Mixed conductivity, thermochemical expansion and electrochemical activity of Fe-substituted (La,Sr)(Cr,Mg)O$_{3-\delta}$ for solid oxide fuel cell anodes

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HIGHLIGHTS

- $(La_{0.9}Sr_{0.1})_{0.98}Cr_{0.9-x}Fe_xMg_{0.1}O_{3-\delta}$ ($x = 0-0.3$) are stable under SOFC anode operation conditions.
- Iron cations substitute in 3+ oxidation state in both oxidized and reduced materials.
- Substitution with Fe increases oxygen deficiency and ionic transport under reducing conditions.
- The materials exhibit moderate TECs and small chemical expansion on reduction.
- Porous anodes ($x = 0.3$) show good electrochemical performance in contact with LSGM.

ARTICLE INFO

ABSTRACT

The effect of iron substitution in perovskite-type $(La_{0.9}Sr_{0.1})_{0.98}Cr_{0.9-x}Fe_xMg_{0.1}O_{3-\delta}$ ($x = 0-0.3$) is evaluated with emphasis on the properties relevant for solid oxide fuel cell anode application including the phase stability, oxygen nonstoichiometry, mixed ionic−electronic transport, thermochemical expansion and electrochemical activity. Thermogravimetric analysis, Mössbauer spectroscopy and electrical measurements in combination with X-ray diffraction confirm the stability of perovskite phase for $x = 0.3$ down to $p(O_2)$ as low as 10^{-19} atm at 1223 K. Mössbauer spectroscopy results indicate also that iron cations substitute in 3+ oxidation state in both oxidized and reduced material. The total conductivity is predominantly p-type electronic, with negligible contribution of ionic transport under oxidizing conditions. Substitution with iron decreases electronic transport, but also leads to higher oxygen deficiency and ionic conductivity under reducing conditions. The oxygen nonstoichiometry variations, determined by coulometric titration, and defect chemistry of $(La_{0.9}Sr_{0.1})_{0.98}Cr_{0.6}Fe_{0.3}Mg_{0.1}O_{3-\delta}$ can be described by non-ideal solution model and site-exclusion effects. The materials exhibit moderate thermal expansion coefficients $(10.1−11.5) \times 10^{-6}$ K^{-1} in air, nearly independent of iron content and $p(O_2)$, and favorably small chemical expansion on reduction. Porous $(La_{0.9}Sr_{0.1})_{0.98}Cr_{0.6}Fe_{0.3}Mg_{0.1}O_{3-\delta}$ anodes applied onto LaGaO$_3$-based solid electrolyte with thin Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ interlayers show a better electrochemical performance compared to $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ under identical conditions.

1. Introduction

Nickel-based composite anodes show a good electrochemical performance in H$_2$-based fuels and have been used in solid oxide fuel cell (SOFC) prototypes for decades. Their often-cited drawbacks include however poor redox stability and large dimensional changes in inevitable redox cycles leading to microstructural and functional degradation [1]. These cermets suffer also from the fast coking and sulfur poisoning in hydrocarbon fuels resulting in blocking of porous anodes and subsequent loss of performance [2]. Significant efforts are focused therefore on the development of alternative electrode components satisfying numerous requirements to SOFC anode such as phase stability and high electrical conductivity under fuel atmosphere conditions, chemical and

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thermomechanical compatibility with solid electrolytes, and superior electrochemical activity. A number of perovskite-like oxide ceramic materials with electronic or mixed ionic-electronic conductivity are considered as potential substituents for nickel in anodes. Representative examples include donor-doped $SrTiO_3$, $Sr_2MgMoO_{6-\delta}$, and solid solutions derived from $SrVO_{3-\delta}$ and $LaCrO_3$ [3–5].

$LaCrO_3$ and, in particular, its alkaline earth-substituted derivatives exhibit an attractive combination of properties making them not only the SOFC interconnect candidate materials [6], but also promising hosts for the development of ceramic anodes. They are stable in both oxidizing and reducing atmospheres and exhibit moderate thermal expansion compatible with that of common solid electrolytes [3–6]. Acceptor-type substitutions with calcium, strontium or magnesium result in improvement of electrical conductivity [6]. Furthermore, Sr- and Ca-substituted lanthanum chromites do not catalyze carbon deposition [7,8] and thus are potential anode materials for direct oxidation of methane-based fuels. Although the electrocatalytic activity of $(La,Sr)CrO_3$-based anodes is often poor [9,10], the performance can be improved by appropriate substitutions into chromium sublattice, provided that its excellent redox stability is retained. One example of efficient anode material is $(La_{1-x}Sr_x)_{1-y}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ ($x = 0.2-0.25$, $y = 0-0.1$) perovskite which demonstrated fairly good electrochemical activity in both hydrogen and wet CH_4 [11–16], and also was suggested for use in symmetrical cells with anode and cathode made of the same material [13]. One drawback of this material is relatively low electronic conductivity in both oxidizing and reducing conditions in combination with p-type conduction behavior [16]. As a result, infiltration of metals (e.g. Cu, Ni) as electronic current collectors and/or electrocatalytically-active additives (e.g., $CeO_{2-\delta}$) are required to minimize anode ohmic and polarization resistance [14–16]. Positive results were also obtained for iron-substituted $(La,Sr)CrO_{3-\delta}$ [17–20]; in particular, $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ electrodes showed lower polarization resistance in symmetrical cells with $LaGaO_3$-based solid electrolyte if compared to the Mn-containing analog [18]. The electrochemical cells with iron-containing electrodes exhibit however a higher series resistance, presumably due to stronger interaction between electrodes and solid electrolyte [18]. Note that introducing a ceria-based buffer layer between lanthanum gallate-based electrolyte and $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ electrodes was reported to prevent diffusion of Cr and Mn cations into electrolyte surface layers [14].

The present work was aimed on the appraisal of iron-substituted $(La_{0.9}Sr_{0.1})_{0.95}Cr_{0.9}Mg_{0.1}O_{3-\delta}$ for possible use as a SOFC anode material. The main attention was focused on the properties relevant for practical application including phase relationships in different atmospheres, ionic and electronic transport properties in connection with the oxygen nonstoichiometry variations and defect chemistry mechanism, thermochemical expansion, and electrochemical behavior. A particular concern is given to stability issues under highly reducing conditions assessed employing a series of techniques including Mössbauer spectroscopy. Note that the low-$p(O_2)$ stability of $(La,Sr)CrO_{3-\delta}$ heavily substituted with iron is questionable [19–21]. For instance, it was reported that the XRD pattern of $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ annealed in 5%H_2 at 1173 K for 120 h shows the trace amounts of metallic iron [19]. In another report [21], XRD analysis of $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ quenched from 1173 K and $p(O_2) = 10^{-20}$ atm demonstrated the segregation of $(La,Sr)_2FeO_4$ secondary phase. Haag et al. [20] indicated that $LaSr_2Fe_2CrO_{9-\delta}$ starts to decompose at $p(O_2) < 10^{-20}$ atm at 1073 K. In the present work, iron concentration was limited therefore to 30 at.% in chromium sublattice. $La_{0.9}Sr_{0.1}Cr_{0.9}Mg_{0.1}O_{3-\delta}$ with a moderate content of acceptor-type dopants, Sr^{2+} and Mg^{2+}, in both sublattices was selected as a parent composition. Minor cation deficiency was also

introduced into the A-sublattice in order to decrease the chemical expansion on reduction [11]. The electrochemical activity of porous anode layers was evaluated in contact with two selected solid electrolytes — perovskite-type $(La_{0.9}Sr_{0.1})_{0.98}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) and apatite-type $La_{10}Si_5AlO_{26.5}$ (LSA) ([22] and references therein). Thin $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO) buffer interlayer was introduced between electrodes and electrolytes, similar to the previous reports [16,17,23].

2. Experimental

The powders of $(La_{0.9}Sr_{0.1})_{0.98}Cr_{0.9-x}Fe_xMg_{0.1}O_{3-\delta}$ ($x = 0-0.3$) were synthesized by the glycine-nitrate self-combustion technique using metal nitrates as oxidant and glycine as fuel and chelating agent. Appropriate proportions of metal nitrates (Sigma–Aldrich) and glycine (SAFC) were dissolved in distilled water. The solution was stirred at room temperature for several hours, and then heated on a hot plate until auto-ignition. The foam-like combustion products were ground and annealed in air at 1273 K for 2 h in order to burn out organic residues. Dense disk-shaped ceramic samples were pressed uniaxially at 40 MPa and sintered in air for 5 h; the sintering temperatures are listed in Table 1. Prepared ceramic samples were cut into rectangular bars and polished for the electrical and dilatometric measurements. The experimental density was calculated from the mass and geometric dimensions of the samples. Powdered samples for X-ray diffraction (XRD), Mössbauer spectroscopy and thermal (TGA/DSC) analysis were prepared by grinding sintered ceramics in a mortar with subsequent annealing (air, 1273 K, 2 h) and slow cooling in order to attain equilibrium with atmospheric oxygen pressure at low temperatures.

Room-temperature and high-temperature XRD patterns were recorded using Rigaku D/Max-B (CuK$_\alpha$, $2\Theta = 10-80°$, step 0.02°, exposition 3 s) and Philips X'pert MPD (CuK$_\alpha$, $2\Theta = 10-80°$, step 0.02°, exposition 15 s) diffractometers, respectively. Unit cell parameters were calculated from the XRD data using Fullprof software (profile matching method). Microstructural characterization was performed by scanning electron microscopy (SEM, Hitachi S-4100 instrument) coupled with energy dispersive spectroscopy (EDS, Rontec UHV detector). Differential scanning calorimetry (DSC) studies were done in air using Netzsch 204HP equipment (300–873 K, 5 K min^{-1}). The dilatometric measurements (vertical Linseis L75V/1250 instrument) and thermogravimetric analysis (TGA, Setaram SetSys 16/18 instrument) were carried out in flowing air, argon, 10%H_2–N_2 and CO–CO_2 mixtures at 298–1373 K with constant heating/cooling rate of 2–3 K min^{-1} or isothermally as function of time. In all cases, the oxygen partial pressure, $p(O_2)$, in a gas atmosphere was monitored using yttria-stabilized zirconia (YSZ) solid-electrolyte sensors; $p(O_2)$ in 10%H_2–N_2 flow corresponded to $\sim 10^{-19}$ atm at 1173 K.

The Mössbauer spectra were collected at room temperature and at 4.2 K; details may be found in Refs. [24,25]. The measurements were performed 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 into perspex holders. Isomer shifts (IS) are given relative to metallic α-Fe

Table 1
Properties of as-prepared $(La_{0.9}Sr_{0.1})_{0.98}Cr_{0.9-x}Fe_xMg_{0.1}O_{3-\delta}$ ceramics.

x	$T_{sintering}$, K	Density ρ_{exp}, g cm^{-2}	ρ_{exp}/ρ_{theor}, %	Unit cell parameters		
				a, Å	b, Å	c, Å
0	2023	5.72	88.4	5.4774(3)	7.7542(4)	5.5199(3)
0.1	2023	6.08	94.1	5.4855(3)	7.7646(4)	5.5250(3)
0.2	2023	6.38	99.1	5.4943(3)	7.7748(4)	5.5295(3)
0.3	1973	6.37	99.0	5.5010(2)	7.7847(3)	5.5328(2)