Mixed conductivity and electrochemical behavior of $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3-\delta}$

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Abstract

The electronic and oxygen–ionic transport in $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3-\delta}$, a member of promising family of solid oxide fuel cell (SOFC) anode materials, was studied at 1023–1273 K in the oxygen partial pressure range from 10^{-20} to 0.5 atm. In oxidizing and moderately reducing atmospheres, this perovskite exhibits a predominant p-type electronic conductivity, which lies in the range 20–35 S/cm and is essentially $p(O_2)$-independent. Reducing $p(O_2)$ below 10^{-16}–10^{-12} atm leads to a drastic increase in the oxygen vacancy concentration, ionic conductivity and oxygen permeability, whilst the total conductivity decreases down to 1–3 S/cm. The ion transference numbers, calculated from the oxygen permeation data and measured by the faradaic efficiency technique controlling oxygen pressures at both sides of dense ceramic membranes, vary in the range 9×10^{-7} to 8×10^{-5} at 1223–1273 K, increasing with temperature. The average thermal expansion coefficients in air increases from 10.8×10^{-6} K^{-1} at 373–923 K up to 14.1×10^{-6} K^{-1} at 1223–1523 K. Under both oxidizing and reducing conditions, the electrochemical behavior of porous $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_3$-based electrodes applied onto $(La_{0.9}Sr_{0.1})_{0.98}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ solid electrolyte suggests a key role of electronic transport-related processes. As a result, the electrode performance can be significantly enhanced by optimizing current collector and/or by introducing an additional electronically-conductive component, such as metallic Ni or Ag. Further decrease of overpotentials may be achieved via incorporation of electrocatalytically active additions, including praseodymium oxide in oxidizing atmospheres and ceria at low $p(O_2)$.
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Keywords: Perovskite; SOFC anode; Mixed conductivity; Oxygen permeation; Faradaic efficiency; Dilatometry; Electrode polarization

1. Introduction

Electrical power generation systems based on solid oxide fuel cells (SOFCs) are beneficial with respect to other energy-conversion engines due to high efficiency, fuel flexibility, environmental safety and possibility to recover exhaust heat [1–3]. At the same time, significant efforts are still necessary to develop commercially feasible fuel cells, in particular to increase their long-term stability and to decrease costs. As the conventional Ni-containing cermet anodes exhibit extensive volume changes on redox cycling and promote carbon

deposition deteriorating their performance, one important aspect in the SOFC developments is the search for new anode materials. A promising combination of properties, including phase and dimensional stability, high electrochemical activity in both reducing and oxidizing atmospheres, and chemical compatibility with various solid electrolytes, was recently reported for $(La,Sr)(Cr,Mn)O_{3-\delta}$ perovskites [4–11]. As an example, porous $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ layers covered with Au paste and mesh, demonstrated anodic polarization resistances of 0.90 $\Omega \times cm^2$ in diluted H_2 and 0.47 $\Omega \times cm^2$ in wet 100% H_2, in contact with yttria-stabilized zirconia (YSZ) solid electrolyte at 1198 K [4]. The use of interfacial $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO) layer between the anode and electrolyte increases electrode performance [4]. Low overpotentials were also observed for $(La_{0.75}Sr_{0.25})_{1-x}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ ($x=0$–0.05) applied onto $LaGaO_3$-based electrolytes [7,9], and for

$La_{0.8}Sr_{0.2}Cr_{0.8}Mn_{0.2}O_{3−δ}–Ni–Ce_{0.9}Gd_{0.1}O_{2−δ}$ cermets in contact with gadolinia-doped ceria [5]. On the contrary, a relatively poor performance was reported for $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3−δ}$| YSZ cells, particularly due to poor electrode adhesion [10]. In the latter case, the electrochemical activity and adhesion were substantially improved by YSZ additions, which also increase the ionic conductivity of anode materials. The level of oxygen ionic conduction in $(La_{0.75}Sr_{0.25})_{1−x}Cr_{0.5}Mn_{0.5}O_{3−δ}$ materials is still unknown.

Other important factors, which may affect performance of manganite–chromite electrodes, are the lattice expansion and electronic conductivity [5,6,10]. In air, the average thermal expansion coefficient (TEC) was reported as low as $9.3 × 10^{−6}$ $K^{−1}$ at 340–1230 K for $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_3$ ceramics [4]; a substantially higher value, $13.7 × 10^{−6}$ $K^{−1}$ at 430–1170 K, was however obtained for $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ [10]. Creation of A-site cation vacancies was found to decrease chemically-induced expansion on redox cycling [4]. The electronic conductivity of $(La,Sr)(Cr,Mn)O_{3−δ}$ perovskites in reducing atmospheres is relatively low, <5 S/cm at 1000–1100 K [4–6]. Note that the current–constriction effects on electrode polarization are significant even for $(La,Sr)MnO_{3−δ}$, where the conductivity is higher than 100 S/cm [11]. For model cells, the limiting effects of electronic transport can be avoided using specific current collectors, such as Au paste and mesh [4,7–9] or Ag paint [5]. This approach cannot be used in real SOFCs; the practical current collectors made of various stainless steels or $LaCrO_3$-based ceramics [1–3] possess considerably higher contact and/or bulk resistances compared to the noble metals. On the other hand, increasing oxygen chemical potential under anodic polarization is expected to increase electronic transport in $(La,Sr)(Cr,Mn)O_{3−δ}$ electrodes [6].

The present work is focused on the studies of partial ionic and electronic conductivities, oxygen permeability, and thermal and chemical expansion of $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3−δ}$ in a wide range of oxygen partial pressures. One particular goal was to assess possible correlations between the transport properties and electrochemical behavior. As serious technological and economic benefits may be expected from the symmetrical SOFCs with similar cathode and anode compositions [8], the performance of manganite–chromite electrodes was evaluated under both reducing and oxidizing conditions. The solid electrolyte selected for this case study, $(La_{0.9}Sr_{0.1})_{0.98}Ga_{0.8}Mg_{0.2}O_{3−δ}$ (LSGM), was characterized elsewhere [12]. Doped lanthanum gallates are well-known for high ionic conduction and moderate TECs [13,14]; chemical reactivity between these electrolytes and $(La,Sr)(Cr,Mn)O_{3−δ}$ at temperatures below 1650–1700 K was reported endurable [9,15].

2. Experimental

2.1. Materials processing and characterization

Submicron powder of $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3−δ}$ was prepared via the glycine–nitrate process (GNP), a self-combustion technique using glycine as a fuel and chelating agent and nitrates of metal components as oxidant [16]. After the GNP, the powder

was calcined at 1273–1573 K for 7 h in air and then ball-milled. Gas-tight ceramic samples with 94–95% density were sintered in air at 1873 K for 5 h with subsequent slow cooling (3 K/min). The porous electrodes (sheet density of $8.6 ± 0.2$ mg/cm^2) were applied onto LSGM substrates and annealed in air at 1473 K for 2 h. This firing schedule was based on optimum conditions reported for $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ — YSZ (50–50 wt.%) composites [10]. Without sintering aids, however, the resultant mechanical strength of electrodes was found insufficient; at higher sintering temperatures an extensive diffusion of Mn and Cr cations into LSGM was observed, which may lead to increasing electronic conductivity of LSGM electrolyte and blocking ionic transport in the electrolyte surface layers [17]. Therefore, 2 wt.% Bi_2CuO_4 sintering aid was introduced in the slurry deposited onto LSGM, as proposed elsewhere [18]. As the performance of oxide cathodes may often be improved by metallic silver dispersion [18,19], a series of electrodes with addition of 10 wt.% Ag powder was prepared and tested; these were sintered at 1273 K during 2 h. For all anodes, an intermediate CGO layer was applied onto LSGM prior to $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3−δ}$ deposition and fired at 1473 K for 2 h; the interfacial layers were made of nanocrystalline $Ce_{0.8}Gd_{0.2}O_{2−δ}$ synthesized by the cellulose-precursor technique [20].

Formation of single perovskite phase in $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3−δ}$ ceramics and electrodes was confirmed by X-ray diffraction (XRD) analysis; examples of the XRD patterns are presented in Fig. 1. The cation composition was verified by inductively-coupled plasma (ICP) spectroscopic analysis, which confirmed that the deviations from nominal composition are lower than 2 at.%. General characterization included also scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM/EDS), dilatometry, determination of the total conductivity (4-probe DC) and Seebeck coefficient as functions of the oxygen partial pressure, and measurements of the steady-state oxygen permeability (OP). Description of the
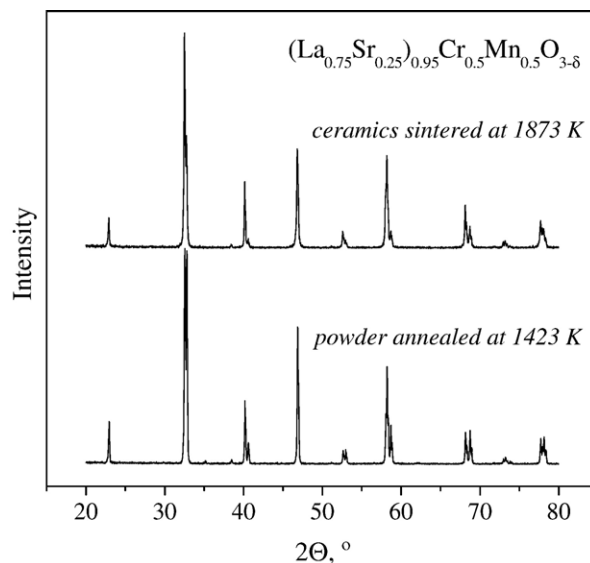

Fig. 1. XRD patterns of $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3−δ}$ after annealing in air at 1423–1873 K.