Lanthanum nickelate thin films deposited by spray pyrolysis: Crystallization, microstructure and electrochemical properties

Thomas Ryll a, *, Philipp Reibisch a, Lukas Schlagenhauf a, Anja Bieberle-Huetter a, Max Döbeli b, Jennifer L.M. Rupp a, Ludwig J. Gauckler a

a Nonmetallic Inorganic Materials, Department of Materials, ETH Zurich, Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland
b Laboratory of Ion Beam Physics, Department of Physics, ETH Zurich, Schafmannistrasse 20, 8093 Zurich, Switzerland

Received 31 August 2011; received in revised form 13 December 2011; accepted 29 December 2011
Available online 23 January 2012

Abstract

Thin films from the Laₙ₋₁NiₙO₃₋δ system exhibit favorable dielectric and electrochemical properties that may prove useful for a variety of devices ranging from ferroelectrics to low-temperature solid oxide fuel cells. The present work covers the compositional, microstructural and electrochemical characterization of thin lanthanum nickelate films deposited by spray pyrolysis. In accordance with the phase diagram, LaNiO₃₋δ or LaₙNiₙO₃₋δ films were obtained during annealing of spray deposited films at temperatures between 540 °C and 1100 °C. Whereas LaNiO₃₋δ films exhibited a high metallic conductivity, LaₙNiₙO₃₋δ films were semiconducting. Electrochemical impedance spectroscopy indicated an increase of the area specific oxygen reduction resistance with the annealing temperature. The study highlights how the phase and microstructure of thin films from the Laₙ₋₁NiₙO₃₋δ system can be tailored by annealing of initially amorphous films. LaNiO₃₋δ films have a high potential for application in electrochemical devices operating at low temperatures where high electrical conductivity is required. © 2012 Elsevier Ltd. All rights reserved.

Keywords: Thin films; Sol–gel processes; Electrical conductivity; Fuel cells; Transition metal oxides

1. Introduction

Due to promising electrical and catalytic properties materials from the lanthanum nickelate system Laₙ₋₁NiₙO₃₋δ (1 ≤ n < ∞) have attracted considerable attention within the past decades. Whereas thin films of the perovskite phase LaNiO₃₋δ (n → ∞) have been applied as electrodes for ferroelectric devices, thin-film capacitors and superconducting films, the higher order Ruddlesden–Popper phases LaₙNiₙO₃₋δ (n = 3) and La₃Ni₂O₇₋δ (n = 2) show great promise for application as cathodes in intermediate temperature solid-oxide fuel cells (SOFCs). LaNiO₃₋δ adopts a rhombohedral perovskite structure and exhibits a metallic conductivity of 600 S cm⁻¹ at room temperature. During heating, LaNiO₃₋δ decomposes forming the Ruddlesden–Popper phases with n = 3, 2 and 1, corresponding to the consecutive reactions (1) → (2) → (3). The equilibrium temperatures for the reactions (1)–(3) in air are 978, 1183 and 1231 °C, respectively.

The Ruddlesden–Popper structure is composed of n layers of the perovskite LaNiO₃₋δ permeated by single LaO layers with rocksalt structure. With decreasing n, the electrical conductivity decreases and a successive change from metallic to semiconducting behavior occurs. In contrast to the pure perovskite, the Ruddlesden–Popper structure can accommodate a considerable amount of excess oxygen on interstitial sites resulting in a high oxygen incorporation rate and high, but anisotropic, oxygen-ion conductivity.

Studies investigating thin films from the Laₙ₋₁NiₙO₃₋δ system have concentrated on films grown by physical vapor deposition (PVD), metal organic chemical vapor deposition (MOCVD) or nebulized spray pyrolysis. These
techniques conjointly yield epitaxial and dense microstructures. However, nanoporous microstructures featuring a high surface area are required for applications of thin films where reactions with a gas phase are essential, e.g. SOFC electrodes. In this regard deposition techniques based on organometallic precursor solutions, e.g. wet spray pyrolysis, have been proven to be well suited, rendering nanoporous and untextured thin films with equiaxed grains in the nanometer range at a high deposition rate and low cost.20–23

In this study, we demonstrate the applicability of wet spray pyrolysis for the deposition of ceramic thin films from the La<sub>n+1</sub>Ni<sub>3n+1</sub>O<sub>6n+6</sub> system. The impact of crystallization and phase transformation on the microstructure and electronic conductivity of porous LaNiO<sub>3</sub>−δ and La<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub>−δ thin films are presented. Furthermore, the performance of porous LaNiO<sub>3</sub>−δ and La<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub>−δ thin films with respect to the oxygen reduction reaction on a Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>1.9</sub> (CGO) electrolyte is assessed.

2. Experimental

2.1. Preparation of thin films

Lanthanum nickelate thin films were deposited by air-pressurized spray pyrolysis on randomly oriented sapphire single crystals (Stettler, Switzerland) and polycrystalline Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>1.9</sub> (CGO) electrolyte pellets. A detailed description of the preparation of CGO electrolyte pellets can be found elsewhere.24 The composition of the spray solution as well as the experimental parameters used during spray pyrolysis are specified in Table 1. During deposition the spray solution was pumped (syringe pump A99, Razel Scientific Instruments, USA) through a nozzle (Binks 460, J92P air nozzle, J920 fluid nozzle, Binks, USA) and atomized by air pressure. The substrate was positioned at a distance of 38 cm below the nozzle on a hot plate (CT 10, Harry Gestigkeit, Germany). Subsequent heat treatments at temperatures between 540 °C and 1100 °C were performed in air (L3, Nabetherm, Germany) using a dwell time of 4 h and a heating and cooling rate of 3 °C min<sup>−1</sup>

2.2. Structural and microstructural characterization

In order to analyze the crystallization and phase transformation behavior of lanthanum nickelate thin films, Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG, both Netzsch STA 449 C Jupiter, Netzsch, Germany) were applied. 20 mg of film material were scratched off the Al<sub>2</sub>O<sub>3</sub> substrate after 10 h of deposition. The resulting powder was investigated in a Pt crucible in air, using a heating and cooling rate of 20 °C min<sup>−1</sup> up to a maximum temperature of 1350 °C.

The crystallinity and crystal structure of lanthanum nickelate thin films were investigated by Grazing Incidence X-ray Diffraction (GIXRD, XPert Pro MPD, Panalytical, Netherlands, Cu anode, 40 mA current, 45 kV acceleration voltage) using a parallel beam geometry and a fixed incidence angle of 1°. Reference peak positions were obtained by the web application of the Inorganic Crystal Structure Database (ICSD).25 For the refinement of GIXRD patterns and the calculation of lattice parameters the software Maud was applied.26,27

The surface structure of lanthanum nickelate thin films was visualized by a Leo 1530 Scanning Electron microscope (SEM, Carl Zeiss SMT, Germany). Images were recorded by an in-lens detector using an acceleration voltage of 3 kV. Cross-sections of thin films were cut, polished and imaged by a Focused Ion Beam (FIB) workstation (Nvision 40, Carl Zeiss SMT, Germany). For the quantitative analysis of SEM images with respect to grain size and porosity software Lince 2.31 was applied.28 The error margins of grain size and porosity were assessed by the analysis of images comprising a statistically significant number of features taken on two identically prepared samples in each case.

The elemental composition of lanthanum nickelate thin films was analyzed by Rutherford Backscattering Spectrometry (RBS) and Particle-Induced X-ray Emission (PIXE) using 2 MeV 4He ions. RBS spectra were evaluated using the software RUMP.29 Concentrations of impurity elements were calculated from the intensity ratios of Ka and Lα lines compared to the Ni Ka line in PIXE spectra using literature values for branching ratios, fluorescence yields and ionization cross-sections.30,31

2.3. Electrical and electrochemical characterization

For measurements of lateral DC conductivity, lanthanum nickelate thin films were deposited through a shadow mask (open area of 1.4 cm × 2.5 cm, 200 µm thick stainless steel) on sapphire single crystals. The films were contacted by four stripes of sputtered platinum, platinum paste (C 3605 S, Heraeus, Germany) and platinum wire. The wires fixed on the film surface by ceramic two-component cement (Feuerfestkitt,
Fig. 1. Schematic cross-section of a symmetrical cell for the characterization of lanthanum nickelate thin films by electrochemical impedance spectroscopy.

Fig. 2. (A) Impedance spectra of a symmetrical cell comprising a lanthanum nickelate thin film on a CGO pellet. The high frequency region is magnified in the inset. The discrete data points represent the original impedance data while the continuous line corresponds to the resulting fit. (B) Equivalent circuit used for the fitting of impedance data. R and CPE refer to ohmic resistances and constant phase elements, respectively.

3. Results and discussion

3.1. Crystallization

During heating, metal oxide thin films deposited by precipitation-based techniques like spray pyrolysis undergo major changes including the evaporation of residual organic solvents and hydroxyl water, crystallization as well as phase transformations of the thin film material. DSC and TG have been shown to be useful techniques for the investigation of such processes.33

In Fig. 3 the evolution of heat and mass of as-deposited thin film material during the first heat-up to 1350°C are plotted. A major mass loss of 15.5 wt.% occurs between the deposition temperature of 350°C and 800°C. In agreement with literature
this loss is attributed to the removal of gaseous species tracing back to the organic solvents in the spray solution and hydroxyl groups. The concurrent volumetric loss between 350 °C and 800 °C is estimated to add up to 54 vol.%, provided that (i) the density of the organic residues in the as-deposited lanthanum nickelate thin films corresponds to the mean density of the spray solution (1.09 g cm⁻³) and (ii) the density of as-deposited lanthanum nickelate is close to the density of crystalline LaNiO₃₋δ (7.09 g cm⁻³ [2]). Around 400 °C, the DSC signal exhibits the onset of an exothermal minimum that passes into a large endothermal peak with a maximum value at 750 °C. Based on the above-mentioned mass loss the endothermal peak is attributed to the removal of gaseous species and most likely superimposes an exothermal crystallization maximum. Further mass losses of 1.6 wt.% and 0.7 wt.% in conjunction with distinct endothermal DSC maxima occur around 1069 °C and 1204 °C, respectively. In DSC experiments involving heating of the LaNiO₃₋δ compound in an oxygen partial pressure of 0.1 bar with 10 °C min⁻¹, literature reports endothermal DSC maxima at 1052 °C and 1171 °C corresponding to the decomposition reactions of the Ruddlesden–Popper phases (1) and (2). The theoretical mass losses due to oxygen formation during the two reactions are 1.63 wt.% and 0.60 wt.% respectively. Based on the agreement of these values with the mass losses and temperatures of the DSC maxima found in this study, the two endothermal reactions are likewise attributed to the stepwise thermal decomposition reactions (1) and (2) of the Ruddlesden–Popper phases. The slightly higher temperatures of DSC maxima compared to literature data result from the higher heating rate (20 °C min⁻¹) and atmospheric oxygen partial pressure applied during the DSC measurements. Given that no temperatures higher than 1350 °C were applied in the DSC experiments shown in this study, the final reaction (3) resulting in the compound La₂NiO₄₊δ was not observed.

Based on the DSC/TG results, annealing temperatures of 540 °C, 660 °C and 800 °C covering the temperature range of solvent evaporation and crystallization, and 1100 °C resulting in the La₄Ni₃O₁₀₋δ phase were chosen for further experiments. GIXRD patterns of as-deposited and annealed lanthanum nickelate thin films are shown in Fig. 4. The GIXRD patterns of as-deposited lanthanum nickelate thin films contain primarily peaks resulting from the CGO substrate. Three minor reflections around 27°, 45° and 54° can neither be assigned to any known lanthanum nickelate phase, ceria phase nor any potential reaction product of the thin film and the electrolyte. However, these peaks do not appear in GIXRD patterns of as-deposited lanthanum nickelate films on Al₂O₃ single crystals, for which reason they most likely trace back to some minor foreign phase in the CGO electrolyte. Hence, GIXRD confirms that as-deposited lanthanum nickelate thin films are amorphous.

After annealing at 540 °C, 660 °C and 800 °C GIXRD patterns comprise additional peaks that are assigned to the rhombohedral perovskite LaNiO₃₋δ with space symmetry R-3m. Accordingly, amorphous lanthanum nickelate thin films deposited by spray pyrolysis begin to crystallize between 350 °C and 540 °C. This substantiates the assumption that the exothermal DSC minimum starting at 400 °C represents the crystallization of the thin film material. The refinement of the spectrum measured after annealing at 660 °C renders lattice parameters of a = 5.45 Å and c = 13.15 Å which are in accordance with literature for bulk ceramics. The diffraction lines in GIXRD patterns recorded after annealing at 1100 °C are attributed to the Ruddlesden–Popper phase La₄Ni₃O₁₀₋δ and NiO. This finding is in accordance with the DSC/TG results and confirms the endothermal decomposition of LaNiO₃₋δ thin films around 1052 °C according to reaction (1). Lanthanum nickelate thin films heat treated at temperatures exceeding 1100 °C exhibit reactions with the substrate and were therefore excluded from this study. As the GIXRD reflections attributed to LaNiO₃₋δ and La₄Ni₃O₁₀₋δ appear in the expected intensity ratio, no indication for a preferred grain orientation is found. This is in contrast to studies where the deposition of thin films from the La₄n₊₁Ni₃O₃n₊₁ series by nebulized spray pyrolysis gave rise to pronounced texturing. The reason for this significant microstructural difference, despite the use of a similar deposition technique, is a different ratio of the substrate temperature during deposition Tₛ and the boiling point of the organic solvent in the precursor solution T_bp. The value Tₛ/T_bp > 5 used in involves complete evaporation of the solvent on the way to the substrate. Accordingly, nucleation occurs from the gas phase resulting in layer-by-layer-like growth and the formation of a preferred grain orientation. By contrast, the value of Tₛ/T_bp = 1.6 used in this study leads to the arrival of liquid droplets on the substrate surface and precipitation of three-dimensional nuclei of amorphous film material. The resulting amorphous matrix transforms into a microstructure without a preferred grain orientation during crystallization. More information on wet spray pyrolysis is available in literature. A similar lack of a preferred orientation has also been observed for thin LaNiO₃₋δ films deposited by spin coating of a polymeric precursor solution containing lanthanum and nickel salts.
It can be concluded that as-deposited lanthanum nickelate thin films fabricated by spray pyrolysis are amorphous. Crystallization starts at 400 °C, whereas the removal of gaseous species originating from the organic solvents in the spray solution and hydroxyl groups continues until 800 °C. This outgassing during crystallization causes a volumetric loss of 54 vol.% compared to the as-deposited state. The perovskite LaNiO$_3$−δ that was found to form up to 800 °C decomposes into the Ruddlesden–Popper phase La$_4$Ni$_3$O$_{10}$−δ around 1052 °C.

### 3.2. Microstructure

SEM images of lanthanum nickelate films after deposition by spray pyrolysis on polycrystalline CGO electrolyte pellets are shown in Fig. 5. As-deposited, amorphous films are dense, smooth and free from cracks. 60 min of deposition result in a film thickness around 350 nm and a corresponding deposition rate of 5.8 nm min$^{-1}$.

The microstructure of lanthanum nickelate films annealed at different temperatures for 4 h is displayed in Fig. 6. Corresponding values of grain size and porosity are plotted in Fig. 7. Thin LaNiO$_3$−δ films annealed at 540 °C (compare Fig. 6A and B) exhibit equiaxed grains with a diameter of 37(7) nm, an equally distributed porosity adding up to 26(1) vol.% and an overall film thickness around 250 nm. An increase of the annealing temperature to 660 °C and 800 °C involves a roughly linear increase of the grain size, whereas the porosity stays constant considering the error margins of the porosity values. In literature, similar microstructures have been observed after the deposition of LaNiO$_3$−δ thin films by repeated spin coating of an organometallic solution and adjacent annealing. Comparing the cross-sections shown in Fig. 6B, D and F, it becomes apparent that the grain growth is accompanied by a decrease of the contact area between the LaNiO$_3$−δ films and the CGO electrolyte. LaNiO$_3$−δ films annealed at 800 °C are approximately 200 nm thick. In consideration of the porosity, this film thickness corresponds to a volumetric loss of 58 vol.% compared to the as-deposited films. This value matches the 54 vol.%, estimated on the basis of TG measurements. Accordingly, the removal of gaseous species gives rise to pore formation and the reduction of film thickness during annealing.

As shown in Fig. 6G, thin La$_4$Ni$_3$O$_{10}$ films annealed at 1100 °C exhibit a dense film surface and a mean grain diameter of 350(60) nm. In FIB-cut cross sections (Fig. 6H) isolated pores at the interface between the film and the CGO electrolyte resulting in a porosity of 14(5) vol.% are observed. In contrary to the LaNiO$_3$−δ films annealed between 540 °C and 800 °C, La$_4$Ni$_3$O$_{10}$−δ films comprise one layer of laterally connected grains in close contact with the CGO electrolyte. The significantly higher grain size and lower porosity of La$_4$Ni$_3$O$_{10}$−δ film compared to LaNiO$_3$−δ films are attributed to sintering processes caused by the comparatively high temperature of 1100 °C which is required to obtain the La$_4$Ni$_3$O$_{10}$−δ phase.

#### 3.3. Elemental composition

The elemental composition of LaNiO$_3$−δ films on sapphire substrates annealed at 660 °C for 4 h was analyzed by RBS and PIXE. The evaluation of the RBS spectrum shown in Fig. 8A yields a La:Ni ratio of 1:1. Besides La and Ni the corresponding PIXE spectrum shown in Fig. 8B points at the presence of impurity elements. Whereas the atomic percentage of S, Pd, Ru and K compared to the total amount of cations is between 0.1 and 0.2 at.%, the amount of Gd and Sc adds up to 0.7 and 2.0 at.%, respectively. It is assumed that the detected impurity elements originate either from the lanthanum and nickelate salts dissolved in the spray solution or from the spray setup. While traces of impurities can hardly be avoided, their quantification is important in order to facilitate the comparison of electrical and electrochemical properties with literature data.

#### 3.4. Electrical conductivity

The electrical conductivity of lanthanum nickelate thin films annealed at different temperatures is plotted in Fig. 9. In order to avoid the distortion of conductivity values by a conductive substrate, thin films deposited on insulating sapphire crystals were used for conductivity measurements.

During the first heating as-deposited films exhibit a low but strongly thermally activated conductivity. As long as the crystallization temperature of 400 °C is not exceeded, this behavior is retained during further heating and cooling cycles. The electrical conductivity of LaNiO$_3$−δ films annealed at 540 °C is around 490 S cm$^{-1}$ at room temperature and exhibits a metal-type temperature dependence. These characteristics correspond well with...
Fig. 6. Microstructure of crystalline lanthanum nickelate films on polycrystalline CGO electrolyte pellets obtained after annealing for 4 h at different temperatures in air. (A–F) LaNiO$_3$–δ; (G–H) La$_4$Ni$_3$O$_{10}$–δ.

Fig. 7. Grain size and porosity of lanthanum nickelate films deposited on polycrystalline CGO electrolyte pellets and annealed for 4 h at different temperatures in air.

literature, even though the exceptionally high conductivity of LaNiO$_3$–δ films presented by Burriel et al.\textsuperscript{9} is not reached. An increase of the annealing temperature results in a stepwise increase of the electrical conductivity up to 1220 S cm$^{-1}$ at room temperature after annealing at 800 °C. We assume that this increase results from a decreasing scattering of charge carriers at residues tracing back to the organic solvents and grain boundaries with increasing annealing temperature and grain size. The overall increase of electrical conductivity with increasing annealing temperature does not impact the metallic conduction characteristics of the LaNiO$_3$–δ films investigated in this study. La$_4$Ni$_3$O$_{10}$–δ thin films annealed at 1100 °C exhibit a slightly thermally activated conductivity which is approximately one order of magnitude lower compared to LaNiO$_3$–δ films. While the overall magnitude of conductivity corresponds well with literature, the Ruddlesden–Popper phase La$_4$Ni$_3$O$_{10}$–δ has been reported to exhibit a metal-type temperature dependence of conductivity.\textsuperscript{4–6,40–42} This disagreement might result from the
incorporation of 2 at.% of the larger impurity ion $^{3+}$ Sc on Ni$_2$+/3+ sites, as detected by PIXE measurements. A comparable transition from metallic to semiconducting behavior was observed after the substitution of Ni in LaNiO$_{3-\delta}$ by Co or Ti.$^{43,44}$

Summing up, both LaNiO$_{3-\delta}$ and La$_4$Ni$_3$O$_{10-\delta}$ thin films fabricated in this study exhibit electrical conductivities above 80 S cm$^{-1}$ in the temperature range between room temperature and 600°C. The observed magnitudes of conductivities correspond with literature data and are adequate for electrode applications.

3.5. Electrochemical performance

The electrochemical performance of lanthanum nickelate thin films on CGO annealed at different temperatures was investigated by electrochemical impedance spectroscopy. The resulting ASRs are plotted in Fig. 10. LaNiO$_{3-\delta}$ films annealed at 540°C exhibit an ASR of 0.59 k$\Omega$/cm$^2$ at 500°C, whereas annealing at 660°C and 800°C results in ASRs around 3 k$\Omega$/cm$^2$. It is interesting to note that, in contrast to the electronic conductivity, the presence of organic remains and hydroxyl groups as well as a potential partial crystallinity promote the cathode performance of LaNiO$_{3-\delta}$ thin films. In addition, the lower grain and pore size of samples annealed at 540°C may contribute to the higher cathode performance compared to samples annealed at 660°C and 800°C. The activation energy for the cathode process in case of thin films annealed at 660°C and 800°C is 1.39(8) eV and 1.31(5) eV, respectively. This value corresponds reasonably well with literature data for thick LaNiO$_{3-\delta}$ films on CGO.$^{45}$ By contrast, the overall ASR of LaNiO$_{3-\delta}$ films annealed at 660°C and 800°C exceeds the literature data by more than one order of magnitude. The reason for this mismatch might be the decreasing contact area between thin film cathode and electrolyte observable in the cross-sections shown in Fig. 6. The ASR of La$_4$Ni$_3$O$_{10-\delta}$ thin films annealed at 1100°C adds up to 16.5 k$\Omega$/cm$^2$ at 500°C and exhibits an activation energy of...
1.13(3) eV. In literature ASR values of La₄Ni₃O₁₀₋δ thick films on a La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃₋δ (LSGM) electrolyte have been reported that are one order of magnitude lower compared to the values measured in this study.⁴ This difference might trace back on the one hand to the different choice of substrate material, as it has been shown that the ASR of lanthanum nickelate based cathodes on LSGM is more than two orders of magnitude lower compared to the same film on CGO.⁴⁶ On the other hand the closed surface, low porosity and relatively high grain size of the La₄Ni₃O₁₀₋δ films annealed at 1100 °C do not provide a promising microstructural basis for high cathode performances. Further studies have to clarify whether the La₄Ni₃O₁₀₋δ phase is accessible in thin films deposited by spray pyrolysis without annealing at high temperatures. Directions in this regard are given by studies where La₄Ni₃O₁₀₋δ films were obtained by nebulized spray pyrolysis⁸,¹⁹ or MOCVD⁹ after an appropriate choice of the La/Ni ratio in the precursor solution.

It is acknowledged that the ASR values measured in this study are comparably high. Further microstructural optimization is required in order to make use of the promising oxygen incorporation and oxygen conduction properties of thin films of the Laₖ₋₁Ni₆O₃ₙ₊₁ system.

4. Conclusions

Thin lanthanum nickelate films deposited on sapphire and CGO substrates by spray pyrolysis are amorphous. After spray deposition, both crystal structure and microstructure of thin films from the La₄₋₁Ni₆O₃ₙ₊₁ system can be tailored by heat treatments: by annealing between 540 °C and 800 °C rhombohedral LaNiO₂₋δ films with equiaxed grains in the 50 nm range and a porosity around 25 vol.% are obtained. Grain and pore size increase with rising annealing temperature. Simultaneously, the metallic conductivity of LaNiO₂₋δ films increases due to the removal of organic remains. Commensurate with the phase diagram, thin La₄Ni₃O₁₀₋δ films with Ruddlesden–Popper structure are obtained after annealing at 1100 °C. La₄Ni₃O₁₀₋δ films exhibit a dense microstructure with grains in the range of 350 nm and are found to be semiconducting in the temperature range between room temperature and 600 °C.

LaNiO₃₋δ and La₄Ni₃O₁₀₋δ thin films deposited by spray pyrolysis qualify for electrode applications due to their high electrical conductivity above 80 S cm⁻¹ between room temperature and 600 °C. However, the ASR values, measured on a CGO electrolyte in air, have been found to suffer from a decreasing contact area between electrode and electrolyte with increasing annealing temperature in case of LaNiO₃₋δ layers, and a dense microstructure with large grains in case of La₄Ni₃O₁₀₋δ films. Microstructural improvements are required in order to enhance the cathode performance of sprayed LaNiO₃₋δ and La₄Ni₃O₁₀₋δ thin films.

Acknowledgments

Financial assistance by the following Swiss institutions is gratefully acknowledged: (i) Competence Centre for Materials Science and Technology (CCMX) within the framework of the NANCER project; (ii) Center of Competence Energy and Mobility (CCEM) within the framework of the ONEBAT project; (iii) Swiss Electric Research (SER) within the framework of the ONEBAT project; (iv) Swiss National Foundation (SNF) within the framework of the Sinergia project ONEBAT.

References

8. Raju AR, Aiyer HN, Rao CNR. Oriented films of LaNiO₃ and other members of the La₈₋₁Ni₆O₃₉₊₃ series, La₈₋₁CuO₃₋δ and Pbl(Zr0.5Ti0.5)O₃-O₃, obtained by nebulized spray pyrolysis. Chem Mater 1995;7:225–31.
19. Aiyer HN, Raju AR, Subbanna GN, Rao CNR. Epitaxial nature of the films of LaNiO₃, Pb(Zr0.5Ti0.5)O₃-O₃, and La₀.95Mn₀.05O₃ obtained by nebulized spray pyrolysis. Chem Mater 1997;9:755–60.


23. Beckel D, Dubach A, Grundy AN, Infortuna A, Gauckler LJ. Solid-state dewetting of La0.6Sr0.4Co0.2Fe0.8O3±δ thin films during annealing. J Eur Ceram Soc 2008;28:49–60.


38. Beckel D, Dubach A, Studart AR, Gauckler LJ. Spray pyrolysis of La0.6Sr0.4Co0.2Fe0.8O3±δ thin film cathodes. J Electroceram 2006;16:221–8.


