Surface states and stability of Fe-containing perovskite electrodes for SOFCs/SOECs by conversion-electron Mössbauer spectroscopy

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A R T I C L E   I N F O

Abstract

Conversion-electron Mössbauer spectroscopy analysis of model electrochemical cells, comprising porous 57Fe-enriched (La0.9Sr0.1)0.98Cr0.6Fe0.3Mg0.1O3 electrodes and lanthanum gallate solid electrolyte, showed no reductive decomposition of the perovskite electrode material in H2-containing atmosphere at 1073 K, even in the steam electrolysis regime. The predominant state of iron cations in the electrode surface layers was found to remain trivalent irrespective of the oxygen partial pressure in surrounding atmosphere and polarization, whilst oxygen coordination of Fe3+ decreases on lowering electrode potential.

1. Introduction

Energy-related systems based on solid oxide fuel cells (SOFCs) and electrolysis cells (SOECs) offer important potential advantages due to a high efficiency, environmental safety, fuel flexibility and possibility to recover exhaust heat [1–5]. Significant efforts are focused on the developments of oxide electrode materials stable under both oxidizing and reducing environments, in order to reduce costs of the electrochemical devices and to suppress degradation phenomena, such as coking and sulfur poisoning of the SOFC anodes. These problems are well known for the conventional Ni-containing cermet electrodes, which also degrade owing to large volume changes on redox cycling and sintering during SOFC operation. A very promising combination of properties was recently reported for perovskite-type (LaSr)3(3−δ)CrδMn1−δO3−δ (LSCM) [2,3], where the presence of rigid CrO6 octahedra in the crystal structure enables its stabilization down to low oxygen chemical potentials necessary for the SOFC anode operation, whilst moderate acceptor-type doping is necessary to improve electronic and ionic transport. The incorporation of iron in LaCrO3 may further enhance electrode performance [3,4]. However, information on phase stability of (LaSr)3(3−δ)CrδFeδO3−δ in reducing atmospheres is still quite contradictory [3–6]. Moreover, no data on surface states in these perovskite electrodes under reducing conditions are available up to now, although the surface defects and oxygen deficiency level are critically important for the electrochemical and catalytic activity [7–9]. It should also be mentioned that under high current densities, the oxygen chemical potentials at an electrode surface and electrode/electrolyte interface differ substantially from the surrounding gaseous phase [1,7], thus raising additional requirements to the redox and dimensional stability of the electrode materials.

The present work was centered on the analysis of iron oxidation states and coordination in the surface and near-surface layers of model 57Fe-enriched (La0.9Sr0.1)0.98Cr0.6Fe0.3Mg0.1O3−δ electrodes by conversion-electron Mössbauer spectroscopy (CEMS). To authors’ knowledge, the CEMS technique is used in this area of solid state electrochemistry for the first time. Although CEMS is a highly-selective and non-destructive method advantageous to study interfacial phenomena, its applications to bulky complex materials are rare as it requires large concentrations of 57Fe isotope on and near the surface. Hence, the conversion-electron Mössbauer (CEM) spectra are usually collected for iron-rich compositions, for 57Fe-doped thin films, or when 57Fe is implanted into surfaces. The maximum depth analyzed by integral CEMS registering all electrons back-scattered from the surface is approximately 200–300 nm [10]. In this work, 57Fe-enriched perovskite (La0.9Sr0.1)0.98Cr0.6Fe0.3Mg0.1O3−δ was selected as a model electrode material with relatively high concentration of iron and moderate content of acceptor-type dopants, Sr2+ and Mg2+; further substitution is expected to significantly decrease thermodynamic stability of the perovskite-type solid solution [5]. The CEM spectra of porous (La0.9Sr0.1)0.98Cr0.6Fe0.3Mg0.1O3−δ electrodes are...
compared to the results of transmission Mössbauer spectroscopy (TMS), collected using powdered samples equilibrated in various atmospheres.

2. Experimental

The experimental conditions used in this work for the electrode preparation and characterization were similar to those described earlier for LSCM anodes[11]. Single-phase (La$_{0.9}$Sr$_{0.1}$)$_{0.98}$Cr$_{0.6}$Fe$_{0.3}$Mg$_{0.1}$O$_{3-\delta}$ powder was synthesized by the glycine–nitrate process (GNP). Prior to the synthesis, the stoichiometric amount of metallic iron enriched with $^{57}$Fe isotope (95.7%, Chemgas, France) was dissolved in diluted nitric acid and then added into the solution used for the GNP. The obtained powders were annealed at 1273–1473 K in air for 12 h with several intermediate regrinding steps. Phase purity was confirmed by X-ray diffraction (XRD), Fig. 1. The porous electrode layers were screen-printed onto dense solid-electrolyte membranes of (La$_{0.9}$Sr$_{0.1}$)$_{0.98}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-\delta}$ (LSGM) tested elsewhere[12], and were sintered in air at 1473 K for 2 h. Examination by scanning electron microscopy (SEM) revealed the formation of homogeneous electrode microstructure with a high porosity and submicron grain size, which was essentially unchanged during polarization tests. Typical SEM micrographs are presented in the inset of Fig. 1. The area, thickness and sheet density of the working electrodes were 1.44±0.01 cm$^2$, 52±6 μm and 16±2 mg/cm$^2$, respectively; the electrolyte membrane thickness was 1.35±0.01 mm. The counter electrodes made of porous Pt were applied onto the opposite side of LSGM and sintered in air at 1273 K for 0.5 h. The model electrochemical cells were placed at 1073 K in flowing wet 10% H$_2$–90% N$_2$ gas mixture where the oxygen partial pressure, $p$(O$_2$), was continuously monitored by an electrochemical oxygen sensor. In this work, $p$(O$_2$) was fixed equal to 1×10$^{-20}$ atm at 1073 K in all cases. After equilibration, DC voltage (U) of $±1.1$ V or $−1.1$ V was applied to the cell electrodes during 24 h. Following fast cooling (8–12 K/min) under the applied DC voltage, the electrochemical cells were analyzed by CEMS and SEM/EDS. For the sake of comparison, a series of powdered samples of (La$_{0.9}$Sr$_{0.1}$)$_{0.98}$Cr$_{0.6}$Fe$_{0.3}$Mg$_{0.1}$O$_{3-\delta}$ were annealed in the same atmosphere at 1023–1223 K during 24 h and then studied by XRD and TMS. The equipment and experimental procedures used for XRD, TMS and SEM/EDS were described elsewhere[9,11–13]. CEMS was performed at room temperature, with the samples mounted inside a...
3. Results and discussion

Fig. 2 compares the CEM and TM spectra of porous (La0.9Sr0.1)0.98Cr0.6Fe0.3Mg0.1O3 ceramics and electrodes after cathodic and anodic polarization tests in wet 10% H2–90% N2 during 24 h, and powders of the same composition equilibrated in reducing and oxidizing atmospheres. The room-temperature and 4.2 K TM spectra of the reduced powder annealed at p(O2) = 10^{-20} atm and 1073 K, consist of two quadrupole doublets and two magnetic sextets, respectively (Fig. 2, bottom). These two subspectra clearly indicate the presence of Fe^{3+} cations with 6- and 5-fold oxygen coordination (Table 1), with considerably higher isomer shifts (IS) than those typical for tetrahedral Fe^{3+}, 0.14-0.22 mm/s at room temperature [13–15]. In addition to lower IS values, the signal of penta-coordinated Fe^{3+} has higher quadrupole splitting (QS) as expected for a site with more distorted coordination polyhedra compared to the iron-oxygen octahedra. The TM spectra of the oxidized perovskite phase equilibrated with atmospheric oxygen show that the octahedrally-coordinated Fe^{3+} state is predominant (Table 1). Moreover, neither Fe^{2+}, Fe^{4+} nor tetrahedrally-coordinated Fe^{3+} can be detected in the reduced and oxidized powders. Notice that, due to the significantly lower IS and magnetic hyperfine fields of 4-fold coordinated Fe^{3+}, at least the peaks located at the highest Doppler velocity of the corresponding sextets should be resolved at 4.2 K if the Fe^{3+}O_{4} tetrahedra were present [9,14,15]. The observed behavior shows hence that the oxygen vacancies formed on reduction of (La0.9Sr0.1)0.98Cr0.6Fe0.3Mg0.1O3 are statistically distributed in the lattice, whereas the oxidation state of iron cations in this perovskite is essentially independent of the oxygen nonstoichiometry and remains 3+ within the limits of experimental uncertainty. The latter means, in particular, that the vacancy formation is charge-compensated by Cr^{3+}/Cr^{4+} redox couple. This trend is opposite with respect to La_{1–x}Sr_{x}Cr_{0.5}Mn_{0.5}O_{3}+δ series [16] where X-ray absorption spectroscopy indicated an essentially constant state of Cr^{3+} cations.

Irrespective of the electronic subsystem, the absence of peaks characteristic of Fe^{2+} and metallic Fe in the TM spectra of reduced (La0.9Sr0.1)0.98Cr0.6Fe0.3Mg0.1O3 (Fig. 2) confirms that the perovskite phase is preserved at p(O2) = 10^{-20} atm and 1073 K. This conclusion is in agreement with the XRD results (Fig. 1) indicating that no extra phases appear on reduction. Decreasing p(O2) leads to a transition from orthorhombic (space group Pnma) to rhombohedrally distorted perovskite structure (S.G. R3c), as reported earlier for La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3}–δ [8], and to a moderate lattice expansion due to the oxygen vacancy formation. For example, the unit cell parameters of oxidized (La0.9Sr0.1)0.98Cr0.6Fe0.3Mg0.1O3–δ, calculated from the room-temperature XRD patterns, were: a = 5.5063(2) Å, b = 5.5156(2) Å, c = 7.7976(4) Å, V = 236.82(2) Å³. After reduction at 1223 K and p(O2) = 5 × 10^{-18} atm, the rhombohedral lattice parameters expressed in hexagonal settings were: a = 5.5363(1) Å, c = 13.4484(3) Å, V = 356.97(1) Å³. The increase in the unit cell volume (V) normalized to orthorhombic perovskite, 0.49%, is comparable to analogous results on La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_{3}–0.31% [8]. Taking into account the TMS data, this volume increment is essentially contributed by increasing radius of chromium cations when their oxidation state decreases.

As for TMS, the room-temperature CEM spectra of the porous electrodes, collected after the polarization tests in flowing 10%H2–90% N2 at 1073 K, exhibit only two doublets corresponding to hexa- and penta-coordinated Fe^{3+} (Fig. 2 and Table 1). Again, no traces of metallic Fe and Fe^{2+} states are visible, even after cathodic polarization (U = –1.1 V). The latter regime corresponds to the water vapor electrolysis, when the oxygen chemical potential at the electrode is much lower than that in the supplied gas flow, p(O2) = 10^{-20} atm. Under anodic polarization (U = +1.1 V), this chemical potential is higher as oxygen is pumped through the solid electrolyte membrane onto the working electrode. The fraction of penta-coordinated Fe^{3+} was found to exhibit a linear dependence on the applied voltage (inset in Fig. 2), reflecting the oxygen deficiency variations induced by the electrode polarization. The changes in Fe^{3+} (CN=5) concentration with respect to the equilibrium conditions are relatively small but statistically significant (Table 1).

In summary, the results demonstrate that CEMS is sensitive enough to the local alterations of oxygen nonstoichiometry in the Fe–containing electrode surface layers under polarization. This makes it possible, in particular, to experimentally study the oxygen chemical potential distribution across electrode bulk and current-dependent defect chemistry in porous electrodes by the differential CEMS enabling to collect signals from different depths, and/or by combining layer-by-layer polishing of the electrode layers and integral CEMS technique. The CEMS and TMS analyses of the model electrochemical cells with (La0.9Sr0.1)0.98Cr0.6Fe0.3Mg0.1O3–δ layers show also that the trivalent state of iron cations remains essentially unchanged under reducing conditions, even in the steam electrolysis regime.

Table 1

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Technique</th>
<th>T, K</th>
<th>IS, mm/s</th>
<th>QS, mm/s</th>
<th>2ε, mm/s</th>
<th>B_{4d}, T</th>
<th>CN</th>
<th>δ, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibration in air at 295 K</td>
<td>TMS</td>
<td>295</td>
<td>0.36</td>
<td>0.38</td>
<td>–0.05</td>
<td>47.2 a</td>
<td>6</td>
<td>100</td>
</tr>
<tr>
<td>Equilibration in 10% H2 at 1073 K</td>
<td>TMS</td>
<td>295</td>
<td>0.35</td>
<td>0.31</td>
<td>–</td>
<td>47.2 a</td>
<td>6</td>
<td>100</td>
</tr>
<tr>
<td>Anodic polarization in 10% H2 at 1073 K</td>
<td>CEMS</td>
<td>295</td>
<td>0.37</td>
<td>0.32</td>
<td>–0.10</td>
<td>46.6</td>
<td>5</td>
<td>31</td>
</tr>
<tr>
<td>Cathodic polarization in 10% H2 at 1073 K</td>
<td>CEMS</td>
<td>295</td>
<td>0.28</td>
<td>1.13</td>
<td>–</td>
<td>5</td>
<td>29</td>
<td></td>
</tr>
</tbody>
</table>

a IS, QS, 2ε = (ε^{2}V_{zz}Q/4) (3cos^{2}θ−1), B_{4d}, I and CN are the isomer shift relative to metallic α-Fe at 295 K, quadruple splitting, quadrupole shift, magnetic hyperfine field, relative area and oxygen coordination number, respectively. Estimated errors are ≤0.2 T for B_{4d}, ≤1% for I, and ≤0.02 mm/s for the other parameters.

b Average values of a magnetic sextet distribution.
Although long-term electrochemical testing in pure H₂–H₂O, CO–CO₂ and converted CH₄ atmospheres is necessary, the data obtained in this work suggest that Fe-substituted chromites and their derivatives may provide a stable operation of intermediate-temperature SOFC anodes.

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References