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Development of new anodes compatible with the solid oxide fuel cell electrolyte $BaIn_{0.3}Ti_{0.7}O_{2.85}$

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ABSTRACT

A new family of MIEC compounds resulting from the electrolyte $BaIn_{0.3}Ti_{0.7}O_{2.85}$ (BIT07) was developed by coupled substitution of titanium by iron and barium by lanthanum. Total conductivity increases significantly with iron and lanthanum content. $BaIn_{0.3}Ti_{0.7}O_{2.85}$ yields a total conductivity in air of 10^{-2} S cm^{-1} at 700 °C whereas that of $Ba_{0.7}La_{0.3}In_{0.3}Ti_{0.1}Fe_{0.6}O_{3-\delta}$ (BLITFe06) is 3 S cm^{-1}. Doped compounds are p-type conductors. In reducing atmosphere the electrical conductivity decreases drastically to $\sigma = 2 \times 10^{-2}$ S cm^{-1} for the best value, which is not sufficient for a use as MIEC anode. Nevertheless, Ni/BLITFe06 cermets seem to be good candidates as SOFC anodes. The total conductivity of Ni/BLITFe cermets is higher than that of 18.7 vol.% Ni/BIT07 ($\sigma_{700\,°C} \approx 10^2$ S cm^{-1}), even for a lower Ni content (16.1 vol.% Ni/BLITFe $\sigma_{700\,°C} \approx 200$ S cm^{-1}). The percolation threshold moves towards the small quantities of nickel (from 15.7 vol.% to 10 vol.%). Ni/BLITFe06 cermets, compared with Ni/BIT07, show a better electrochemical behaviour towards fuel oxidation.

1. Introduction

The development of new electrolyte materials with improved properties is essential to the future of intermediate temperature solid oxide fuel cells (IT-SOFCs) technology. Several electrolytes have been described as finding practical application in SOFCs: ZrO_2-, CeO_2-, $LaGaO_3$-, and $La_{10}Si_6O_{27}$-based [1,2]. Jayaraman et al. [3] reported a new family of anionic conductors $Ba_2In_{2(1-x)}Ti_{2x}O_{5+x}\square_{1-x}$ with $0 \le x \le 0.7$ (called BITx) which can be also considered as potential electrolytes for SOFC, mainly the phase $BaIn_{0.3}Ti_{0.7}O_{2.85}$ (BIT07).

In order to design anodes chemically and mechanically compatible with BIT07 electrolytes, Ni/BIT07 cermets were prepared and characterized [4]. Authors obtained a cermet containing only 18.7 vol.% of nickel with an open porosity of 40%. Its electronic conductivity ($\sigma_{700\,°C} \approx 10^2$ S cm^{-1}) is higher than that of Ni/YSZ cermets with a larger nickel content and the thermal expansion coefficient measured, 11.4×10^{-6} K^{-1}, is close to that of the electrolyte compound BIT07 (9.9×10^{-6} K^{-1}). The Ni/BIT07 cermet was used as anode in single-cells based on BIT07 electrolyte and using $La_{0.8}Sr_{0.2}MnO_3$ as cathode [5]. The value of P_{max} at 690 °C under dry hydrogen was found to be 100 mW cm^{-2} whereas that under dry natural gas was 8 mW cm^{-2}. Indeed, Ni-based anodes are usually unstable in the presence of hydrocarbons because Ni catalyzes the formation of coke unless large amounts of steam are also present. High currents and low concentration (4–9%) of dry CH_4 can also prevent coke build-up for operating temperatures less than 700 °C.

Since oxides catalyze less cracking, anodes based exclusively on ceramic mixed ionic–electronic conductors (MIECs) have been extensively studied in the literature [6–9]. However, it proved to be difficult to obtain good electronic conductivity and good catalytic activity, in the same ceramic material, even if promising properties were reported for some perovskite like $La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$ ($x = 0.2$–0.3; $y \le 0.5$) and $Sr_2MoMg_{1-x}Mn_xO_{6-\delta}$ [6–9]. However, the most crucial factor for these materials is a relatively low electronic conduction leading to electronic transport limitations.

On the other hand, Hamakawa et al. [10] described a Ni-based catalyst composed of a MIEC support oxide which induces a self anti-coking phenomenon during methane conversion. In fact, the self-migration of lattice oxygen inside the support like the balance between the oxide ionic and electronic conductivities, play an important role to prevent accumulation of deposited carbon over the catalysts. Consequently, another way to prepare anodes resistant to coke while preserving Ni, which exhibits excellent electrocatalytic properties, could be to use a MIEC as component of the anode, i.e. a Ni–MIEC cermet. A potential way to improve the stability of the Ni/BIT07 cermets under dry natural gas possibly will be to induce electronic conductivity into BIT07 compounds. In this work a new family of MIEC compounds derivate from BIT07 by substitution of Ti by Fe (Fe → Ti) $BaIn_{0.3}Ti_{0.7-y}Fe_yO_{3-\delta}$

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(BITFey) has been synthesized and characterized. La-derivate compounds $Ba_{1-z}La_zIn_{0.3}Ti_{0.7-y}Fe_yO_{3-\delta}$ (BLITFey) were also prepared and studied. Finally, Ni/MIEC cermets based on BLITFe phases were elaborated and investigated as potential anode material.

2. Experimental

$BaIn_{0.3}Ti_{0.7-y}Fe_yO_{3-\delta}$ (BITFey) compounds were synthesized by solid state reaction of $BaCO_3$, In_2O_3, TiO_2 and Fe_2O_3. Reactants were mixed in stoichiometric proportions, ground thoroughly in acetone and calcinated at 1200 °C for 24 h. Powders thus obtained were ground, passed through the 100 mesh sieve and uniaxially pressed into disks. Finally the samples were sintered in air at 1350 °C for 24 h. $Ba_{1-z}La_zIn_{0.3}Ti_{0.7-y}Fe_yO_{3-\delta}$ (BLITFey) compounds were prepared according to the same protocol as BITFey. La_2O_3 was used as precursor of lanthanum.

Ni/BLITFe06 cermets were elaborated from powders of as prepared $Ba_{0.7}La_{0.3}In_{0.3}Ti_{0.1}Fe_{0.6}O_{3-\delta}$ (grain size 100 μm) and NiO (grain size 0.5–1 μm) mixed in different BLITFe06/NiO weight ratios: 75/25, 70/30, 60/40. Both mixtures were introduced with twenty glass balls (Ø 5 mm) into a 30 mL glass vessel and then placed on a roller bank for 2 h at 30 rpm. Samples of the resulting $Ba_{0.7}La_{0.3}In_{0.3}Ti_{0.1}Fe_{0.6}O_{3-\delta}$/NiO mixture were pressed to obtain pellets of Ø 10 mm (thickness 2 mm) that were heated at 1200 °C for 6 h in order to get a porous matrix, while minimizing shrinkage.

A multilayer tape casting and co-sintering processes were used for fabricating Ni/BIT07//BIT07//Ni/BIT07 and Ni/BLITFe06//BIT07//Ni/BLITFe06 symmetrical cells. The slurries for tape casting process were prepared by a ball milling process including two steps. In the first step, ceramic powders of BIT07 and of cermets were milled in a planetary mill for 1 h using zirconia balls as milling medium with ethanol and 2-butanone as the solvents, and oleic acid as dispersant. Secondly, polyvinyl butyral (PVB) and polyethylene glycol (PEG) used as binder and plasticizer, respectively, were added, then milled for another 24 h. Before tape casting, the slurries were deaerated for 24 h using a roller bank.

The cermet film was cast first onto the glass plate by a "doctor blade" method and dried in air for several minutes; then BIT07 electrolyte and cathode substrate were cast on top of the tape. After drying overnight at room temperature, the multilayer tape was detached, waiting for co-sintering. The multilayer tape was co-sintered at 1300 °C during 6 h and circular symmetrical cells (diameter 10–13 mm) were cut.

X-ray powder diffraction (XRD) patterns of all materials were recorded using a Brüker "D8 Advance" powder diffractometer operated in Bragg–Brentano reflection geometry with a Cu anode X-ray source, a focusing Ge(1 1 1) primary monochromator (selecting the Cu $K\alpha_1$ radiation) and a 1-D position-sensitive detector ("Vantec" detector). Refinements of cell parameters were carried out using the program FULLPROF [11]. Thermal expansion coefficient (TEC) was inferred from X-ray diffraction patterns recorded from room temperature up to 1000 °C.

The temperature-programmed reduction (TPR) studies were performed in a chemisorption unit Micromeritics AutoChem 2910 using powdered samples of 100 mg. Before reaction, samples were treated with helium at 300 °C for 10 min and cooled to room temperature. The TPR experiments were carried out under a 5.1% H_2/Ar mixture flowed through the sample at 50 mL min^{-1}, raising the temperature at 10 °C min^{-1} up to 850 °C. The consumption of hydrogen was monitored on-line with a thermal conductivity detector.

Transmission electron microscopy (TEM) study was carried out with a Hitachi H9000NAR electron microscope, operating at 300 kV equipped with an energy dispersive X-ray (EDX) analyzer. The compounds were gently ground in ethanol and microcrystals were deposited on a holed carbon film supported by a copper grid.

^{57}Fe Mössbauer spectra were recorded in transmission geometry with a constant acceleration spectrometer using a room temperature ^{57}Co(Rh) source. α-Fe foil was used at 300 K as standard to calibrate velocity and isomer shift. Powdered samples were studied at 300 K and 77 K using a cryostat. The spectra were computed with a least squares routine using quadrupolar components based on lorentzian lines.

The standard DC four-probe method was used to measure the electrical conductivity in air and under reducing atmosphere (95% Ar/5% H_2) between 300 °C and 800 °C. Sintered pellets densified to over 95% of theoretical density were cut to rectangular-shaped samples with dimensions 2 mm × 2 mm × 10 mm and subjected directly to electrical conductivity measurements.

Symmetrical cells were studied by electrochemical impedance spectroscopy (EIS). The measurements were carried out using a frequency response analyzer Solartron 1260. The impedance spectra were recorded over a frequency range 2 MHz to 0.01 Hz with signal amplitude of 50 mV and with 10 points per decade under open circuit conditions. A stabilisation time of one hour was considered between each temperature change.

3. Results and discussion

3.1. The iron substituted BIT07 compounds: $BaIn_{0.3}Ti_{0.7-y}Fe_yO_{3-\delta}$

The XRD patterns of $BaIn_{0.3}Ti_{0.7-y}Fe_yO_{3-\delta}$ (BITFey) compounds prepared as described in the experimental section are shown in Fig. 1(a). Single phase compounds were obtained in the composition range $0 \leq y \leq 0.4$. They exhibit a cubic perovskite structure which can be described in space group P*m*-3*m*. The cell parameter *a* increases weakly with increasing Fe content as illustrated in Fig. 1(b).

For $y \geq 0.5$, even if no extra peaks corresponding to secondary phases were observed in XRD patterns, the full width at half maximum (FWHM) of the diffraction peaks (e.g. see Fig. 1(b) for the (1 1 0) reflection ($2\theta \approx 31°$)) is much larger. This feature indicates a structural distortion or a biphased compound.

In order to go further in the characterization of this specific aspect, a TEM study of $BaIn_{0.3}Ti_{0.1}Fe_{0.6}O_{3-\delta}$ was performed. No secondary phase was detected. The reciprocal lattice of this compound was studied by selected area electron diffraction (SAED). No sign of amorphisation was detected. Main reflections could be indexed in the space group P*m*-3*m* (see Fig. 2(a) and (b)). However, for some zone axes (i.e. [1 1 5] in Fig. 2(c)), a phenomenon of diffuse scattering is observed, which could be due to a short range order of oxygen vacancies and/or B-site cations. Moreover, in some crystals forbidden reflections in P*m*-3*m* S.G. are observed, even if they are very diffuse, indicating a lowering of symmetry. Nevertheless, it should be noted that the stacking of the layers remains very regular, as evidenced from the [1 1 0] high resolution image illustrated in Fig. 2(d).

As will be discussed below, a mixed-valence Fe(III/IV) state occurs in these materials at room temperature, thus the aliovalent substitution of Ti(IV) by Fe(III/IV) implies the formation of charge-compensating oxygen vacancies which number increases with the iron content. For $y \geq 0.5$, the oxygen vacancies content becomes high enough to destabilize the cubic perovskite structure. This feature is translated into the XRD pattern by a broadening of the diffraction peaks.

To stabilize the cubic structure for high iron rates the substitution of Ti by Fe was coupled to that of Ba by La (La → Ba). This double substitution is expected to limit the number of charge-compensating oxygen vacancies formed during reaction and obtain a better mismatch between AO and BO_2 layers