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Electrochemical and Raman study of $La_{0.7}Sr_{0.3}Co_{0.8}Fe_{0.2}O_{3-\delta}$ reduction

E. Siebert [a], A. Boréave [b], F. Gaillard [b], T. Pagnier [a,*]

[a] LEPMI, UMR 5279, CNRS, Grenoble INP, Université de Savoie, Université Joseph Fourier, BP75, 38402 Saint Martin d'Hères, France
[b] IRCELYON, UMR5256 CNRS — Université Claude Bernard Lyon 1, 2 Av. Einstein, F-69626 Villeurbanne Cedex, France

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ABSTRACT

The reduction of $La_{0.7}Sr_{0.3}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF7382) by heat-treatment in H_2 atmosphere or by electrochemical polarization has been followed by X-ray diffraction and Raman spectroscopy. The transition from perovskite ABO_3 to brownmillerite $A_2B_2O_5$ occurs at 250–300 °C in 10% H_2 atmosphere and is reversible. The Raman spectrum of brownmillerite shows two bands at 560 and 640 cm^{-1} that we attribute to CoO_4 tetrahedron stretching. Above 600 °C the sample starts to decompose irreversibly into Co, La_2O_3, SrO, and $LaSrFeO_4$. This confirms that Co cations are more reducible than Fe ones. The Raman spectra obtained under cathodic polarization of the LSCF7382/CGO interface at 300 °C and $PO_2 = 10^{-4}$ or 0.1 atm show the same bands as for the $A_2B_2O_5$ structure. This indicates that electrochemical reduction produces Co^{2+} in tetrahedral environment, even at low reducing overpotentials. Two reduction steps have been observed by linear sweep voltammetry and open circuit voltage relaxation. In both cases, Raman spectra indicate the presence of Co^{2+} in tetrahedral environment. The first reduction step is thus attributed to the reduction of B^{4+} within the perovskite phase and the second one to the reduction of Co^{3+} to Co^{2+} associated to the transition from perovskite to brownmillerite phase. Thermodynamic calculations from published literature support this idea. The association of n-type mobile species (Co^{2+}) with oxygen vacancies is confirmed.

1. Introduction

$La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) perovskite oxides have been shown to possess good electronic conductivity at intermediate temperatures and high oxygen exchange and bulk diffusion characteristics [1] as well as good catalytic activity [2]. LSCF materials are also known to be chemically and thermally compatible with gadolinia doped ceria (CGO) electrolytes [3,4]. Those properties make LSCFs good candidates as cathode materials for solid oxide fuel cells operating at intermediate temperature (IT-SOFCs) [5] or low temperature (μ-SOFC) [6], oxygen separation membranes [7] and catalyst for electrochemical promotion (EPOC) of combustion reactions [8]. Cathode materials or catalysts operating under EPOC conditions can be locally exposed to low oxygen partial pressure due to polarization. Membranes are also likely to operate in a reducing environment [9]. Therefore, it is essential to know the structural property changes of LSCF in low oxygen partial pressure atmosphere as well as under polarization as they are at the origin of the electrochemical performances.

Phase stability of LSCF in reducing atmosphere is well documented (see below). Structural data originate from in-situ and ex-situ X-ray diffraction measurements in various conditions: (i) low oxygen partial pressure and high temperature (T > 600 °C), (ii) hydrogen atmosphere at intermediate temperatures, and (iii) oxygen gradient at high temperature.

In a previous paper [10], the reduction processes taking place in the Co rich phase LSCF7382 were studied by H_2 temperature programmed reduction techniques (H_2-TPR) as well as cyclic voltammetry performed on the LSCF/CGO interface. Two processes retaining the perovskite structure in LSCF were evidenced by heat treatment under H_2 or electrochemical reduction near 300 °C. They were tentatively assigned to the successive reduction of Co^{4+} to Co^{3+} and Co^{2+}. However, both kinds of reduction were not connected through a common characterization technique. In this work, we want to concentrate on this latter aspect. The study of the phase stability and transformations of electrochemically reduced samples needs a characterization tool able to work in in-situ conditions. Raman spectroscopy is sensitive to chemical structure and is a powerful technique for the characterization of electrochemically active materials (e.g. see Refs. [11–13]). In-situ Raman measurements were performed on LSCF6482 in order to observe carbon deposition during

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* Corresponding author. Tel.: +33 4 76 82 66 82; fax: +33 4 76 82 67 77.
E-mail addresses: elisabeth.siebert@lepmi.grenoble-inp.fr (E. Siebert), antoinette.boreave@ircelyon.univ-lyon1.fr (A. Boréave), francois.gaillard@ircelyon.univ-lyon1.fr (F. Gaillard), thierry.pagnier@lepmi.grenoble-inp.fr (T. Pagnier).

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partial oxidation of CH_4, while phase stability was studied by ex-situ post Raman [14]. To the best of our knowledge, no in-situ characterization of the phase stability of LSCF under electrochemical polarization is reported in the literature.

The paper is organized as follows. A first part makes a literature survey of the structure and stability of LSCF compounds. Then, an X-ray diffraction study of the reduction of LSCF7382 in H_2 atmosphere allows us to determine a temperature domain in which the brownmillerite phase $A_2B_2O_5$ is stable. In the same conditions, and with the same powder, the Raman spectrum of this brownmillerite phase is obtained. Finally, a LSCF7382 film is studied by in-situ Raman spectroscopy under electrochemical reduction near 300 °C for $PO_2 = 0.1$ or 10^{-4} atm. The results are analyzed in view of the preceding ones and thermodynamic data from the literature. From a practical point of view, the conditions of the present study correspond to those of EPOC or μ-SOFC which operate near 300 °C.

2. Structure and stability of LSCF compounds

LSCF materials can be considered as solid solutions between $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC) and $La_{1x}Sr_xFeO_{3-\delta}$ (LSF). At room temperature, LSCF are nearly cubic perovskites, with an orthorhombic distortion at low Co and low Sr content, rhombohedral otherwise. At high temperature and/or high Sr content, the structure becomes cubic [15–19]. The ionic conductivity and the electrochemical performances increase with Sr and Co contents [20,21] whereas there is an opposite trend for chemical stability. Substitution of Sr for La in $LaMO_3$ compounds induces a decrease of the mean valence state of the A-site ion of the perovskite, which is compensated partially by the creation of oxygen vacancies and by the increase of the oxidation degree of the transition metal. In reducing atmosphere, the creation of new oxygen vacancies is compensated by the reduction of the transition metal ion.

2.1. Thermo-chemical stability under low PO_2

Under low oxygen partial pressure at high temperature, instability of LSCF perovskite may occur with possible formation of $A_2B_2O_5$ brownmillerite or A_2BO_4 Ruddlesden–Popper phase, depending on T, PO_2, and LSCF composition. In Sr rich compounds, the large concentration of oxygen vacancies yields a structural transformation from the perovskite to the brownmillerite phase at quite high PO_2 [19,22]. In the case of LSCF1982, this occurs for $PO_2 = 10^{-3}$ atm at 550 °C [19]. The ABO_3 to $A_2B_2O_5$ transition becomes more difficult with increasing La content. High temperature X-ray diffraction (HTXRD) performed on LSCF4682, in N_2 (PO_2 near 10^{-5} atm) showed that the ABO_3 phase was stable in the temperature range 20–900 °C [19]. Recently, Hashimoto et al. [16] studied the oxygen nonstoichiometry and the thermo-chemical stability of $La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-\delta}$ by combining high temperature gravimetry and coulometric titration for the intermediate PO_2 range with XRD and in-situ HTXRD. The Co rich compounds were found to decompose into A_2BO_4 and CoO at relatively high PO_2, i.e. 10^{-9} atm at 600 °C for LSCF6482. This decomposition occurred when the average valence of B-site ions became 3+. It shifted to lower PO_2, i.e. 10^{-20} atm for the Fe rich compounds. After re-oxidation of the Fe rich compounds, A_2BO_4 and CoO transformed back to LSCF phase. Phase stability of the Fe rich compound was studied as a function of oxygen activity at high temperature (1000–1200 °C) [23]. XRD on quenched samples showed that a series of distinct reactions and reduction processes occurred as the oxygen activity decreased. The major transient compound could be represented by a general formula of $(LaSr)(FeCo)O_4$ in which the ratio of La/Sr and Fe/Co changed with oxygen partial pressure and temperature. For example, $LaSrFeO_4$ and La_2CoO_4 were evidenced for LSCF6428 at 1200 °C, in $PO_2 = 10^{-14}$ atm, where Fe and Co ions exist in trivalent and divalent states respectively. At such a temperature, the average valence of all B cations was suggested to be +3 in the 10^{-5}–10^{-3} PO_2 range. Preferential reduction of Co^{3+} to Co^{2+} was also reported in LSCF6428 by Mineshige et al. [24] while Fe was proposed to preserve its higher valence above +3, with decreasing PO_2 from 1 to 10^{-4} atm at 1000 °C.

2.2. Thermo-chemical stability under H_2

The reducibility of LSCF by heat treatment under H_2 has been studied by H_2-TPR and XRD analysis. (e.g. see Ref. [10] and references herein). LSCF7382 was reduced in two steps, the first one in the temperature range 300–500 °C with a broad band composed of at least two processes and the second one near 700 °C with a rather sharp peak corresponding to the decomposition of LSCF7382. The thermal reduction of LSCF5555 in 10% H_2 in N_2 at 500 °C allowed Shinawi et al. [25] to obtain $LaSrCoFeO_5$ with the brownmillerite structure. The reduced material showed relatively good stability in air for 1–2 days. X-ray diffraction pattern refinements at 20 K indicated an Icmm space group with equally distributed Co and Fe over the tetrahedral and octahedral sites. The average B site oxidation state is +2.5. Moreover, magnetic and Mossbauer measurements showed that Co is mostly in +2 state, while Fe state is +3.

2.3. Thermo-chemical stability under oxygen potential gradient

The stability of LSCF compounds has also been investigated under oxygen chemical potential gradient in connection with its potential use as a catalytic membrane. LSCF6428 was found to be very stable in air/N_2 gradients at temperatures up to 960 °C [26]. Recently, kinetic demixing due to cationic transport was reported at high temperature in LSCF6428. Co oxide as well as Sr and Fe enrichment was evidenced on the air side of the membrane [27,28]. Cationic transport was also proposed by Baumann et al. [29] in order to explain the strong performance improvement induced by a cathodic DC bias of −1 V of LSCF6482 SOFC cathodes deposited on YSZ. Surface compositional changes under electrochemical polarization corresponded to depletion of La while the concentration of Sr and Co increased on the air side. Sr surface segregation in LSCF cathodes was also proposed to be at the origin of the efficiency degradation over time during long-term operation [30,31]. In all these studies, pre- and post-test analyses were carried out mainly by ex-situ X-ray photoelectron spectroscopy (XPS).

3. Experimental

3.1. Sample preparation

The LSCF7382 powder was prepared by a combined citrate-EDTA complexing method as described elsewhere [32,33]. The X-ray diffraction pattern of the powder showed that LSCF7382 had the perovskite structure (JCPDFile n°(1)-89-1265) without any detectable impurity phase. It was indexed as trigonal (rhombohedral) with the $R\overline{3}c$ symmetry. The lattice parameters deduced from the diffraction patterns were equal to a = 5.45 Å and c = 13.2 Å. The corresponding pseudo-cubic lattice parameter calculated as defined in Ref. [15] was equal to 3.84 Å. Those parameters agreed well with those from the literature [16]. According to the Scherrer equation, the size of the crystallite was of the order of 20 nm. The specific surface area of the powder was equal to 22 $m^2\ g^{-1}$ (BET measurement). The powder was constituted of agglomerates. It was ground by attrition before use for sample and thin film preparation in order to diminish the agglomerate size.

LSCF7382 pellets were prepared for Raman measurements as a function of the temperature in air as well as in reducing atmosphere. The samples were obtained by isostatic pressing and annealing at 1000 °C in air for 1 h.

For Raman measurements under electrochemical polarization, LSCF7382 thin films were deposited on a gadolinia doped ceria (CGO, 10 mol% Gd_2O_3 in CeO_2) pellet as described in our previous study [10]. Deposition was made by spraying a slurry containing (wt.%): 40% LSCF7382 powder, 30% ethylic alcohol, 27% terpineol, 2% polyvinil-