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Oxygen nonstoichiometry, Mössbauer spectra and mixed conductivity of $Pr_{0.5}Sr_{0.5}FeO_{3-\delta}$

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Abstract

The oxygen deficiency of perovskite-type $Pr_{0.5}Sr_{0.5}FeO_{3-\delta}$, studied by coulometric titration, thermogravimetry and Mössbauer spectroscopy, is significantly higher than that in $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ at 973–1223 K. The variations of hole mobility and Seebeck coefficient in oxidizing atmospheres, where the total conductivity of praseodymium-strontium ferrite is predominantly p-type electronic, suggest progressive delocalization of the p-type charge carriers on increasing oxygen chemical potential. As for other perovskite-type ferrites, reduction leads to the co-existence of vacancy-ordered and disordered domains. The n-type electronic conductivity of $Pr_{0.5}Sr_{0.5}FeO_{3-\delta}$ at reduced $p(O_2)$ and the hole transport under oxidizing conditions are both lower compared to the La-containing analogue. Analogous conclusion was drawn for the ionic conductivity, calculated from the steady-state oxygen permeation data under oxidizing conditions and from the $p(O_2)$-dependencies of total conductivity in the vicinity of electron-hole equilibrium points where the average iron oxidation state is 3+. The similar activation energies for partial ionic and electronic conductivities in $Ln_{0.5}Sr_{0.5}FeO_{3-\delta}$ ($Ln = La$, Pr) indicate that the presence of praseodymium does not alter any of the conduction mechanisms but decreases the charge-carrier mobility due to the smaller radius of Pr^{3+} cations stabilized in the perovskite lattice.

Keywords: A. Oxides; C. Mössbauer spectroscopy; D. Defects; D. Diffusion; D. Electrical properties

1. Introduction

Partial oxidation of methane to synthesis gas, a mixture of CO and H_2, may take place efficiently on the surface of a mixed oxygen-ion/electron conducting membrane, which integrates oxidation with controlled oxygen separation in a single reactor [1–3]. The simplicity of the system implies significant savings in energy and capital compared to the conventional technologies of natural gas conversion via steam reforming. Commercialization of the ceramic membrane reactors, however, requires achieving the often incompatible aims of high oxygen permeability, chemical stability and moderate thermal expansion for both oxidizing and reducing conditions, respectively, encountered at the membrane feed and permeate sides. One group of promising materials with high oxygen permeability is the perovskite-type system based on (La, Sr)$FeO_{3-\delta}$ [4–10]. The ideal composition has not been fully established for the range of oxygen partial pressures relevant to membrane-reactor operation. A maximum of electronic and oxygen ionic conductivity in undoped $La_{1-x}Sr_xFeO_{3-\delta}$ was observed for $x = 0.5$ [9,10]; further strontium doping results in oxygen vacancy ordering and deterioration of transport properties. The ferrite-based perovskites with a high mixed ionic-electronic conductivity may also be of interest for another important application, namely as the cathode materials in solid oxide fuel cells (SOFCs) operating at 800–1100 K [11,12].

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The present work is focused on the studies of oxygen nonstoichiometry, electronic transport and ionic conduction in $Pr_{0.5}Sr_{0.5}FeO_{3-\delta}$. The structural, electronic and magnetic properties of praseodymium–strontium ferrites at low temperatures are well documented in literature (e.g., [13–16] and references cited), although there are several debatable issues, such as the simultaneous presence of low- and high-spin iron species and the Mössbauer spectroscopy analysis of mixed-valence $Fe^{(3+n)+}$ at 296 K. However, the information on transport phenomena and defect formation mechanisms in (Pr, Sr)$FeO_{3-\delta}$ at elevated temperatures is scarce. The incorporation of praseodymium cations leads often to an enhanced oxygen exchange kinetics of various perovskite-related phases and an improved electrochemical performance of SOFC electrodes [17–20]. The effects of A-site cation radius on the oxygen ionic conduction in perovskite-type ferrites are still unknown, in spite of the economic benefits which may result from the substitution of lanthanum oxide with less expensive mixed-lanthanide precursors [12,21]. In the case of isostructural cobaltites, gallates and aluminates, the ionic transport decreases with decreasing rare-earth cation size [22–24]; a similar tendency was found for rare-earth cuprates $Ln_2CuO_{4+\delta}$ (Ln = La, Pr, Nd) with K_2NiF_4-type structure [25]. The data on oxygen nonstoichiometry and hole mobility in $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ used in this work for comparison, are more detailed and refined with respect to the previous reports [9,10].

2. Experimental

The submicron powder of $Pr_{0.5}Sr_{0.5}FeO_3$ was synthesized by the glycine-nitrate process (GNP). Glycine was added as the fuel and chelating agent in 100% excess to an aqueous solution of the metal nitrate precursors in appropriate ratios. The solution was dried and heated until auto-ignition occurred, leaving a foam-like reaction product; this powder was annealed in air at 1273 K for 2 h to remove remaining organic content and then ball-milled. The gas-tight ceramics with density higher than 93% of theoretical were sintered in air at 1540 K for 5 h. The synthesis procedure and sintering conditions of $La_{0.5}Sr_{0.5}FeO_3$ ceramics were described in previous work [9]. The powdered samples, used for X-ray diffraction (XRD) and Mössbauer spectroscopy studies, were obtained by grinding of dense ceramics and treatment in various atmospheres. The samples equilibrated at atmospheric oxygen pressure were annealed at 1023 K in air for 5 h, and then either slowly cooled (1–2 K/min) down to room temperature or quenched in liquid nitrogen. Another series of the powdered samples were treated in flowing H_2–H_2O–N_2 mixture with subsequent fast cooling (10–12 K/min); the oxygen partial pressure in the H_2-containing atmosphere, measured by an electrochemical oxygen sensor, was 3×10^{-16} atm.

Characterization of the materials was conducted employing XRD analysis, scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS), inductively coupled plasma (ICP) spectroscopic analysis, and measurements of the total conductivity (4-probe DC), Seebeck coefficient and steady-state oxygen permeation fluxes. Detailed descriptions of experimental techniques and equipment can be found in previous publications ([8,9,25–27] and references therein). The XRD patterns were collected at room temperature in the 2Θ range 10–110° (CuK_α radiation, step 0.02°, 8 s per step). Structure refinement was performed by the full-profile Rietveld method using FullProf package [28], taking into account the scale factor, zero shift, background parameters, lattice parameters, atomic coordinates and fractions, isotropic temperature factors, peak profile and texture parameters. The total conductivity and thermopower were studied at 300–1300 K in an oxygen partial pressure ranging from 10^{-18} to 0.5 atm, as described elsewhere [26]. The criteria for equilibration of a sample after a change in either oxygen partial pressure or temperature included the relaxation rates of the conductivity and Seebeck coefficients less than 0.05%/min and 0.001 μV/(K min), correspondingly. The oxygen nonstoichiometry at 923–1223 K in the oxygen partial pressure range 10^{-17} to 0.7 atm was studied by the coulometric titration (CT) technique and thermogravimetry [26,29,30]. The CT data were verified by pumping oxygen into the electrochemical cells and reproducing the nonstoichiometry data after each isothermal titration cycle, which confirmed zero leakage (Fig. 1a). Also, the nonstoichiometry variations calculated from TGA and CT data, showed an excellent agreement within all studied temperature range (Fig. 1b). The ionic conductivity in air was calculated from the steady-state oxygen permeation fluxes and total conductivity [27].

Mössbauer spectra were collected at room temperature and at 4.1 K, in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi ^{57}Co source in a Rh matrix. The velocity scale was calibrated using α-Fe foil. The absorbers were obtained by pressing the powdered samples (5 mg of natural Fe/cm^2) into perspex holders. Isomer shifts (IS, Table 1) are given relative to metallic α-Fe at room temperature. Low-temperature spectra were collected using a JANIS bath cryostat, model SVT-400, with the sample immersed in liquid He. The spectra were fitted to Lorentzian lines using a non-linear least-squares method [31]. The relative areas and widths of both peaks in a quadrupole doublet were kept equal during refinement. Distributions of magnetic splittings were fitted according to the histogram method [32].

3. Results and discussion

3.1. Crystal structure

XRD analysis showed that all $Pr_{0.5}Sr_{0.5}FeO_3$ samples studied in this work are single-phase and have perovskite-type structure. Taking into account peak splitting and