ni/BIT07 cermets (50% wt.%).

1. Introduction

In the last years, solid oxide fuel cells (SOFCs) withdraw intense research and development efforts due to the benefit of getting a clean electrical power by the conversion of chemical energy into electrical energy. Reducing the usual operating temperature from 1000 °C to 500–600 °C presents one of the main challenges to expect near a commercialization of this technology and is essential to reduce the cost to be competitive with the other alternatives available today. However, the reduction of operating temperature is followed by a decrease of electrochemical performance of each material constituting the fuel cell.

$BaIn_{0.3}Ti_{0.7}O_{2.85}$ (BIT07) electrolyte exhibits an ionic conductivity of 10^{-2} $S \cdot cm^{-1}$ at 700 °C and can be considered as a potential electrolyte material for intermediate temperature solid oxide fuel cells (IT-SOFCs) [1,2]. Currently, the most widely used anodes are cermets (ceramic-metal) composed of nickel (Ni) which is an excellent catalyst for hydrogen oxidation, and a ceramic material often similar to the electrolyte used in the cell.

Tape casting was widely used to fabricate electronic devices [2–5] and is also an attractive process to obtain planar anode supporting SOFCs because of the low cost for mass production [6–8]. Anode supported half-cell electrolyte/anode, BIT07-Ni/BIT07, has been prepared by tape casting and complete cells have been also realized and tested, with power densities of 336 $mW \cdot cm^{-2}$ at 0.7 V [9]. Improvements must therefore be done in order to reduce the overall cell resistance and increase the performances in terms of power density. In this work, we focus on anode by developing alternative materials derived from BIT07.

Recently, mixed ionic electronic conductor (MIEC) anode materials have received great attention [10–14]. New MIEC anode material was obtained from BIT07 by substitution of Ba by La (La → Ba) and In by Mn (Mn → In) to get $Ba_{0.5}La_{0.5}Ti_{0.3}Mn_{0.7}O_{3+}$ (BLTM). $Ba_{0.5}La_{0.5}In_{0.3}Ti_{0.1}Mn_{0.6}O_{3-\delta}$ (BLITIM) has been also synthesized by co-substitution of La → Ba & Mn → Ti and studied as potential MIEC anode materials in terms of chemical expansion and stability, as well as electrical performances.

Moreover, symmetrical cells based on BIT07 electrolyte and Ni-BLTM or Ni-BLITIM cermet anodes were prepared using a tape casting process. Their microstructure and electrochemical properties were also investigated.

2. Experimental

2.1. Powders

$Ba_{0.5}La_{0.5}Ti_{0.3}Mn_{0.7}O_{3-\delta}$ (BLTM) was synthesized by a solid state reaction by using stoichiometric amounts of $BaCO_3$, La_2O_3, TiO_2 and MnO_2. Reactants were thoroughly mixed using acetone in agate mortar and calcined at 1350 °C for 24 h. The obtained powder was again ground well, mixed, pressed into pellets and sintered at 1350 °C for 24 h. $Ba_{0.5}$

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Table 1
Specific surface areas of compounds after synthesis and ball milling.

Compound	Specific surface area (m^2/g)	
	Sieved with mesh size of 100 μm	Ball milling for 60 h at 500 tr·min^{-1}
BIT07	1.51 ± 0.05	18.23 ± 0.07
BLTM	1.06 ± 0.05	13.66 ± 0.07
BLITIM	1.83 ± 0.09	12.95 ± 0.10

$La_{0.5}In_{0.3}Ti_{0.1}Mn_{0.6}O_{3-\delta}$ (BLITIM) compound was prepared according to the same protocol. In_2O_3 was used as a precursor of indium.

2.2. Physicochemical characterization

X-ray powder diffraction (XRPD) data were collected at room temperature (RT) using a Brüker D8 Advance diffractometer working in Bragg–Brentano reflection geometry with a Cu anode X-ray source, a focusing Ge(111) primary monochromator (selecting the Cu $K\alpha_1$ radiation) and a 1-D position-sensitive detector ("Vantec" detector). Data were collected in the range $2\theta = 20$–$90°$, with a 0.02° step and a 10 s counting time per step. The FULLPROF program [15] was used for cell parameter refinements.

High-temperature X-ray powder diffraction (HT-XRPD) patterns were collected using a D8 Bruker diffractometer equipped with an Anton Paar HTK1200N furnace and a Vantec1 linear detector, with the Cu K_α radiation ($\lambda = 1.54056$ Å) and 2θ varying from 20 to 90° by steps of 0.0146° and 0.4 s counting time per step. Each pattern was collected in 30 min. Measurements were carried out between RT and 800 °C, each at 50 °C, under wet air, and dry and wet H_2 flow on heating and cooling with a rate of 0.2 °C s^{-1} between each temperature step. For each temperature, the measurements were performed for 2 to 6 h to reach thermodynamic equilibrium (4 to 12 XRPD patterns per temperature, respectively). Gas humidification was performed by passing the gasses through water at room temperatures.

Thermal expansion coefficient (TEC) was inferred from XRPD patterns recorded from room temperature up to 800 °C.

TGA measurements were carried on ~100 mg of powder using a Netzsch STA 449F3 Jupiter. Wet hydrogen was obtained by passing the gas through a glass tube containing distilled water at 20 °C.

The microstructure of the compounds and the quality of the different interfaces have been observed by scanning electron spectroscopy (SEM) performed on a JEOL 7600 apparatus equipped with an X-ray analyzer for energy-dispersive X-ray spectroscopy (EDX).

Table 2
Unit cell parameters of BLTM and BLITIM at room temperature.

Compound	Space group	Cell parameters	χ^2	R_{wp}
BLTM	$Pm\bar{3}m$	a = 3.940(3) Å	1.30	7.5
BLITiMn	*P4/mmm*	a = 3.983(3) Å c = 3.981(7) Å	1.34	8.5

2.3. BLTM-Ni//BIT07 and BLITIM-Ni//BIT07 symmetrical cell manufacturing

The anode and the electrolyte were prepared by tape casting. First, the electrolyte slurry is prepared by mixing the ball milled BIT07 powder, a dispersant (oleic acid) and an azeotropic mixture of solvents (ethanol and methyl ethyl ketone) in a 45 ml silicon nitride pot with 12 silicon nitride balls at 240 rpm for 1 h. Polyvinyl butyral (PVB-90 and PVB-98) used as binders and plasticizers (Polyethylene glycol PEG-400 and dibutyl phthalate) was added to the former preparation and ball-milled for 24 h at 180 rpm [16].

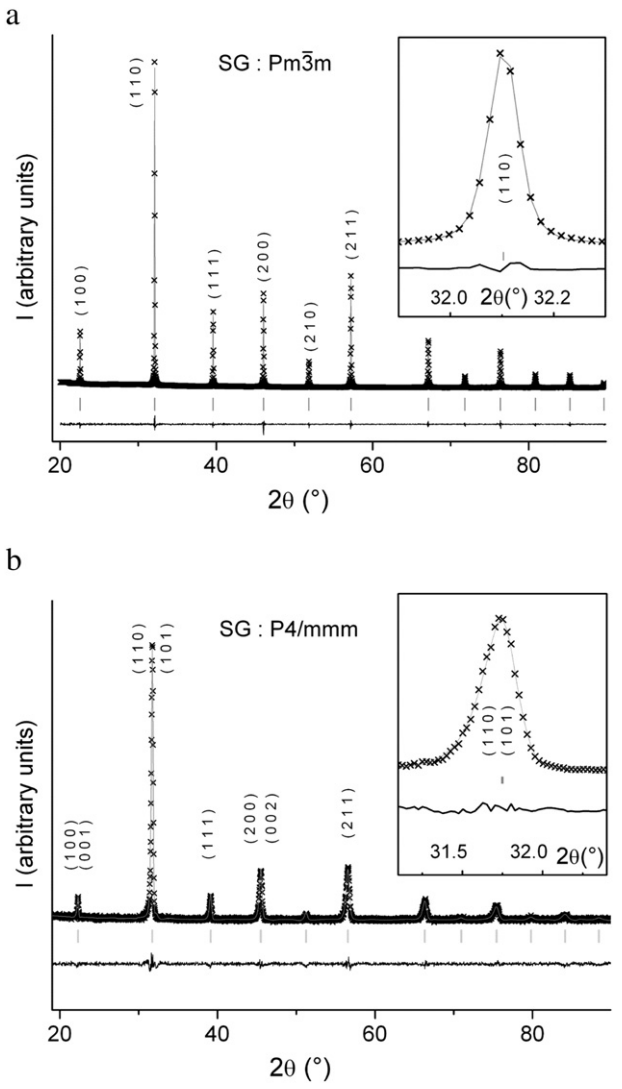

Fig. 1. XRD patterns of a) $Ba_{0.5}La_{0.5}Ti_{0.3}Mn_{0.7}O_{3+\delta}$ and b) $Ba_{0.5}La_{0.5}In_{0.3}Ti_{0.1}Mn_{0.6}O_{3-\delta}$ under air at RT.

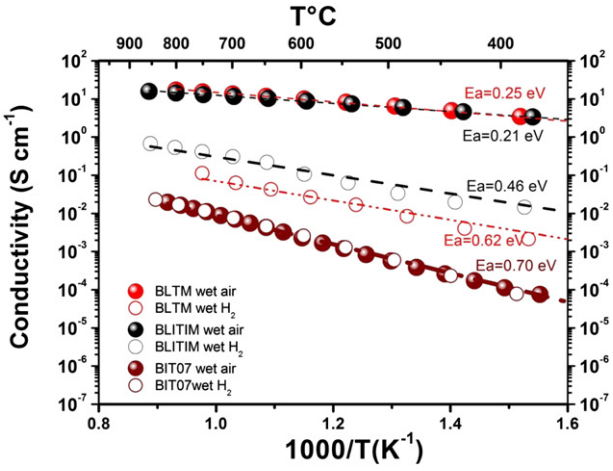

Fig. 2. DC conductivity vs. temperature for $Ba_{0.5}La_{0.5}Ti_{0.3}Mn_{0.7}O_{3+\delta}$ under air (red close circle) and under wet ($P_{H2O} = 0.025$ atm) 5%H_2/95%Ar atmosphere (open red circle) like for $Ba_{0.5}La_{0.5}In_{0.3}Ti_{0.1}Mn_{0.6}O_{3-\delta}$ under air (black close circle) and under wet reducing atmosphere (open red circle).