

Article

Electrical Conductivity of Thin Film $\text{SrTi}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ -Supported $\text{Sr}_{0.98}\text{Zr}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$ Electrolyte

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Abstract: Thin films of $\text{Sr}_{0.98}\text{Zr}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$ (SZY) electrolyte were grown on porous supporting $\text{SrTi}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ electrodes by the chemical solution deposition method from a low-viscous solution of inorganic salts. The films were characterized by X-ray diffraction and scanning electron microscopy. The gas-tightness of the films was evaluated using the differential-pressure method. The across-plane electrical conductivity of 1 mm thick SZY film was measured by impedance spectroscopy and compared to that of a massive ceramic sample. The revealed difference in electrical properties of the film and massive SZY samples indicates that diffusional interaction between the film and the substrate influences the performance of the supported electrolyte.

Keywords: SOFC; thin film electrolyte; Y-doped SrZrO_3 ; electrode-supported SOFC; chemical solution deposition; electrical conductivity; Fe-doped SrTiO_3



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1. Introduction

Solid oxide fuel cells (SOFCs) are considered to be the most promising type of fuel cells for highly efficient power generation, with zero levels of pollutant emissions and noise [1,2]. However, SOFCs operate at high temperatures (800–1000 °C), which entails significant problems on materials selection. Reliability and durability issues are the most essential obstacles for mass production because of degradation of SOFC components—an electrolyte, electrodes, interconnects, etc.—in harsh operating conditions. The current trends in the SOFC development field are focused on reducing the operating temperature to 500–700 °C. An effective way to decrease this temperature is using the proton-conducting electrolytes instead of the oxide-ion ones (typically, yttria-stabilized zirconia) due to the higher mobility and the lower activation energy of proton charge carriers [3,4]. Proton-conducting oxides with a perovskite structure are promising candidates for application as electrolytes in SOFCs [5,6].

A further decrease in the SOFC operating temperature is possible by lowering a thickness of a solid-oxide electrolyte, which allows us to lessen the ohmic losses [7–9]. However, in the case of thin-film electrolytes, the issue of chemical stability becomes more serious than for the bulky ones. The electrolyte material must stay chemically inert in both fuel and oxidizing atmospheres at high temperatures, being in contact with electrodes, to ensure a long lifespan of a SOFC. Therefore, the chemically and thermally stable AZrO_3 ($A = \text{Ca}, \text{Sr}$) oxides with a perovskite-type structure, possessing appreciable proton conductivity in wet atmospheres [1,6,10], are considered as promising materials for application as a thin film electrolyte in SOFCs.

In contrast to the electrolyte-supported SOFCs, in which a solid-oxide membrane ensures mechanical strength of the cell, in the case of the SOFCs with a thin-film electrolyte, one of the electrodes usually serves as a support [11,12]. It should be noted that the electrolyte must be dense to prevent the gas leakage, which could entail decreasing an output voltage, while the electrodes must be porous in order to promote transportation of the electrochemically active gas components to/from the three-phase boundary, where

the electrochemical reactions occur. Therefore, for fabrication of an electrode-supported SOFC, a dense thin electrolyte is to be deposited on a porous supporting electrode. Solid oxide films can be obtained by chemical vapor deposition (CVD) [13–16], physical vapor deposition (PVD) [17–19], or chemical solution deposition (CSD) [17–19] methods. PVD methods are based on evaporation or sputtering a target and transportation of these particles to a substrate surface, where they condense forming a film. PVD technologies require high vacuum conditions to avoid dissipation of energy of the film-forming particles during collisions with gas molecules [19]. CVD methods include the atomic layer deposition (ALD), plasma enhanced CVD (PECVD), metalorganic CVD (MOCVD), etc. These methods are based on a heterogeneous reaction of gaseous precursors on a substrate surface, which results in formation of a film [16]. Chemical solution deposition method is founded on application of a solution containing the film-forming cations onto substrates by dip-coating, spin-coating or spraying, followed by synthesis of a target oxide film. CSD is a technologically simple and cost-effective way to fabricate solid-oxide films of complex composition. Another notable advantage of CSD is the possibility to deposit films on substrates with various shapes; so, it can be used for fabrication of not only planar, but also tubular or other types of SOFCs.

In our previous studies, it was shown that the gas-tight films of CaZrO_3 - and SrZrO_3 -based electrolytes on porous supporting electrodes can be grown by CSD from low-viscous solutions of inorganic salts through the multi-step dip-coating/annealing process [20–24]. Upon the multi-step deposition of a low-viscous solution onto a porous substrate, the solution first gradually fills the pores, thus creating the electrode–electrolyte composite layer, until a continuous coating is formed. The intermediate composite layer is expected to adjust the differences in the structural, thermal and chemical properties of the electrolyte and electrode materials, and thus improve the film adhesion. Additionally, this composite layer enlarges the three-phase boundary length, which should improve the SOFC performance. The disadvantage of using the low-viscous solutions is the need for multiple deposition in order to achieve the target thickness and gas-tightness of the film, e.g., the gas-tight 3 mm thick $\text{CaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ film on the porous $\text{SrTi}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ supporting electrode (28% porosity) was obtained by the 15-fold solution deposition [23]. Fe-doped SrTiO_3 is a mixed oxide-ion and electronic conductor possessing the thermal expansion coefficient (TEC) (10.7×10^{-6} – $13.7 \times 10^{-6} \text{ K}^{-1}$ in a hydrogen atmosphere [25]) similar to those of typical solid oxide electrolytes ($\sim 10 \times 10^{-6} \text{ K}^{-1}$ for yttria-stabilized zirconia [26,27]), which is important for the selection of the electrode material. Therefore, the Fe-doped strontium titanates can be considered as promising supporting electrodes of a thin-film SOFC. In the recent studies [23,24], we found that $\text{CaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ films deposited on $\text{SrTi}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ substrates by CSD contained some amounts of Sr, Fe and Ti, which was explained by the diffusion process occurring during the film synthesis. However, the diffusional interaction between the film and the substrate was shown not to deteriorate the electrolyte performance: the film demonstrated high ionic transport numbers of 0.93–0.97 at 500–600 °C [24].

According to the data on the electrical conductivity of the alkaline-earth zirconates reported in [6], the SrZrO_3 -based electrolytes possess higher ionic conductivity than calcium zirconates. The calculations based on the DFT method had shown that In, Yb, and Y were the most effective dopants ions for improving the protonic conduction in SrZrO_3 [28]. Recently, we studied the influence of Sr nonstoichiometry on electrical conductivity of the SrZrO_3 and $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$ ceramics and revealed that small Sr deficiency (2 at.%) resulted in a rise of ionic conductivity due to increasing the concentration of oxygen vacancies [29]. The further decrease in Sr content led to a decrease of the conductivity that was explained by self-compensation of the dopant ions because of partitioning over the Sr- and Zr-sites in the zirconate.

That is why, in the present study, the $\text{Sr}_{0.98}\text{Zr}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$ (SZY) and $\text{SrTi}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (STF) compositions were selected for fabrication of the electrode-supported thin film electrolyte using the CSD technology. Phase and elemental compositions, microstructural features and electrical conductivity of the obtained films were studied using X-ray diffraction

(XRD) method, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), differential-pressure method and AC impedance spectroscopy. The electrical behavior of the films was compared to that of a massive ceramic sample of the same composition, which was studied in our recent research [29], and the revealed differences in electrical properties were discussed.

2. Materials and Methods

2.1. Film Deposition

STF substrates were prepared by the solid-state reaction method using SrCO_3 , Fe_2O_3 and TiO_2 (all with 99% purity) as precursors. Appropriate amounts of the initial reagents were mixed in an agate mortar in the ethanol media. The powders were calcined at $1100\text{ }^\circ\text{C}$ for 3 h, then re-ground, pressed into pellets at 130 MPa, and sintered at $1400\text{ }^\circ\text{C}$ for 2 h in air. The open porosity of the samples determined by the kerosene absorption method was $20 \pm 3\%$. The density of the sintered STF ceramics was 72% from the theoretical density.

SZY films were grown on the STF substrates by the CSD method. The film-forming solution of inorganic salts, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (all with 99% purity), was made as follows. Initially, the individual solutions of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in ethanol, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in ethanol, and $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in a mixture of ethanol and distilled water were prepared. The water is needed to attain the necessary concentration of Sr in the solution, because strontium nitrate is poorly soluble in ethanol. Further, the individual solutions were mixed in the ratio corresponding to the target composition, $\text{Sr}_{0.98}\text{Zr}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$. The concentration of the solution containing 8 wt.% water corresponded to 18 g SZY per 1 L. To increase the concentration of the solution, it is necessary to increase the water content, which, however, was shown to negatively affect the morphology of the SrZrO_3 -based films because of the formation of highly porous layers [26]. The dynamic viscosity of the prepared film-forming solution measured by a vibration viscometer (AND SV-1A, Tokio Japan,) was $1.7\text{ mPa}\cdot\text{s}$ at $25\text{ }^\circ\text{C}$.

The SZY films were fabricated by the multi-step (25 and 30 cycles) dip-coating and withdrawal of the STF substrates from the solution with a rate of $0.1\text{--}0.2\text{ cm min}^{-1}$, followed by drying at room temperature and synthesis at $1000\text{ }^\circ\text{C}$ for 1 h in air. The film synthesis temperature and the heating rates were chosen on the basis of the thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) with the ability to mass-spectrometric detection of emitted gases (STA 449 F1 Jupiter with QMS 403C Aëolos, NETZSCH). The TGA/DSC measurements were performed on the sediment powder obtained by drying of the solution in ambient air, in the temperature range from 35 to $1200\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C min}^{-1}$. As can be seen from the obtained TGA/DSC data shown in Figure 1, the main mass loss (about 50% of the initial sample mass) occurs upon heating the sample from room temperature to $\sim 630\text{ }^\circ\text{C}$ and is accompanied by the removal of water ($m/z = 18$), nitrogen monoxide ($m/z = 30$), nitrogen dioxide ($m/z = 46$) and chlorine ($m/z = 35$). Taking into account the TGA/DSC data, the temperature ramp rate for the film synthesis was as slow as $1\text{ }^\circ\text{C min}^{-1}$ upon heating to $650\text{ }^\circ\text{C}$ and $3\text{ }^\circ\text{C min}^{-1}$ upon the further heating to $1000\text{ }^\circ\text{C}$.

2.2. Preparation of SZY Bulk Samples

To compare the linear thermal expansion of the SZY and STF ceramics, the bulk samples of SZY were prepared as follows. SZY powder was obtained by drying of the film-forming solution and calcining the sediment powder at $1100\text{ }^\circ\text{C}$ for 2 h in ambient air. The obtained powder was thoroughly ground, pressed into pellets at 130 MPa, and sintered at $1650\text{ }^\circ\text{C}$ for 5 h in air. The density of the sintered SZY samples was 80% from the theoretical density. The rectangular samples for the dilatometric studies were cut from the pellets, polished and calcined at $1000\text{ }^\circ\text{C}$.

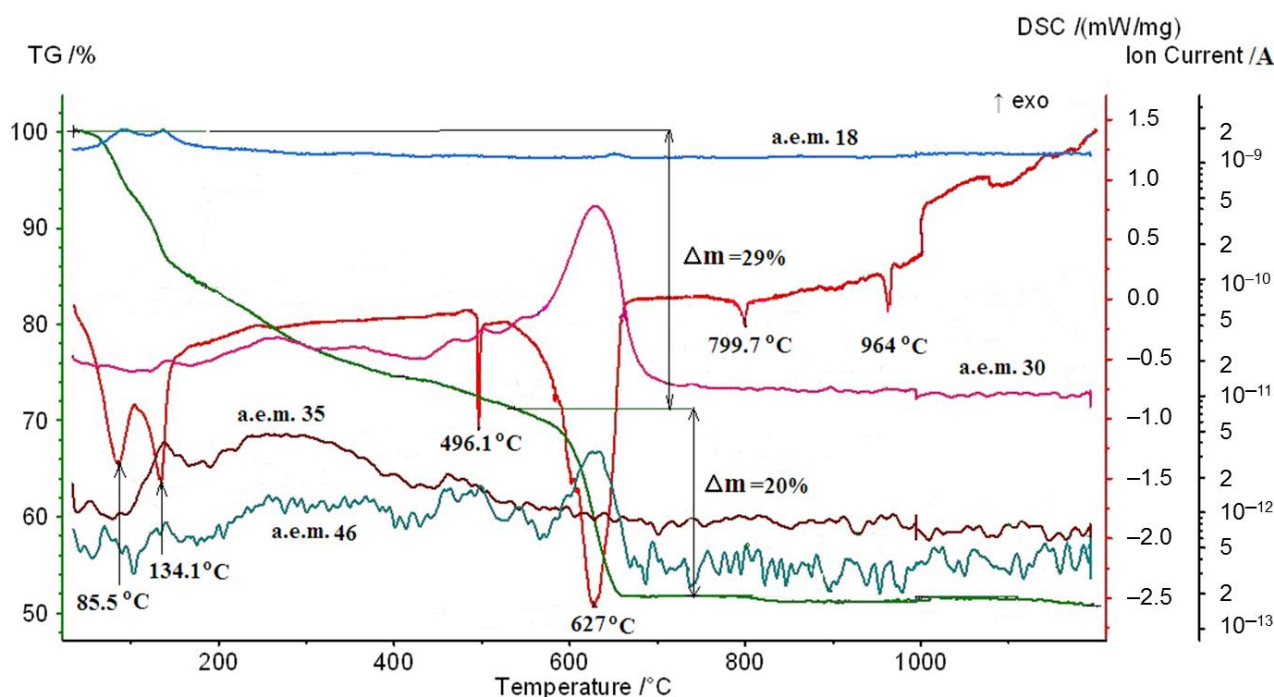


Figure 1. TGA/DSC and ion currents for the sediment powder obtained by drying of the film-forming solution.

2.3. Sample Characterization

The phase composition of the STF and SZY powders, obtained by grinding the sintered samples, and the SZY films was studied using X-ray diffraction (XRD) method. The measurements were performed on a Rigaku D-Max 2200 (Tokyo, Japan) diffractometer with Cu K α 1 radiation. The films were studied in the mode of grazing incidence diffraction with the angle of incidence of 1.5°.

Morphology and elemental composition of the films were investigated using a scanning electron microscope (SEM) MIRA 3 LMU (Tescan, Brno, Czech Republic) equipped with an energy-dispersive X-ray spectroscopy (EDX) system (Oxford Instruments X-MAX 80, Abingdon, UK). Microimages of the film surface and the cross-section of the SZY-film/STF sample were analyzed. The film thickness was evaluated from the cross-sectional views.

Gas-tightness of the films was evaluated using the differential-pressure method. In this technique, the target sample separates two chambers with different pressures, which causes gas leakage through the sample. The gas leakage coefficient (K) is determined by the Darcy's law:

$$K = \frac{d\Delta P}{dt} \times \frac{\eta h V_0}{\Delta P S P_0} \quad (1)$$

where P_0 is the atmospheric pressure, ΔP is the pressure change in the low-pressure side during time t , h is the sample thickness, S is the surface area of the sample, η is the gas viscosity, and V_0 is the volume of the low-pressure chamber. The measurements were performed in air at room temperature upon the pressure of 10^{-4} Pa in the low-pressure side, which was created using a vacuum pump.

The linear thermal expansion of the samples was studied by the dilatometric method in a quartz cell using a Tesatron TT 80 length meter with a high-precision axial probe GT 21 HP (TESA, Renens, Switzerland). The measurements were performed in air and in wet hydrogen atmosphere ($H_2 + 1\% H_2O$) in the temperature range of 30–870 °C at a heating rate of 2 °C/min.

2.4. Measurement of Electrical Conductivity

The across-plane electrical conductivity of the SZY films deposited on the STF supporting electrodes was measured using the two-probe AC impedance spectroscopy (Parstat

2273-SVS, Advanced Measurement Technology Inc., Oak Ridge, TN, USA) in the frequency range of 0.1 Hz–1 MHz with an amplitude of 30 mV. For these measurements, the SZY-film/STF samples were prepared by grinding and polishing one of the two faces of the film-coated STF pellets to remove the coating. The symmetrical Pt electrodes were applied to the opposite faces of the SZY-film/STF pellets by painting a platinum paste and sintering at 1000 °C for 1 h. To evaluate the substrate contribution into the impedance of the Pt/SZY-film/STF/Pt cell, the cell with the bare STF pellet and symmetrical Pt electrodes, Pt/STF/Pt, was also prepared. Schematic views of the prepared cells are given in Figure 2. The impedance measurements on the both cells were carried out in the temperature range of 100–800 °C in dry air. The air was dried by passing through the column filled with zeolite beads ($p_{H_2O} = 40$ Pa).

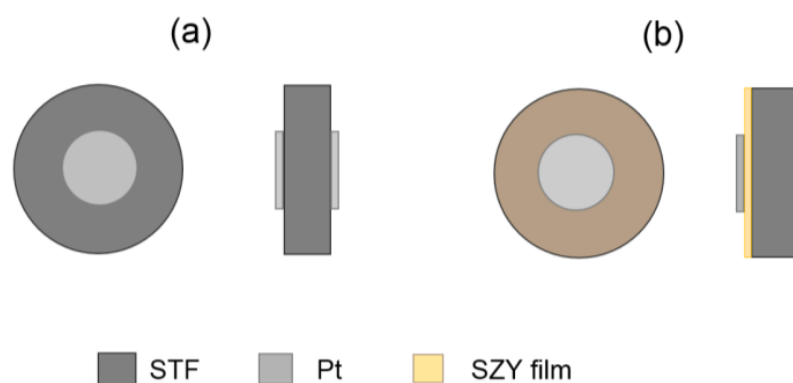


Figure 2. Schematic views of (a) Pt/STF/Pt and (b) Pt/SZY-film/STF/Pt cells.

3. Results and Discussion

3.1. Phase Composition of the Samples

XRD patterns of the STF and SZY powders, and the STF-supported SZY film are presented in Figure 3. According to the XRD data, the STF samples are single phase and possess a cubic perovskite crystal structure ($SrTiO_3$, ICDD 79-0176). The SZY sample has an orthorhombic perovskite structure ($SrZrO_3$, ICDD 44-0161). No traces of the secondary phases can be seen in the both diffractograms. The XRD pattern of the SZY film exhibits the peaks corresponding to STF and SZY phases. The presence of STF reflexes is explained by the high penetrating ability of X-rays and the small thickness of the film. As the film was studied in the grazing incidence diffraction mode, the reduction of the SZY diffraction peaks intensity is observed. The impurity phases were not detected, which indicates that the contacting materials of the film and the substrate are chemically stable.

3.2. Thermal Expansion of STF and SZY

The relative linear expansion of the SZY and STF samples as a function of temperature measured in air and hydrogen atmosphere ($H_2 + 1\% H_2O$) is shown in Figure 4. As can be seen, the relative linear expansion of SZY almost does not change upon the change of the ambient atmosphere; the dependences on temperature are nearly linear, with a slight deviation from linearity observed at the temperature of ~750 °C. This deviation can be caused by the second-order phase transition from the orthorhombic distorted perovskite with the space group Pbnm to the one with Ibmm, which occurs at 769 °C [30]. STF exhibits the linear thermal expansion in the ranges of low (30–320 °C) and high (420–900 °C) temperatures; whereas an inflection is observed in the intermediate temperature range of 320–420 °C, which is especially pronounced in hydrogen atmosphere. Similar thermal behavior of Fe-doped strontium titanate, $Sr_{0.97}Ti_{0.6}Fe_{0.4}O_{3-\delta}$, was observed earlier [31]: the temperature dependence of thermal expansion showed a discontinuity at approximately 450 °C. This behavior was suggested to be due to the loss of oxygen with an increasing temperature. The fact that the change of the relative linear expansion of STF in the range of 320–420 °C is much greater in a hydrogen atmosphere than in air can be explained by

the higher reduction degree of iron and the related increase of oxygen loss. The values of TEC for STF and SZY calculated from the temperature dependences of the relative linear expansion are summarized in Table 1.

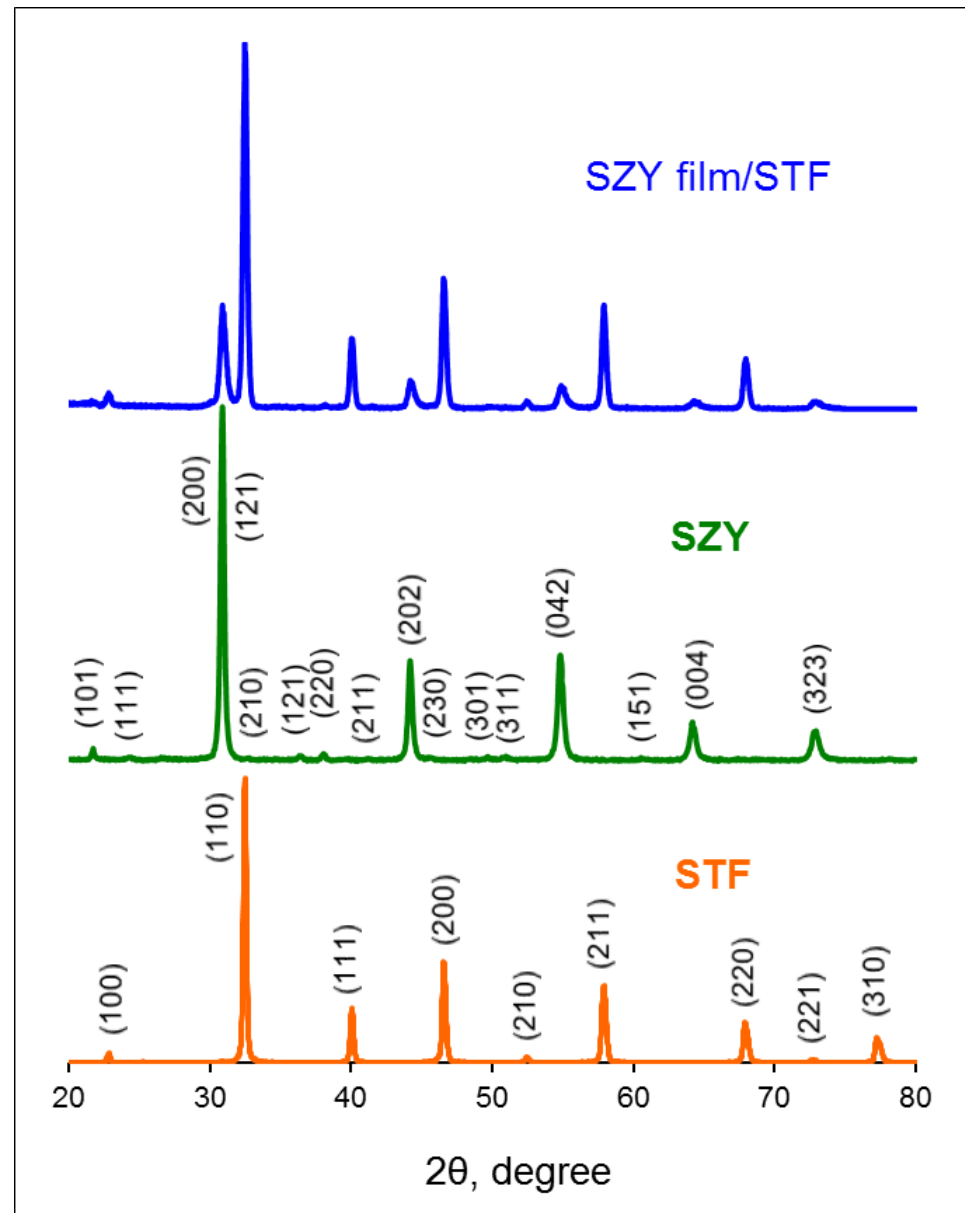


Figure 3. XRD patterns of STF and SZY powders, and SZY film on STF substrate.

As it was mentioned above, compatible thermal behavior of materials of a film and a substrate is required for fabrication of well adhered continuous films, whereas a significant difference in TECs might lead to the emergence of various defects in a film such as cracking, exfoliation and delamination, which might lead to fast SOFC degradation. As it follows from Table 1, in a hydrogen atmosphere, the TEC values for SZY and STF are similar; however, the peculiarities of thermal expansion of STF in the temperature range of 320–420 °C can negatively affect the thermal cycling ability of the STF-supported SZY films. In air, although the difference between the TEC values for SZY and STF is larger, the thermal expansion of STF is more uniform, which is beneficial for the film thermal stability.

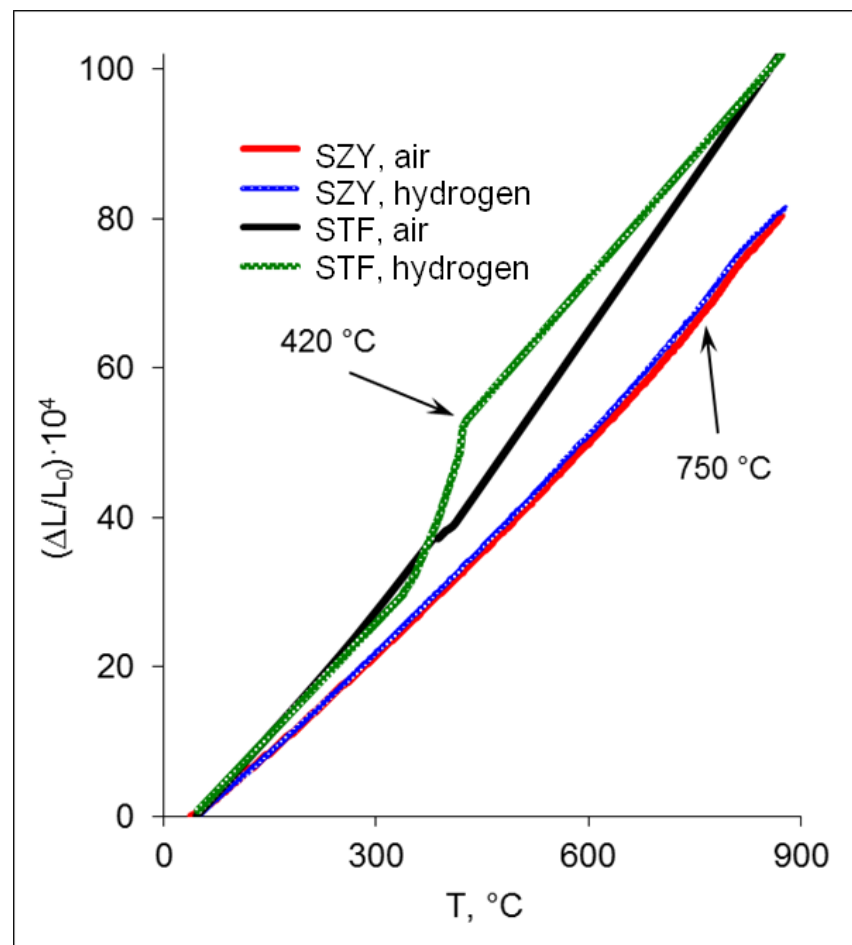


Figure 4. Relative linear expansion of SZY and STF vs. temperature in air and hydrogen atmosphere ($H_2 + 1\% H_2O$).

Table 1. TECs of STF and SZY.

Atmosphere	STF	SZY
air	50–320 °C 11.3×10^{-6}	50–750 °C 10.3×10^{-6}
	420–870 °C 14.0×10^{-6}	
$H_2 + 1\% H_2O$	50–320 °C 10.4×10^{-6}	50–750 °C 10.4×10^{-6}
	420–870 °C 11.2×10^{-6}	

3.3. Morphology and Gas-Tightness of the Films

Figure 5 presents the surface and cross-sectional images of the SZY films deposited on the STF substrates after 25 and 30 dip-coating/annealing cycles. As can be seen, the film possesses the fine-grained nanoporous morphology with the average grain size of about 100 nm. The film thickness estimated from the cross-sectional images was $0.8 \pm 0.1 \mu m$ and $1.0 \pm 0.1 \mu m$ after 25 and 30 cycles of solution deposition. The films are well adhered to the substrate; no cracking or exfoliation is observed, which proves the satisfactory compatibility of thermal behavior of STF and SZY. Adhesion of the films is enhanced by the formation of the intermediate layer between the film and the substrate because of the infiltration of the low viscous film-forming solution into the porous STF during the first dip-coating steps, as

can be seen in Figure 5d. This composite layer should smooth the differences in the thermal and mechanical properties of the materials.

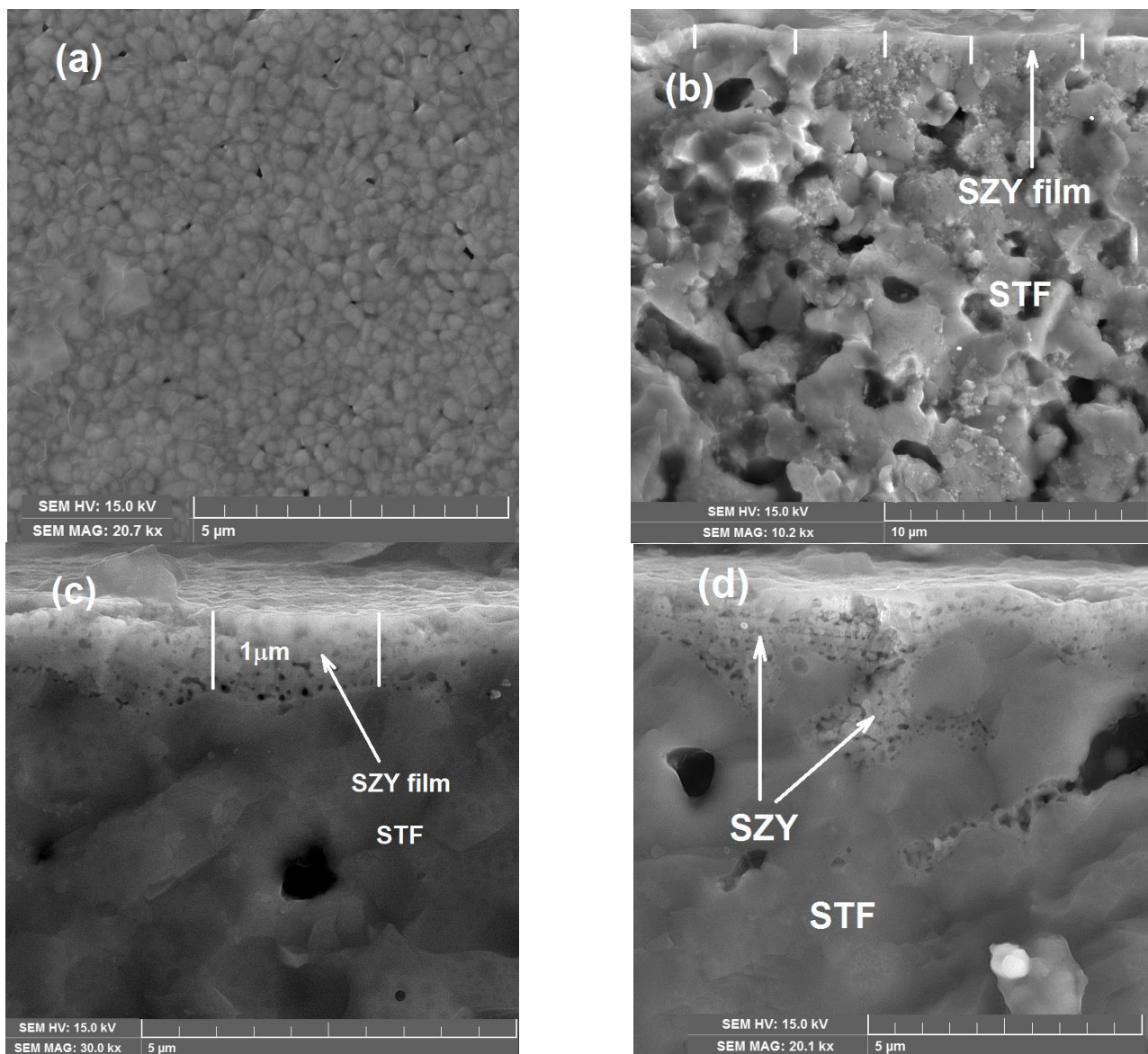


Figure 5. SEM-images of the surface (a) and the cross section of SZY films deposited on STF substrates by (b) 25 dip-coating/annealing cycles and (c,d) 30 dip-coating/annealing cycles.

A study of elemental composition along the cross section of the 1 mm thick film revealed the presence of a small amount of Ti and Fe (up to 6 at.%), which can be explained by diffusional interaction between the film and substrate materials during the film annealing. Similar results were obtained for a 6 mm thick film of $\text{CaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ deposited on STF [24]. An exact evaluation of the Ti and Fe contents in the 1 mm thick film is difficult since X-rays are formed in $\sim 2\text{ }\mu\text{m}$ depth area; therefore, the image of the elements includes not only the film response, but also the STF substrate contribution. Nonetheless it is reasonable to assume the probability of surface diffusion of Ti- and Fe-ions from the substrate toward the film, taking into account the nanoporous morphology of the film and the fact that diffusion in solid oxides proceeds more rapidly along the grain boundaries than through the grain interior.

A SOFC membrane must be gas-tight to avoid gas leaks, which lead to a decrease of the fuel cell efficiency. The gas-tightness of the deposited films was controlled by the

differential pressure method after every 5–10 deposition steps. The determined gas leakage coefficients are summarized in Table 2. As can be seen, the film gas-tightness is enhanced with an increase of the deposition/annealing cycles, attaining a saturation after 25 cycles. Thus, in spite of the nanoporous morphology of the films, the 25-fold deposition results in good gas-tightness of the film.

Table 2. Gas-tightness of SZY films.

Number of Deposition/Annealing Cycles	Gas-Tightness, μm^2
10	9×10^{-5}
20	3×10^{-5}
25	$<1 \times 10^{-5}$
30	$<1 \times 10^{-5}$

3.4. Electrical Conductivity of SZY Films

The electrical conductivity of the STF-supported SZY films was determined from the impedance spectra of the Pt/SZY-film/STF/Pt cells. Impedance of the Pt/STF/Pt cell with the bare STF pellet was also measured to evaluate the substrate contribution. The hodographs were treated using Zview software. As can be seen in Figure 6a, the impedance spectra of the Pt/STF/Pt cell display a part of a single semicircle, which possesses a capacitance below 10^{-9} F/cm². The semicircle can be attributed to the STF response; therefore, the low frequency intersection of the semicircle with the real axis was considered as a resistance of STF. The hodographs of the Pt/SZY-film/STF/Pt cell with the 1 mm thick SZY film measured at 150 and 200 °C are displayed in Figure 6b, together with those of the Pt/STF/Pt cell. The hodographs of the cell with the film consist of a large low-frequency semicircle characterized by a capacitance of $\sim 10^{-8}$ F/cm², and a fragment of a high frequency arc possessing a capacitance of 10^{-9} – 10^{-10} F/cm². The low-frequency semicircle can be ascribed to the response of grain boundaries in the film, while the high frequency part of the spectra is supposed to be a superposition of responses of the STF substrate and the grain interior of the film. At higher temperatures, the hodographs of the Pt/SZY-film/STF/Pt cell consist of an uncompleted suppressed semicircle (see Figure 6c) with a characteristic capacitance of $\sim 10^{-8}$ F/cm². The semicircle was ascribed to the film grain boundaries, whereas the intersection of the extrapolated semicircle with the real axis at high frequencies can be considered as the bulk resistance of the film plus the resistance of the STF substrate. Notably, the electrode polarization response of the electrode-supported cell, which is expected to appear in the low-frequency range of the spectra, is negligibly small. This can be explained by the proper combination of electrical properties and microstructure of the STF substrate, as well as by the extending the triple phase boundary due to formation of the composite layer between the electrolyte and the porous electrode. The equivalent circuits used for deconvolution of the hodographs of the Pt/SZY-film/STF/Pt cell are shown in Figure 6b,c.

Electrical resistance of the film (R_{film}) was calculated by subtracting the resistance of STF from the Pt/SZY-film/STF/Pt cell resistance, the resistance of the film grain boundaries ($R_{\text{film,gb}}$) was determined as the section of the real axis cut by the low-frequency semicircle, and the resistance of the grain bulk of the film ($R_{\text{film,b}}$) was evaluated as a difference between the section of the real axis cut by the semicircle at high frequencies and the resistance of STF. The corresponding electrical conductivities were calculated as follows:

$$\sigma = L/SR, \quad (2)$$

where L denotes the sample thickness, S is the electrode area, and R is the related resistance.

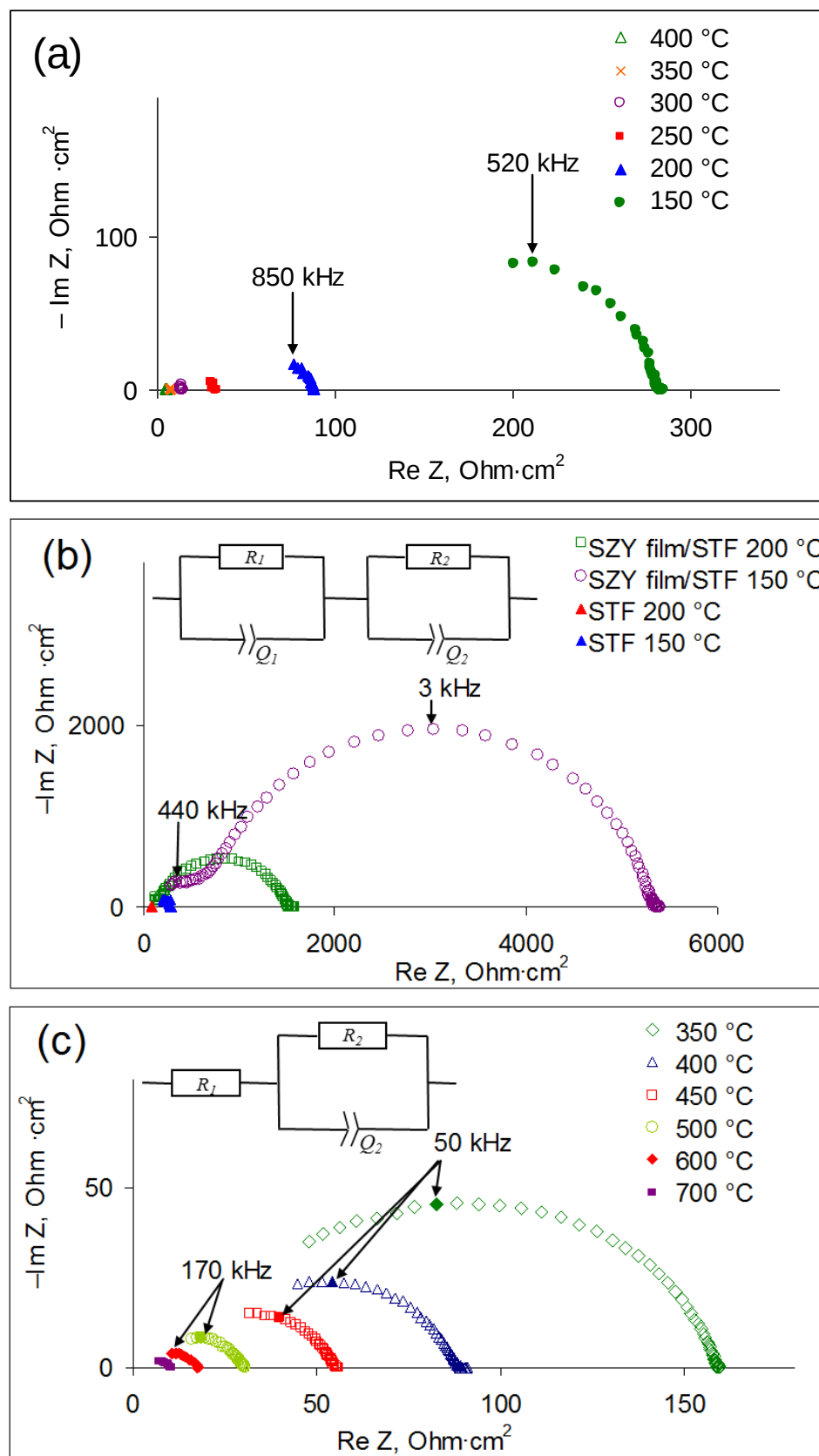


Figure 6. Impedance spectra of (a) Pt/STF/Pt cell, and Pt/SZY-film/STF/Pt cell with the 1 mm thick film at (b) 150–200 °C and (c) 350–700 °C. All spectra were measured in air ($p\text{H}_2\text{O} = 40 \text{ Pa}$).

Arrhenius plots for the total, bulk and grain boundary conductivities of the SZY film, together with the conductivities of the massive ceramic sample of the same composition measured earlier [29], are shown in Figure 7. As can be seen, all the conductivities exhibit the Arrhenius behavior. The dependences of the total conductivity of the film and massive samples possess different slopes, which indicate that the related activation energies are different. The activation energies of the total, bulk and grain boundary conductivities of the film and massive samples calculated from the Arrhenius plots are summarized in Table 3. The activation energy of the total conductivity of a massive sample with similar composition, $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$, reported in [32] is given for comparison. For both the film and massive samples, the low conductivity of grain boundaries limits the total conductivity. It is essential that the bulk conductivity of the film is well correlated with that of the massive sample, which means that the bulk properties of the nanoporous film and the dense ceramic sample are similar. However, the difference in the grain boundary conductivities is more significant: the activation energy for the massive sample is about twice greater than for the film. This can be caused by the change of composition of grain boundaries in the film because of diffusional interaction with the substrate. As a result, the grain boundary and total conductivities of the film exceed those of the massive sample in the low temperature range (below 400 °C). This effect can be used for tuning the properties of thin films.

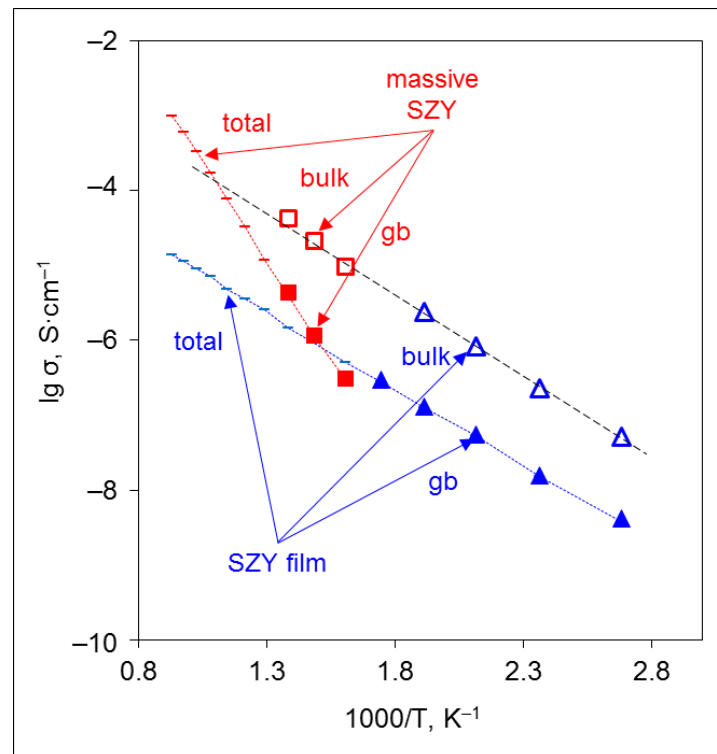


Figure 7. Temperature dependences of the total, bulk and grain boundary conductivities of the film and massive ceramic samples of SZY. Conductivity of massive SZY was reported in [29].

Table 3. Activation energies of total, bulk and grain boundary conductivities for the film and massive samples of SZY in dry air.

Sample	Activation Energy, eV		
	Total Conductivity	Bulk Conductivity	Grain Boundary Conductivity
SZY film	0.42 ± 0.02	0.43 ± 0.02	0.42 ± 0.02
Massive SZY [29]	1.02	0.6	1.03
Massive $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ [32]	1.29	–	–

4. Conclusions

Thin films of $\text{Sr}_{0.98}\text{Zr}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$ electrolyte were grown on the porous supporting $\text{SrTi}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ electrodes by the chemical solution deposition method using the low-viscous solution of inorganic salts. It was shown that for attaining the satisfactory gas-tightness of the film, at least 25 cycles of dip-coating followed by the synthesis are required; after 30 cycles, the 1 mm thick film was obtained. The deposited films possessed a fine-grained nanoporous morphology with an average grain size of 100 nm. The porous microstructure of the substrates and the high wetting ability of the film-forming solution promoted formation of the oxide–oxide composite layer due to the solution penetration into the pores; this is expected to be beneficial for lowering the electrode polarization resistance. The across-plane electrical conductivity of the films is limited by the poor conducting grain boundaries. The bulk conductivity of the nanoporous film correlates with that of the massive ceramic samples of the same composition, whereas the behavior of grain boundaries is significantly different. The difference was explained by diffusional interaction of the film and the supporting electrode. The presented results show the possibility to tune the properties of thin film electrolytes by the proper choice of a supporting electrode.

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