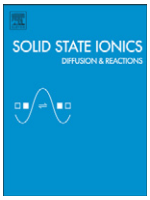
Solid State Ionics 232 (2013) 68–79

Contents lists available at SciVerse ScienceDirect

Solid State Ionics

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



Defect chemistry, thermomechanical and transport properties of $(RE_{2-x}Sr_x)_{0.98}(Fe_{0.8}Co_{0.2})_{1-y}Mg_yO_{4-\delta}$ (RE = La, Pr)

C. Chatzichristodoulou [a,*], C. Schönbeck [b], A. Hagen [a], P.V. Hendriksen [a]

[a] Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark
[b] Department of Science, Systems and Models, Roskilde University, Universitetsvej 1, DK-4000 Roskilde, Denmark

ARTICLE INFO

Article history:
Received 31 July 2012
Received in revised form 18 October 2012
Accepted 25 October 2012
Available online 23 December 2012

Keywords:
Ruddlesden-Popper
Oxygen permeation
XANES
Mixed conductor
Defect chemistry
Thermal expansion

ABSTRACT

The oxygen nonstoichiometry of Ruddlesden-Popper compounds with chemical composition $(RE_{2-x}Sr_x)_{0.98}(Fe_{0.8}Co_{0.2})_{1-y}Mg_yO_{4-\delta}$ (RE = La, Pr, x = 0.9–1.2 and y = 0, 0.2) was measured as a function of temperature and oxygen activity (a_{O2}) by coulometric titration and thermogravimetry. All compositions were found to be approximately stoichiometric in air ($\delta \approx 0$). The oxidation state of Fe and Co was determined by XANES. Fe retains an oxidation state of +3 upon reduction of the sample, whereas Co is reduced to an oxidation state of +2. A model of the defect chemistry is proposed that can account well for the measured oxygen activity dependence of the oxygen nonstoichiometry at all temperatures investigated. The studied compositions exhibit remarkable thermodynamic stability under reducing conditions. Decomposition was only observed for temperatures above 800 °C in a hydrogen water vapor gas mixture ($[H_2]/[H_2O] = 50$). The thermal and chemical expansion coefficients of these compounds are significantly decreased compared to those of $(La_{0.6}Sr_{0.4})_{0.99}Fe_{0.8}Co_{0.2}O_{3-\delta}$, a well studied perovskite with related composition. The transport properties were investigated by conductivity relaxation and the potential of using these materials as oxygen separation membranes was assessed by calculating the oxygen flux that can be delivered through a 30 μm thick membrane.

1. Introduction

Materials with mixed oxide-ionic and electronic conductivity (MIEC) are required for a variety of applications, such as solid oxide fuel cells (SOFC), solid oxide electrolysis cells and oxygen permeation membranes (OPMs). Perovskites with the general formula $RE_{1-x}AE_xTMO_{3-\delta}$, where RE stands for rare-earth, AE for alkaline-earth and TM for transition metal elements, have been widely investigated as mixed oxide-ionic and electronic conducting materials [1–4]. A large number of compositions are known to exhibit sufficiently high electronic and ionic conductivity for OPM applications [1,5,6]. The compositions that exhibit the highest ionic conductivity though, are generally found to have high coefficients of thermal expansion and to be prone to decomposition under reducing conditions [3,7].

Compounds in the Ruddlesden-Popper (RP) type structure ($A_{n+1}B_nO_{3n+1}$), with the general formula $RE_{2-x}AE_xTMO_{4-\delta}$, have also been identified as MIEC materials. The Ruddlesden-Popper is a layered structure, comprising alternating perovskite and rock–salt layers. Compounds with RP structure have been reported to show improved thermodynamic stability and smaller TEC [8] as compared to perovskites of comparable composition. They have also been reported to possess very small chemical expansion coefficients in the hyperstoichiometric regime [9]. Development of materials with small chemical expansion coefficient is beneficial for oxygen membrane applications, as it allows for reduced chemical strain across the membrane under operation, thereby reducing the risk of mechanical failure.

$La_2NiO_{4+\delta}$, and its modifications by A and B-site doping, have received considerable attention as novel cathodes for intermediate temperature SOFCs and OPMs [8,10–17]. The oxide ion migration occurs via interstitials in the rock salt layers and vacancies in the perovskite planes [11,14,18]. The interstitial mechanism determines ionic conductivity and oxygen permeation at high P_{O2} whereas the vacancy mechanism dominates at low P_{O2} [11]. Therefore, RP compositions possessing increased concentrations of oxide ion vacancies may hold greater promise as OPMs operating at low P_{O2} at the permeate side.

The reduction stability of RP ferrites and manganites is superior to that of nickelates and cobaltites [8,19]. It is therefore interesting to investigate the thermodynamic and transport properties of RP ferrites with AE substitution at the A-site and Co substitution at the B-site, as this may lead to a good compromise between oxygen vacancy formation and thermodynamic stability upon reduction. Furthermore, RP compounds are reduction products of perovskites [8,20]. Therefore $(La,Sr)_2(Fe,Co)O_{4-\delta}$ RP compounds are likely to form at the permeate side of a $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSFC) OPM and in LSFC based SOFC cathodes under strong polarization. Knowledge of their defect thermodynamic and transport properties is therefore important in evaluating their impact in LSFC based components of electrochemical devices.

---

[*] Corresponding author.
E-mail address: ccha@dtu.dk (C. Chatzichristodoulou).

0167-2738/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ssi.2012.10.026

In this study, the oxygen nonstoichiometry and redox properties of Fe and Co in Ruddlesden-Popper compounds having the general formula $(RE_{2-x}Sr_x)_{0.98}(Fe_{0.8}Co_{0.2})_{1-y}Mg_yO_{4-\delta}$ are determined by thermogravimetry, coulometric titration and X-ray absorption near edge spectroscopy (XANES). Furthermore, the thermomechanical and transport properties of these compounds are investigated and compared with those of LSFC, a well studied perovskite with related composition (the same transition metal elements on "B-site" and the same ratio between these).

2. Experimental

2.1. Sample preparation

Powders of composition $(RE_{2-x}Sr_x)_{0.98}(Fe_{0.8}Co_{0.2})_{1-y}Mg_yO_{4-\delta}$ (RE = La, Pr), with $0.6 \le x \le 1.4$ and y = 0, 0.2, were synthesized by the glycine–nitrate combustion process [21]. Aqueous solutions of the metal nitrate salts were prepared and their concentrations were determined gravimetrically. After mixing stoichiometric amounts, glycine was added to the mixture at a glycine/nitrate molar ratio of 0.548. The container was placed on a hot plate at 300 °C. After evaporation of a sufficient amount of water, a self-sustaining combustion process initiated, resulting in a very homogeneous, submicron powder. The powders were calcined at 1000 °C for 24 h, and ball milled in a $Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ) container with ethanol using a planetary mill and YSZ balls. The resulting fine powders were shaped into bars ($\sim 28 \times 7 \times 2$ mm^3) at a uniaxial pressure of 35 MPa and further compressed isostatically at a pressure of 325 MPa. The bars were sintered at 1350 °C for 12 h in air or N_2 and cooled to room temperature at a rate of 30 °C/h. Phase purity and structural analysis was performed by room temperature X-ray diffraction (XRD), on polished pellets sintered at 1350 °C in air or N_2, using a Bruker D8 Advance diffractometer with Cu K_α radiation and a PSD LynxEye detector.

2.2. Coulometric titration and thermogravimetry

As-sintered bars were crushed into powders and used for coulometric titration (CT) and thermogravimetric analysis (TG). A small alumina cup with a known mass of sample powder (~1.5 g) was fitted in a (YSZ) cup covered with a YSZ lid and sealed with glass at 1000 °C. A detailed description of the CT measurements including a schematic can be found elsewhere (19).

Thermogravimetry was performed using a Netzsch STA 409CD thermogravimeter. The P_{O2} of the sample atmosphere was varied, by the use of appropriate gas mixtures (of air, N_2 and H_2), and measured downstream with a YSZ P_{O2} sensor operating at 900 °C. The temperature was varied between 500 °C and 1000 °C at each gas mixture, in steps of 100 °C. After each change in temperature or gas mixture the sample was allowed to equilibrate for 1 to 4 h. This duration is considered adequate, taking into account the fact that the time constant for the relaxation is $\tau \sim 5$ s, as estimated from the relation $\tau = r^2/2D_{chem}$ using a value as low as 1×10^{-7} cm^2/s for the chemical diffusion coefficient, D_{chem}, and a particle size $r \approx 1$ μm. At the end of each measurement, the samples were heated up to 1400 °C in $[H_2]/[H_2O] = 50$, in steps of 100 °C, in order to achieve complete decomposition to metals and metal oxides. The measured weight loss was corrected for buoyancy effects using an alumina powder reference sample of the same volume, measured under identical conditions.

2.3. X-ray absorption near-edge spectroscopy (XANES)

Powders obtained from bars sintered at 1350 °C in N_2 were used for XANES measurements, as well as powders obtained from bars that were further annealed at 900 °C in air for 200 h and cooled to room temperature in air at a rate of 60 °C/h, and from bars further annealed at 900 °C in $[H_2]/[H_2O] = 3$ for 200 h and cooled to room temperature in $[H_2]/[H_2O] = 3$ at a rate of 180 °C/h. Finally, measurements were also performed on $LaFeO_3$, $LaCoO_3$, Fe(II)-oxalate and Co(II)-acetate, which are used as references for the 3-valent and 2-valent states of Fe and Co. Approximately 5 mg of the powdered bars were thoroughly mixed with 50 mg of cellulose in a mortar and subsequently pressed into discs. XANES measurements at the Fe and Co K-edges were performed in transmission mode at HASYLAB/DESY (EXAFS E4 beamline), at room temperature and at a pressure of 10^{-9} atm, using a Si (111) double-crystal monochromator at 40% detuning to suppress harmonics. A Fe or Co metal foil was measured as a reference along with each sample in order to accurately calibrate and align the energy scale for all spectra. In the near-edge region, equidistant energy steps of 0.2 eV were used. Leaking of the incident beam, through parts of the sample having less absorbent material, results in amplitude reduction of the XANES signal and an apparent shift of the absorption edge to lower energies [22]. To minimize the effects of sample inhomogeneity, we scanned the X-ray beam along the diameter of the disc and carefully selected a region of homogeneous absorption. Analysis of the XANES spectra was performed with the IFEFFIT program package ATHENA [23].

2.4. Dilatometry

The thermal and chemical expansion coefficients were measured by dilatometry using a NETZSCH DIL 402CD differential dilatometer with a sample load of 0.3 N. The thermal expansion of the sample-rods was measured in flowing air (100 Nml min^{-1}) by heating the samples from room temperature to 1250 °C at a rate of 1 K/min. The samples were then cooled to 1050 °C, where the chemical expansion coefficient was determined by varying the P_{O2} of the surrounding atmosphere, using mixtures of air, CO_2 and H_2. Finally, the thermal expansion coefficient was measured in $[H_2]/[H_2O] = 3$ during cooling. The P_{O2} was measured downstream with a YSZ P_{O2}-sensor operating at 900 °C. An Al_2O_3-rod, measured simultaneously with the sample-rod, served as a standard for the calibration of the instrument.

2.5. Conductivity relaxation

Conductivity measurements were performed on rectangular bars ($\sim 2 \times 0.2 \times 0.2$ cm^3) using the four-probe dc technique in a controlled atmosphere furnace. The surfaces of the samples were polished with SiC paper of decreasing roughness and diamond paste of 1 μm particle size. The samples were electrically contacted with platinum wires and platinum paste, and then fired at 1000 °C for 1 h prior to the conductivity measurements to ensure good contacting. The oxygen activity of the sample environment was controlled by flowing gas mixtures of O_2/N_2 or $N_2/H_2/H_2O$ and monitored by a YSZ-sensor placed downstream, operating at 1000 °C. Brooks mass flow controllers were used to adjust the flow of the various gases, keeping the total gas flow constant at 250 Nml min^{-1}. A four-way valve was used to enable fast change of the gas atmosphere in the sample environment. The non-ideal stepwise change of the oxygen activity in the sample environment was recorded by the YSZ-sensor and fitted to an exponential decay, $a_{O_2}^{\infty} = a_{O_2}^{0} + \Delta a_{O_2}\left(1 - \exp\left(-\frac{t}{\tau}\right)\right)$, to obtain the time constant, τ, of the response of the sample compartment to a change in oxygen activity from an initial value, $a_{O_2}^{0}$, to a final value, $a_{O_2}^{\infty}$. Stepwise changes of the oxygen activity were performed both in oxidizing and reducing directions. The time constant, τ, was evaluated for each individual gas change and used in the fitting of the electrical conductivity relaxation with the following expression [24]:

$$\frac{\sigma(t) - \sigma^{\infty}}{\sigma^{0} - \sigma^{\infty}} = \exp\left(-\frac{t}{\tau}\right) + \sum_{k=1}^{\infty} \sum_{j=1}^{\infty} A_{x,k} A_{y,j} T_{xy,kj} \qquad (1)$$