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Chemical Interaction between Perovskite $La_{0.6}Sr_{0.4}FeO_3$ and Super-Ionic $Zr_{0.84}Y_{0.16}O_x$

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Perovskites are materials of very versatile properties. They may be used in various ways and structures. In this work the results of investigation of the $Zr_{0.84}Y_{0.16}O_x$ electrolyte on $La_{0.6}Sr_{0.4}FeO_3$ perovskite support are presented. The perovskite support was fabricated by iso-axially die-pressing of $La_{0.6}Sr_{0.4}FeO_3$ powders and sintering at 1150°C. The $Zr_{0.84}Y_{0.16}O_x$ layer was deposited on $La_{0.6}Sr_{0.4}FeO_3$ by a combination of colloidal suspension and polymer precursor methods. In this way the dense electrolyte layer was prepared at as low temperature as 400°C. This method may be also useful for high-T_c superconductor layers deposition. The chemical interaction between the electrolyte layer and perovskite support was investigated by X-ray diffraction. It was shown that no reaction occurs between cathode and electrolyte until 900°C. Above 1200°C, parameters of the $La_{0.6}Sr_{0.4}FeO_3$ unit cell increase. It suggests that the reaction between $Zr_{0.84}Y_{0.16}O_x$ and $La_{0.6}Sr_{0.4}FeO_3$ is accompanied by substitutional changes in the $La_{0.6}Sr_{0.4}FeO_3$.

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1. Introduction

Perovskites are widely known as materials of very versatile properties. They may be superconductors, insulators, ferroelectrics, ionic conductors, magnetic materials, or even materials of extraordinary mechanical properties. In many cases it is beneficial to use the perovskite as a support of the electroceramic device. In this work a perovskite is used as a support for a thin electrolyte layer. There are several technologies, which allow deposition of a relatively thin electrolyte layer on porous structures [1, 2]. Those methods include chemical and physical deposition, such

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as electrochemical vapor deposition (EVD) or magnetron sputtering, and liquid precursor and powder processing techniques such as polymer spin coating or tape casting. Powder based techniques require high temperature co-sintering of the perovskite and electrolyte, which frequently leads to formation of high resistance interfacial layers. Chemical and physical deposition techniques allow deposition of dense electrolyte layers at low temperature, but the cost of such kind of processing is too high for widespread applications. An alternative technology, which seems to overcome those problems, is a combination of colloidal suspension and polymer precursor deposition methods [3, 4]. It allows deposition of 1–10 μm dense electrolyte layers on porous perovskite support. $La_{1-x}Sr_xFeO_3$ (LSFx) are a group of perovskites, which are perspective cathode materials for solid oxide fuel cells (SOFCs). In comparison to lanthanum manganites they exhibit superior performance as SOFC cathode [5, 6]. Many attempts have already been made to investigate electrochemical properties and synthesis routes involving both solid state and preferred "soft chemistry" methods [7, 8]. It is also investigated as possible thin film cathode material for micro SOFCs applications [9].

In literature, the interactions between cathode materials and $Zr_{0.84}Y_{0.16}O_x$ (YSZ) electrolyte were investigated in order to understand observed degradation of electrical parameters of SOFCs (e.g. [10–14]). Mainly, $La_{0.8}Sr_{0.2}MnO_3$ (LSM20) and $La_{0.8}Sr_{0.2}FeO_3$ (LSF20), which have relatively low content of Sr ions, were tested. In those studies powders of electrolyte and cathode materials were mixed and sintered and the resulting phases were evaluated mainly by X-ray diffraction (XRD) analysis. It was found that at temperatures $\approx 1000°C$ the diffusion between cathode and electrolyte takes place leading to an increase in the unit cell of cathode material. Moreover, at these temperatures secondary phases can be formed. For instance, in case of the LSM mainly $La_2Zr_2O_7$ and $SrZrO_3$, while for LSF $SrZrO_3$ was observed [11]. Some discrepancy in literature data is noted. For example, Simner et al. [12–14] reported no formation of $SrZrO_3$ in a LSF20/YSZ system, while in Kindermann et al. works [11] this phase is always formed in a LSFM40/YSZ system. Either the amount of strontium or the substitutions for the Fe ion seem to play important role in those interactions.

In this work the results of investigation of the $Zr_{0.84}Y_{0.16}O_x$ electrolyte on $La_{0.6}Sr_{0.4}FeO_3$ perovskite (LSF40/YSZ) are presented. The chemical interaction between the electrolyte layer and perovskite support was investigated by XRD. It should be also stressed that similar problems of solid-state chemical interaction between a perovskite and other material may be encountered in other fields of materials engineering, solid state physics or chemistry. For instance, they may be relevant in high-T_c superconductor thin layers deposition or preparation of composite superconductors.

2. Experimental

The LSF40 ($La_{0.6}Sr_{0.4}FeO_3$) perovskites were prepared by a modified Pechini method [15]. Metal nitrates of $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$ and $Fe(NO_3)_3 \cdot 8H_2O$

in stoichiometric ratios were dissolved in deionized water and ethylene glycol. The solution was stirred for 12 h at 75°C to evaporate water and obtain viscous liquid. Then it was pyrolized at 400°C on a hot plate. The obtained powders were first calcined at 1050°C and then iso-axially die-pressed into pellets [16].

The YSZ film was deposited by net-shape technique, which is a combination of colloidal suspension and polymer precursor deposition methods. The colloid contained $\mathrm{Zr}_{0.84}\mathrm{Y}_{0.16}\mathrm{O}_x$ microcrystallites suspended in mixture of deionized water, ethanol and ethylene glycol. The polymer precursor was prepared in a similar manner as LSF using stoichiometric amounts of zirconium chloride and yttrium nitrate. They were dissolved in ethylene glycol and deionized water and stirred for 12 h at 75°C to evaporate water and obtain viscous liquid [17]. First, the YSZ colloidal suspension was spin-coated on the fabricated cathode support at 7000 rpm and fired at 360°C to obtain electrolyte skeleton. Then the YSZ polymer precursor was used to impregnate the YSZ skeleton. To obtain dense YSZ film the precursor was deposited several times by spin-coating at 3000 rpm. After each deposition the sample was fired at 360°C in order to decompose the organics of polymer and as a result create thin nanocrystalline YSZ layer. The samples were sintered at various temperatures between 600°C and 1200°C for 2 h.

The LSF support and composite of YSZ film on LSF support were investigated by XRD using Phillips X'Pert system with Cu K_α radiation. The samples were scanned over the 2θ range from 20° to 90° with scan rate 0.6°/min at room temperature.

3. Results and discussion

The $\mathrm{La}_{0.6}\mathrm{Sr}_{0.4}\mathrm{FeO}_3$ perovskite as a support for the electrolyte layer should be porous to maximize the permeability of oxygen molecules through the support. Simultaneously, it should be mechanically strong and a good electronic conductor. These three features contradict one another and therefore a kind of a compromise has to be reached. Namely, sintering temperature and compacting pressure should be high enough for the material to be a single-phase perovskite, a good electronic conductor and a good mechanical support. On the other hand, they should be low enough to ensure high porosity of the material. In order to meet those requirements the properties of the $\mathrm{La}_{0.6}\mathrm{Sr}_{0.4}\mathrm{FeO}_3$ supports sintered at different temperatures were evaluated. The compacting pressure of powder of 100 MPa was used. Figure 1 presents scanning electron microscopy (SEM) images of LSF support sintered at 1100°C and 1200°C. It can be seen that porosity of the sample sintered at 1200°C is significantly lower than that sintered at 1100°C. XRD analysis shows that the sample sintered at 1050°C does not contain secondary phases. However, this temperature might be rather low to obtain satisfactory level of electronic conductivity. Taking all the above results into consideration the sintering temperature of 1150°C and the compacting pressure of 100 MPa have been chosen as optimal preparation conditions. As a result, the LSF perovskite supports were fabricated, which were thinner than 0.8 mm, mechanically stable and porous (60% of theoretical density) and their conductivity was higher than 30 S/cm.

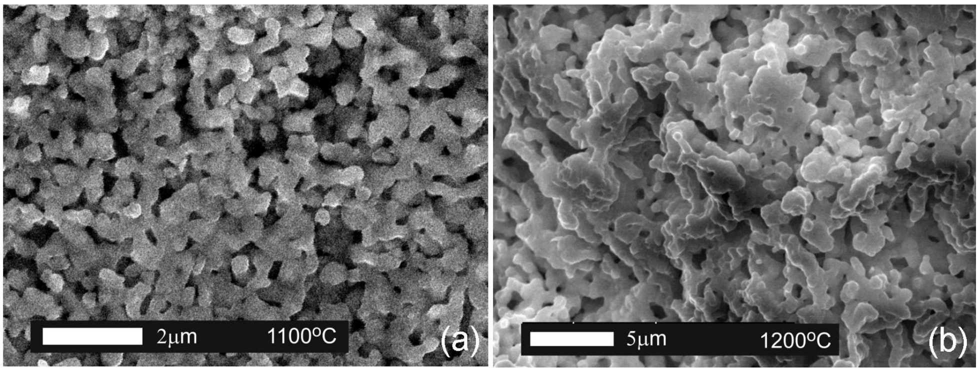

Fig. 1. SEM images of LSF perovskite: surface of LSF sintered at 1100°C (a) and cross-section of LSF sintered at 1200°C (b).

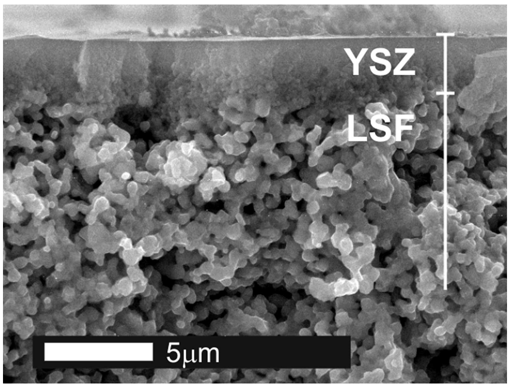

Fig. 2. SEM image of cross-section of YSZ film deposited on LSF (film sintered at 360°C).

The LSF supports were used to deposit the $Zr_{0.84}Y_{0.16}O_x$ electrolyte film. The composite electrolyte–support structure was evaluated and the results are presented in Figs. 2–4. Figure 2 presents SEM image of cross-section of the film–support structure. The film is about 3 μm thick. Neither pinholes nor cracks are observed. The crystallization of the electrolyte layer and chemical interaction between the electrolyte and perovskite support were investigated by XRD. The results are shown in Fig. 3. X-ray diffraction shows that no reaction occurs between cathode and electrolyte until 900°C. Above 900°C a $SrZrO_3$ crystallizes on the interface between the support and the electrolyte. Moreover, above 1200°C, volume of the LSF unit cell significantly increases, while the cell unit of YSZ remains

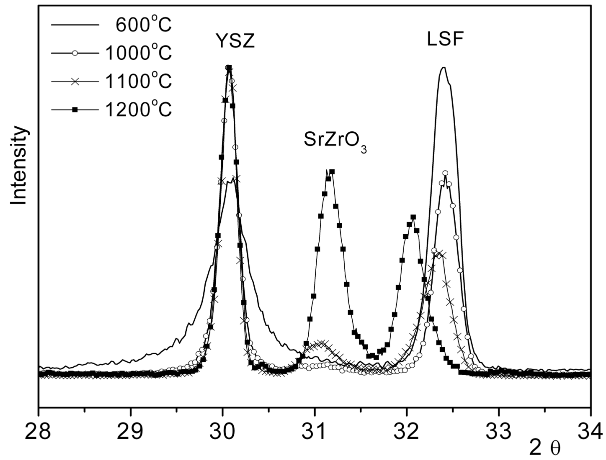

Fig. 3. XRD spectra of YSZ film on LSF perovskite (film sintered at various temperatures).

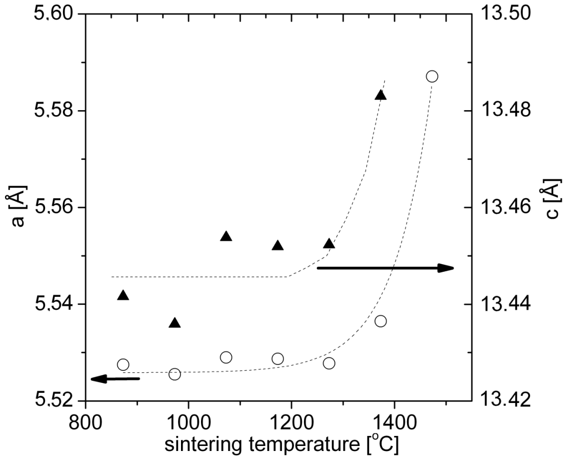

Fig. 4. Unit cell parameters of LSF perovskite as a function of sintering temperature of YSZ film.

unchanged (Fig. 4). Similar increase in the unit cell has been reported before by Simner et al. [12, 13]. When the temperature is sufficiently high (above 1100°C), Zr ions diffuse into the LSF and take the vacant Fe sites. This is accompanied by an increase in the unit cell volume [12]. The unit cell of the YSZ electrolyte does not change significantly despite the possible presence of point defects. It has been shown before that this unit cell is relatively not sensitive to such changes [18].

On the other hand, Simner et al. did not observe crystallization of $SrZrO_3$ even at 1200°C. This contradiction may be caused by the fact that the LSF supports studied in the present work contained more strontium than those investigated by Simner et al. ($La_{0.8}Sr_{0.2}FeO_3$ in their case). As a result, the chemical interaction between the LSF and YSZ can be more clearly seen. In our case the thin film crystallizes during sintering on the cathode substrate and therefore undergoes physicochemical changes. All of the above reasons can attribute to the observed differences.

4. Conclusions

Lowering to minimum the compacting pressure and adjusting sintering temperature allows obtaining LSF perovskite support with 60% of theoretical density and conductivity of more than 30 S/cm. Those LSF are no more than 0.8 mm thick and mechanically stable and therefore can be used as supports for electrolyte films. Employed in this work deposition technique of electrolyte films allows obtaining continuous and crack free 3 μm thick YSZ layers.

The chemical interaction between the electrolyte layer and perovskite support was investigated by XRD. It has been shown that no reaction occurs between cathode and electrolyte until 900°C. Above this temperature Zr and Fe ions diffuse out of the YSZ and LSF, respectively. As a result of those processes, the $SrZrO_3$ phase is formed. Above 1100°C substitutional changes in the LSF perovskite also occur.

Acknowledgments

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