INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–6

Available online at www.sciencedirect.com

ScienceDirect

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

Electrical conductivity of NiMo–based double perovskites under SOFC anodic conditions

Sabrina Presto [a,1], *Pravin Kumar* [b,1], *Salil Varma* [c], *Massimo Viviani* [a,*], *Prabhakar Singh* [b,**]

[a] CNR-ICMATE, c/o DICCA-UNIGE, Via all'Opera Pia 15, 16145 Genova, Italy
[b] Department of Physics, Indian Institute of Technology (Banaras Hindu University), Varanasi, 221005, India
[c] Chemistry Division, Mod. Labs., Bhabha Atomic Research Centre, Trombay, Mumbai, 400085, India

ARTICLE INFO

Article history:
Received 15 November 2017
Received in revised form
9 January 2018
Accepted 13 January 2018
Available online xxx

Keywords:
Double perovskite
Reduction
Electrical conductivity
Anodic materials
SOFC

ABSTRACT

Three different materials are prepared by chemical reaction route, Sr_2NiMoO_6 (SNM00), $Sr_{1.96}La_{004}NiMoO_6$ (SLNM04) and $Sr_{1.99}Ce_{0.01}NiMoO_6$ (SCNM01) and conductivity is measured under reducing atmosphere, in order to study their suitability as anode materials in SOFC application. Selected materials correspond to compositions reported with highest conductivity in air at operative temperatures of a SOFC among the systems SLNM ($Sr_{2-x}La_xNiMoO_6$, $0.02 \leq x \leq 0.10$) and SCNM ($Sr_{2-x}Ce_xNiMoO_6$, $0.01 \leq x \leq 0.05$). The end member Sr_2NiMoO_6 (SNM) is also considered as reference.

Their conductivities considerably increase in wet hydrogen and follow Arrhenius behavior with lower activation energy. Effects of reduction on microstructure and phase stability are also studied by scanning electron microscopy and X–ray diffraction.

The enhancement in conductivity is discussed in terms of defects chemistry. Amongst all measured samples, SLNM04 shows the highest conductivity in reducing atmosphere without phase degradation, which makes it a promising anode material for Solid Oxide Fuel Cells (SOFC).

Introduction

Over the last few decades, various research groups are improving the performance of Solid Oxide Fuel Cells (SOFC) by enhancing the structural, mechanical, and electrical properties of the electrode materials also proposing double perovskite based systems [1]. In general, double perovskite systems are represented with basic formula units of A'A″B'B″O_6 (AB-site ordered), A'A″B_2O_6 (A-site ordered) and A_2B'B″O_6 (B-site ordered). However, there are more reports available about B-site ordered double perovskite systems as electrode materials for intermediate-temperature SOFC devices [2]. The particular, alternating arrangement of B′ and B″ cations in A_2B'B″O_6 can be of great interest from the electrical conductivity point of view [3]. Recently, many groups are exploring B-sites ordered double perovskite materials A_2B′B″O_6 (B′ = Fe, Co, Ni, Cr, Mg etc. and B″ = Mo, W, Nb, etc.) that exhibit interesting electrochemical properties and attractive technological applications [4–7]. Prior studies on Mo-based double perovskite

* *Corresponding author.*
** *Corresponding author.*
E-mail addresses: massimo.viviani@ge.icmate.cnr.it (M. Viviani), psingh.app@iitbhu.ac.in (P. Singh).
[1] Equally contributed to this paper.
https://doi.org/10.1016/j.ijhydene.2018.01.066

systems were found to improve the electrical conductivity in SOFC anodes [8–10]. Various factors play a key role on the properties of this system, such as doping, presence of additional phases, and gas phase composition.

The study of rare earth (La^{3+} or Sm^{3+}) doped Sr_2MgMoO_6 systems showed suitable electro-catalytic activity for better fuel oxidation and electrochemical performance [11,12]. In reducing atmosphere, phase impurity of $SrMoO_4$ in Sr_2MgMoO_6 was found to enhance the electrical conductivity due to reduction of $SrMoO_4$ into $SrMoO_3$. Further, $SrMoO_4$ impurity was found to stabilize the evaporation of Mo during high temperature synthesis process of Sr_2MgMoO_6 [13]. Consequently, electrical conductivity of Mo based double perovskite oxides was studied at a large scale in reducing atmosphere such as $Sr_2Mg_{1-x}Fe_xMoO_{6-\delta}$ ($x = 0.0–0.5$) [14], Sr_2MMoO_6 ($M = Co, Ni$) [5], $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ [15], Ni-doped $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ [16], $Sr_2MgMoO_{6-\delta}$ [17], and $Sr_2NiMoO_{6-\delta}$ [18]. In particular, Ni containing double perovskite oxides, Sr_2NiMoO_6 [5,18] offered excellent electrical conductivity and high catalytic activity leading to anode application for SOFC. $Sr_{2-x}Sm_xNiMoO_{6-\delta}$ ($0.01 \leq x \leq 0.05$) was investigated and proven to have mixed ionic electronic conductivity under reducing atmosphere [19]. Although Ni-based composites have excellent performance as SOFC anodes, they are severely affected by carbon surface deposition and sulfur poisoning. In order to obtain higher coking resistance and redox stability, nickel-free double perovskites were also studied [1,20]. In particular, $Sr_2FeNb_{0.2}Mo_{0.8}O_{6-\delta}$ showed satisfactory conductivity associated to a good coking resistance and redox stability.

$Sr_2FeCo_{0.5}Mo_{0.5}O_{6-\delta}$ double perovskite was investigated as potential anodic material for Symmetrical Solid Oxide Fuel Cells (SSFC) using hydrogen sulfide as a fuel directly, showing high catalytic activity, good conversion efficiency of the H_2S and a certain sulfur tolerance [21].

The double perovskite $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ found applications in Direct Methanol Fuel Cells [22] due to its resistance to coking and stability in reducing atmosphere. Very recently $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ was also studied, mixed to Sm-doped ceria, as functional layer in Electrolyte-layer Free Fuel Cells (EFFC) and performance obtained was compared to a conventional SOFC with the same composite as cathode [23]. In fact, double perovskites found application also as cathode for SOFC, thanks to their low average TEC [24,25].

Other approaches are being studied to improve performances of double perovskites as electrode materials. Pd- and Ni-Co-Mo alloys–impregnated $Sr_2FeMoO_{6-\delta}$ resulted, for example, to be also a very promising bi-functional (air-fuel) electrode for symmetrical SOFC, showing higher power density than non–impregnated material [26]. The addition of $SrMoO_4$ oxide to $Sr_2Mg_{1-x}Ni_xMoO_{6-\delta}$ phases with the formation of (1-y) $Sr_2Mg_{1-x}Ni_xMoO_{6-\delta}$ – $ySrMoO_4$ composite materials was also explored. In particular, the composites with $y = 0.15$ and 0.3 can be considered as perspective fuel electrodes because they exhibit: (1) satisfactory phase stability in the atmospheres with very low and high pO_2 values; (2) good thermal properties, including the monotonic thermal expansion behavior in wet air and hydrogen without tangible bends and acceptable TECs values; (3) enhanced transport properties in comparison with the basic $Sr_2Mg_{1-x}Ni_xMoO_{6-\delta}$ materials in reducing atmospheres [27].

Recently, SNM ($Sr_2Ni_{1+x}Mo_{1-x}O_6$, $0.00 \leq x \leq 0.15$), SLNM ($Sr_{2-x}La_xNiMoO_6$, $0.02 \leq x \leq 0.10$) and SCNM ($Sr_{2-x}Ce_xNiMoO_6$, $0.01 \leq \times \leq 0.05$) systems were studied in air and their structural and electrical properties were reported [28–30]. In this paper, most promising compositions for their electrical conductivity, i.e. SNM00 (Sr_2NiMnO_6), SLNM04 ($Sr_{1.96}La_{0.04}NiMoO_6$) and SCNM01 ($Sr_{1.99}Ce_{.01}NiMoO_6$), were investigated under reducing atmosphere. The conductivity was measured at different temperatures and the effects of reducing atmosphere on microstructure and phase stability were also studied in view of the application as anode materials in SOFC.

Materials and characterizations

Three different double perovskite powders, Sr_2NiMnO_6 (SNM00), $Sr_{1.96}La_{0.04}NiMoO_6$ (SLNM04) and $Sr_{1.99}Ce_{0.01}NiMoO_6$ (SCNM01), synthesized by chemical reaction route, were uniaxially pressed and sintered in proper conditions to obtain dense pellets [28–30]. Ag electrodes (Ag paste, Euroinks) were painted on pellets by screen printing and cured at 700 °C. Electrical measurements were carried out in a commercial test rig (Probostat, Norecs), in 4-wires configuration, by using a digital multimeter (DMM-Keithley 2000, Tektronics). The d.c. resistance was measured at different temperatures after reduction at 700 °C for 24 h under a flow of wet hydrogen ($H_2O = 3$ wt%). Cooling was carried out under wet hydrogen in order to keep the reduced state of the materials for microstructural characterization.

Microstructure of pellets, after conductivity measurements, was characterized by SEM (1450VP, LEO) and the chemical composition was determined by an energy-dispersive electron microprobe (EDS-INCA 300, Oxford Instruments); both analyses were performed on cross sections. Finally, phases were studied by X-ray diffractometry, (XRD-CubiX, Panalytical, Cu–Kα radiation) at room temperature.

Results and discussion

Arrhenius plots of Log($T^*\sigma$) are reported in Fig. 1, for each composition, measured respectively in air and in wet H_2. From comparison of obtained values, the sample SLNM04 showed the highest value of conductivity in air. Moreover, the reduction process considerably increased conductivity of all materials in the whole temperature range. The sample SNM00 also showed in hydrogen two linear regions respectively above and below the temperature 250–300 °C. This behavior is reported in literature due to a phase transition from tetragonal to cubic symmetry at about 250 °C [31]. Such a phase transition is not detected in SCNM01 and SLNM04, probably due to stabilization of the tetragonal phase by Ce– and La– doping. From Fig. 1, it can be observed that, for all systems, both in air and in H_2–atmosphere, the conductivity follows Arrhenius equation:

$$\sigma = \sigma_0/T \cdot \exp(-E_a/kT) \quad (1)$$

where, σ_0 is pre-exponential factor, E_a is the activation energy of conduction, k is the Boltzmann constant and T is the absolute temperature.

Please cite this article in press as: Presto S, et al., Electrical conductivity of NiMo–based double perovskites under SOFC anodic conditions, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.01.066