Nanocrystalline cathode functional layer for SOFC

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Abstract

Recently, it was shown that thin functional layers introduced between an electrolyte and cathode might improve cathode performance. However, the mechanism of this improvement still needs analysis. In this paper, a thin (~140 nm), spin-coated perovskite layer ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$) was placed between a cathode ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$) and an electrolyte ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$) and the effects of this investigated. The microstructure of this layer was varied in order to determine its impact on the electrical and electrochemical properties. It has been shown that a mesoporous, nanocrystalline layer increases the active area for oxygen reduction and charge transfer through the cathode/electrolyte interface, which improves performance. Moreover, the stability of the cathode from thermal stresses is increased. In contrast, the coarsening of the grain and the layer densification has a reduced impact on the cathode performance.

1. Introduction

For several years, Solid Oxide Fuel Cells (SOFC) have been widely studied as a very efficient source of electrical energy. Despite many obvious advantages, widespread commercialization of this technology has been significantly limited by high costs. One way to reduce the price is to decrease the operating temperature of the cell, in order to allow the use of less expensive materials [1].

Unfortunately, lowering of the operating temperature is associated with a decrease in ionic conductivity and with a reduction in catalytic activity of both electrodes. To maintain the efficiency of

the fuel cell, the objective should be to reduce the polarization resistance of the electrodes, as well as the electrolyte ohmic resistance. Processing of the cathode has shown to have an especially strong impact on the polarization resistance [2, 3]. Cathode parameters such as composition, thickness, and microstructure have proven to strongly affect electrochemical performance of SOFC [4].

The $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (LSCF) cathodes family has attracted much attention for intermediate temperature SOFCs because it has both high electronic and oxygen ion conductivity, and also high activity towards oxygen reduction at temperatures as low as 600 °C [5]. Additionally, the oxygen reduction reaction on the LSCF cathode is limited by the surface exchange process rather than the bulk charge transport process [6]. It also shows good compatibility with YSZ electrolytes if doped ceria is used as a buffer layer between an YSZ and the LSCF cathode [7]. Apart from the bulk properties of the cathode material, the microstructure may also have a significant impact on the operation of the cathode, in particular the cathode-electrolyte interface. Early studies carried out in the mid-90s by Van Herle et al [8] have shown that a cathode in the form of a two-layered structure with an inner thin dense layer covered by an outer thick porous cathode is advantageous from the standpoint of the operation of the fuel cell. Subsequent studies carried out by Hildenbrand et al [9] and Dumaisnil et al [10] consistently confirmed that the use of thin (200–400 nm) and dense cathode functional layers leads to a reduction in the polarization resistance of the cell, when using a mixed conducting cathode.

Our previous study has shown that the optimum thickness of the functional layer should be around 120–150 nm for both symmetrical cells [11] and fuel cells [12]. The improvement in polarization resistance was obtained by using an electrode with dominating electronic conductivity ($\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$, LNF) and for the cathode with mixed conducting LSCF as a thin cathode layer. However, it was pointed out that while the thin functional layer is initially dense and nanocrystalline, it becomes porous due to grain growth during the cathode sintering step. The fact that the final thin layer structure is different from that which was assumed, and strongly depends on the cathode sintering temperature, has not been addressed in previous articles on the subject. The focus of this study is the investigation of the influence of grain size and structure of the cathode thin functional layer on the cathode-electrolyte interface performance. The structure and electrical properties of

LSCF functional layers prepared at different temperatures were measured. Moreover, the influence of the thin layer on the cathodes stability during thermal stress was investigated for the first time. The LSCF layer was applied on a $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (CGO) substrate to illustrate a typical arrangement in which the LSCF cathode is applied onto a CGO buffer layer deposited onto an yttria stabilized zirconia electrolyte. The thin LSCF layers were fabricated by spin coating a metallo-organic precursor. This method allowed the microstructure of the required layers to be easily varied by controlling the annealing temperature and deposition parameters.

2. Experimental

Two types of samples were used in the experiment. The first was a CGO substrate with a single thin $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) layer for DC measurements and SEM analysis. The second type used was a symmetrical cell with a dense thin LSCF layer on both sides of a CGO electrolyte covered with porous LSCF cathode, along with a silver current collector (see Fig. 1). This second setup was used for impedance analysis.

CGO pellets with a diameter of 13 mm were prepared from the CGO powder (GDC-20K, Daiichi Kigenso Kagaku Kogyo), which was uniaxially pressed under a pressure of 100 MPa and sintered at 1350 °C for 4 hours. Their density was measured using a fluid displacement method as 99% of the theoretical. Afterwards their surface was grinded to a thickness of approximately 0.9 mm and polished. The thin layer precursor was prepared using a modified Pechini method [13]. Lanthanum, strontium, cobalt and iron nitrates were dissolved in distilled water with citric acid and mixed with ethylene glycol (all reagents by Sigma-Aldrich). After evaporation of the distilled water (on a hot plate), the precursor was diluted with 2-ethoxyethanol, which decreased the viscosity and increased the wetting properties. Thin layers were deposited by spin coating for 2 minutes at 4000 rpm. After each deposition, the samples were dried at 500 °C on a hot plate. In this state, the organic components of the precursor had mostly decomposed and evaporated. Five depositions were needed in order to obtain a thickness of 140 nm. For the symmetrical cells, this procedure was repeated on the other side of the CGO. After the deposition process, the CGO substrates with thin layers were annealed at temperatures ranging from 500 °C to 1200 °C for 1 hour. The sides of the pellets were ground down to remove

excess LSCF. A LSCF paste (4421-A, ESL Europe) was brush painted three times on each side yielding a flat, approximately 60 μm thick, porous electrode. After it had dried, a single layer of an Ag/YSZ paste was brush painted forming porous a current collector layer. Then the structure was sintered at 800 $^{\circ}\text{C}$ for 1 hour. The samples for DC measurements and SEM analysis were coated with LSCF on one side of the CGO and annealed without deposition of any additional layers.

The High Temperature X-Ray Diffraction (HT-XRD) of the LSCF precursor dried at 400 $^{\circ}\text{C}$ and mixed with CGO powder was used to determine the crystallization process, structure and crystalline size. A Bruker D8 diffractometer with MRI high temperature stage and PSD Lynx Eye detector using $\text{CuK}\alpha$ (1.542 $\text{\AA}$) radiation was applied within a temperature range of 500 to 1000 $^{\circ}\text{C}$ with holding time of 80 minutes at each measurements temperature. The morphology of the samples was analyzed using a FEI Quanta FEG 250 Scanning Electron Microscope (SEM) operating with a secondary electron detector in a high vacuum mode with an accelerating voltage of 10 kV. A layer of gold was deposited on the samples prior to SEM examination. DC conductivity of thin LSCF layers was measured using the van der Pauw method for samples with thin layers deposited onto the CGO substrate. Point contacts were prepared on the circumference of the sample with silver paste (4922N, Du Pont). Since CGO becomes conductive at high temperatures, the measurements were performed at temperatures ranging from 150 to 600 $^{\circ}\text{C}$ (except for the samples annealed at 500 and 600 $^{\circ}\text{C}$) and CGO conductivity was taken into account to calculate the LSCF thin layer conductivity. Electrochemical impedance spectroscopy of the symmetrical cells was performed in dry air using Novocontrol Alpha-A in the temperature range of 500 to 800 $^{\circ}\text{C}$, with a frequency range of 100 mHz to 1 MHz and an amplitude of 20 mV. Two symmetrical samples with the layer annealed at 700 $^{\circ}\text{C}$ and a reference without the layer were chosen for stability tests. These were repeatedly heated-up to 700 $^{\circ}\text{C}$ and then cooled-down to 100 $^{\circ}\text{C}$ to accelerate cathode/electrolyte interface degradation due to a thermal expansion coefficient mismatch. Each time the sample was stabilized at 700 $^{\circ}\text{C}$, a impedance measurement was performed.

Selected measurements were compared using *ADIS* analysis [14]. This was performed by subtracting the derivative of the real part of the impedance Z_{SAMPLE}' with respect to the natural logarithm of the frequency of the sample from the similar derivative of the reference $Z_{REFERENCE}'$, which is written as:

$$ADIS = \frac{\partial Z'_{SAMPLE}(\omega)}{\partial \ln(\omega)} - \frac{\partial Z'_{REFERENCE}(\omega)}{\partial \ln(\omega)}$$

This method enables easy visual comparison between different spectra as a function of frequency. For this reason, it can be used to better understand the nature of the differences between the electrochemical responses of cathodes with altered microstructure [15]. Moreover, *ADIS* analysis is particularly useful when small changes in behaviour of single sample occur, e.g. when working conditions slowly change or the sample degrades [16]. It is worth noting that derivative of Z' is negative thus positive *ADIS* values should be interpreted as lowered impedance of the sample in respect to the reference.

3. Results and discussion

The precursor used for cathode thin layer preparation after drying at a temperature of 500 °C has an amorphous structure. In order to investigate the crystallization temperature, pure LSCF precursor and LSCF precursor mixed with CGO powder were examined using HT-XRD. In Figure 2A XRD spectra at 550 °C (lower plot) and at 600 °C (upper plot) of LSCF mixed with CGO powder are shown. At 550 °C only maxima originating from the CGO phase and a Pt holder are visible, while at 600 °C peaks from the perovskite LSCF phase can be observed. Thus, between 550 ° and 600 °C LSCF crystallization occurs. To present the crystallization process clearly, Figure 2B shows the main peak of the LSCF phase ($2\theta \approx 31.7^\circ$) measured at increasing temperatures. The presence of the perovskite phase can be observed beginning at a temperature of 600 °C. Further increases of temperature lead to a change in the peak shape (narrowing) due to the increased size of the grains. Moreover, the shifting of the peak occurs as a result of the lattice thermal expansion [17]. Figures 3A-C present the surfaces of 140 nm thick cathode layers annealed at 800 °C, 1000 °C, and 1200 °C, respectively. One can see that this results in an increase of the grain size from 50 nm for the annealing temperature of 800 °C,

through 150nm for 1000 °C, to 300 nm for 1200 °C. The roughness of the continuous layers visible in Figures 3A and B reflects the shape of CGO substrate grains. The cumulative result of the thin layer grain size measurements, obtained by both Scherrer analysis of the XRD peaks broadening and analysis of the SEM images is shown in Figure 4. It can be seen that the annealing temperature of 900 °C -1000 °C leads to the formation of the a layer at which the particle size equals the thickness of the applied layer. At temperatures higher than 1000 °C, a change in the thin layer coverage of the electrolyte substrate can be seen. The growth of particles over the size of 140 nm, thus over the layer thickness, leads to inhomogeneities, discontinuities and, in an extreme case (annealing at 1200 °C), to the formation of isolated islands, as seen in Figure 3C. This phenomenon was also observed for YSZ sol-gel films in [18]. In the case of the smaller grains, layers uniformly cover the surface of the electrolyte. A dense layer annealed at 800 °C has a thickness of approximately 140 nm, which corresponds at this temperature to a size of three grains. The cross-section of the sample prepared under these conditions is shown in Figure 3D. Well-established contact with the surface of the electrolyte is visible. Furthermore, small pores between 10-30 nm are observed in the layer annealed at 800 °C (with a grain size of approximately 50 nm). Pores of this size may be classified as mesoporosity [19]. These mesopores are more visible in the SEM micrographs shown in Figure 5. Figure 5A presents the surface of the layer with pinholes. In the cross-section presented in Figure 5B, potentially percolating pores can be seen. This suggests that the layer annealed at 800 °C may be neither perfectly dense, nor gas-tight.

As described above, the structure of the cathode functional layer is significantly affected by the method of its preparation. Further studies were carried out to ascertain the influence of the microstructure of the cathode functional layer on its electrical and electrochemical properties. Namely, DC electrical conductivity studies of thin films were performed. Figure 6A shows the electrical conductivity of the layers plotted as a function of annealing temperature. Figure 6B shows the electrical conductivity measured at 500 °C for the different annealing temperatures. It is visible that the initial increase of the annealing temperature from 500 °C to 800 °C and the related increase of the grain size, leads to an increase in the electrical conductivity. The highest conductivity was obtained for

the annealing at 800 °C, namely 106 S cm⁻¹ at 600 °C. For this layer the size of the grains is still three times smaller than the thickness of the layer. At higher annealing temperatures, a linear decrease in conductivity is observed, most likely, associated with the lower effective grain-to-grain connection due to grain spheroidization once the grain size becomes comparable with the layer thickness. For the sample annealed at 1100 °C (and above), at which the formation of isolated islands was observed, the electrical conductivity is not measurable. The highest measured conductivity of 106 S cm⁻¹ is about third the value reported by Tai [17] for bulk sample, namely 330 S cm⁻¹.

The electrochemical studies performed on the symmetrical cells with porous cathodes using impedance spectroscopy allowed the determination of the area specific resistance (ASR). ASR values obtained were no higher than 960, 122 and 36 mΩ cm² at 600, 700 and 800 °C, respectively. Figure 7 shows the Nyquist plots at 700 °C (with series resistance subtracted) of the most distinctive symmetrical samples, namely without a LSCF layer (a reference) and with a thin LSCF layer annealed at 700 °C, 1000 °C and 1200 °C. Points denote experimental data, while solid lines are calculated fits of the equivalent circuits. The equivalent circuit consisted of three parallel R–CPE (constant phase element) elements, which represent three spectrum features recognizable at 700 °C. The equivalent circuit is shown in Figure 7. At the measurement temperature of 700 °C, the series resistance mostly originates from both bulk and grain boundary CGO conductivity, since their characteristic frequencies are above the measurable spectrum [20]. The CGO properties are not investigated in this paper, thus the series resistance is omitted. High (R1–CPE1) and middle (R2–CPE2) frequency features are the result of electrode reaction, most likely the higher frequency signal is related to surface oxygen exchange, while the lower frequency is a result of cathode/electrolyte interfacial resistance [21]. However, these two features have similar characteristic frequencies and for most of the cases, it is impossible to correctly distinguish each contribution. At 700 °C and above, R3–CPE3 becomes visible within the low frequency range, i.e. below 10 Hz. It is usually associated with limited gas diffusion through an electrode [9]. At 700 °C ASR₃ values were in the range of 4-15 mΩ cm². It is visible that the layer annealed at 700 °C affected the impedance spectrum in comparison to the reference sample. All three resistances decreased, while the capacitances of the electrode reactions increased. As a result,

the characteristic frequencies of processes 1 and 2 were lowered from 83.0 kHz to 0.9 kHz and from 1.7 kHz to 0.1 kHz, respectively. The sample with the thin layer annealed at 700 °C was the only one to exhibit a significant difference during the third, diffusive process, as its resistance decreased. In addition, processes shifting resulted in the overlapping of features 2 and 3. It may be explained, that the thin cathode layer increases the surface over which charge transfer between the cathode and electrolyte occurs, which enables more oxygen ions to diffuse through the bulk of the LSCF. Furthermore, the surface exchange on the thin layer may additionally occur due to its mesoporous nature. This directly leads to smaller resistance and larger capacitance of these processes. On the other hand, in the case of the layer annealed at 1000 °C the increase in *ASR* occurs, namely from 103 to 122 mΩ cm², compared to the reference. This diminished performance may be explained by the fact that the layer annealed at 1000 °C has grains of a similar size to the actual layer thickness, forming a thin film which is both coarser and denser. In this case, the surface area for oxygen reduction is decreased and the length of the triple phase boundary is lowered, because the electrolyte is separated from the molecular oxygen. When the layer was annealed at 1200 °C and its grains were completely separated from each other, the impedance spectrum of the cathode became similar to the reference. Small deviations may be a result of inter-diffusion between the LSCF and CGO, which can occur at 1200 °C [22,23] or slightly altered sintering of the cathode/electrolyte interface, which can improve cathode preparation repeatability [11].

Figure 8 shows the *ADIS* plots of the impedance spectra shown in Figure 7, calculated in relation to the reference sample (without the LSCF thin layer). It is visible that the differential of the real part of impedance at frequencies above 1 kHz shows improvement over the reference and is almost identical for two samples, namely, those with layers annealed at 700 and 1000 °C. However, at frequencies below 1 kHz the sample annealed at higher temperature shows significant deterioration of the impedance. The sample with a layer annealed at 1200 °C became similar to the reference except for increased capacitance of electrode processes (the decrease in the *ASR* was not significant). As a result, characteristic frequencies shifted slightly towards lower values. At the lower frequencies (<10 Hz)

related to diffusion processes, the impedances are very similar and as a result the ADIS values are relatively low.

In Figure 9, the symmetrical cell polarization resistance measurements carried at 700 °C for thin LSCF layers annealed at different temperatures are presented. The reference sample without thin layer showed an *ASR* value of 103 mΩ cm². The lowest and very similar polarization resistances were obtained for the annealing temperatures at and below 700 °C (~60 mΩ cm²). This suggests that the annealing of the layers far below the cathodes sintering temperature does not have much influence on the obtained results. The final microstructure and properties of the cathode functional layer, in these cases, will be developed during the porous cathode sintering step and operation of the cell. However, it is worth noticing that the cell with the layer annealed at 800 °C showed a higher *ASR* value (78 mΩ cm²) than the layer annealed at 700 °C (60 mΩ cm²). This may indicate, that the layer annealed at 700 °C sinters better with the porous cathode, because it still undergoes grain growth at the cathode sintering temperature of 800 °C. A thin layer obtained at low annealing temperatures allows the formation of an improved interface between the electrolyte and cathode enabling effective charge transfer. Moreover, small grains form additional triple phase boundary, as stated previously.

Increasing the sintering temperature and the related grain growth, resulted in an increase of polarization resistance. At an annealing temperature of 1000 °C, this value is higher than for the cell without the cathode functional layer, at this temperature polarization resistance reaches its maximum of 122 mΩ cm², as stated before. In this case, the temperature causes the grains to grow to a level comparable with the thickness of the applied layer. This leads to the formation of a solid boundary layer, which limits the effective exchange of oxygen. Further grain growth (at 1100 °C and more) creates a discontinuous layer, which results in a reduction of polarization resistance. The discontinuous layer no longer meets the role of the functional layer, and the investigated system ceases to differ significantly from the traditional system with a direct interface between the porous cathode and the electrolyte. As noted previously, at this temperature inter-diffusion between CGO and LSCF may occur.

As presented above, the introduction of the nano-structured cathode functional layer leads to the 40% decrease in the polarization resistance of the interface between the electrolyte and the cathode.

Improvement in this range is in agreement with previous studies by Hildenbrand [9] and Dumaisnil [10] who reported decrease of ASR at 600 °C from 0.67 $\Omega \text{ cm}^2$ to 0.21 $\Omega \text{ cm}^2$ and from 0.38 $\Omega \text{ cm}^2$ to 0.26 $\Omega \text{ cm}^2$, respectively. An additional advantage of using the above-described layers is in improved stability of the entire system. In order to enforce faster ageing of the cathode, samples with and without 140 nm thick thin layers annealed at 700 °C were periodically heated-to 700 °C and cooled-down to 100 °C. The measurements taken at 700 °C showed deterioration of the polarization resistance possibly due to cathode cracking and delamination. Figure 10A presents changes of the cathode ASR both with and without a functional layer during ageing of the samples. A noticeable difference in the level of the initially measured resistance can be seen. Besides this, a systematic increase in the ASR for a typical interface and practically stable operation for a system with cathode functional layer during ageing may be observed. The increase in the ASR value of the reference sample is linear, namely 1.3 m $\Omega \text{ cm}^2$ per cycle. On the other hand, both cathodes show deterioration of apparent electrolyte conductivity σ (calculated from series resistance), which is shown in Figure 10B. In this case, the conductivity of the sample with the LSCF layer decreases at a the rate of 12 $\mu\text{S cm}^{-1}$ per cycle, which is twice as fast as the sample without the LSCF layer. It is however, only 0.02% of initial conductivity (60.4 mS cm^{-1}), which is 5 mS cm^{-1} more than the initial conductivity of the reference sample. As a result, the increase in total resistance was significantly larger for the reference sample. Figure 11 shows ADIS analysis of aged samples with respect to the initial measurements. It is visible, that the sample without the layer, suffered from an increase in Z' within the range of frequencies between 5 Hz and 2 kHz. The change was visible mainly for the second R–CPE element, for which both ASR and capacitance increased. As a result, the characteristic frequency was reduced from 1.4 to 0.7 kHz. This can be attributed to the deterioration of the cathode/electrolyte interface, and thus the charge transfer occurring over a smaller area. On the other hand, in the case of the sample with the LSCF layer, a small decrease in the characteristic frequency of the electrode reaction is visible. It progresses during the ageing, however, the polarization resistance is virtually unaffected.

There was no visible difference in cathode/electrolyte interface morphology observed before and after the ageing process (SEM micrographs not shown here).

4. Conclusion

The study showed that the microstructure of the cathode functional layer with a thickness of 140 nm has a significant impact on cathode electrochemical performance. It was shown, that this layer should be mesoporous and its desirable grain size should be as small as possible. Such mesoporous and nanocrystalline structure can reduce the polarization resistance of the cathode – electrolyte interface by about 40% and can improve the stability of cell performance. Spin coating of metallo-organic precursor allows a very fine grain structure to be obtained, however the final size of the crystalline structure is determined by the sintering temperature of the cathode.

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Figure captions

Fig.1 Schematic representation of the symmetrical cell.

Fig.2 A) HT–XRD patterns of the LSCF precursor mixed with CGO powder obtained at 550 °C and at 600°C, B) main peak of LSCF perovskite phase during heating to 1000 °C.

Fig.3 SEM micrographs of the 140 nm LSCF thin layer deposited on CGO substrate. A-C) Surfaces of the layer annealed at 800 °C, 1000 °C, 1200 °C, respectively. D) Cross-section of the sample with thin layer annealed at 800 °C and sintered with porous cathode, I – porous cathode, II –thin layer, III – CGO substrate..

Fig.4 Grain size of LSCF layer as a function of annealing temperature, measured by Scherrer analysis of the XRD peaks broadening and analysis of the SEM images.

Fig.5 SEM micrographs of the 140 nm LSCF thin layer annealed at 800 °C with visible mesoporosity.

A) Surface scan, B) cross–section.

Fig.6 A) Temperature dependence of the DC electrical conductivity of the layers annealed at different temperatures. B) Sintering temperature dependence of the DC electrical conductivity, measured at 500 °C.

Fig.7 Equivalent circuit and Nyquist plots for symmetrical samples with and without a thin LSCF layer annealed at 700, 1000 and 1200 °C. Measurements performed at 700 °C. Solid lines denote equivalent fits. Numbers over the empty symbols indicate logarithm of the frequency.

Fig.8 ADIS plots of samples with the LSCF layer annealed at selected temperatures in relation to reference without the LSCF layer.

Fig.9 Area specific resistance of symmetrical cells measured at 700 °C as a function of thin layer annealing temperature.

Fig.10 Relative change of A) the area specific resistance of the symmetrical cell, B) electrolyte apparent conductivity as a function of number of heating/cooling cycles.

Fig.11 ADIS plots of samples during the ageing with respect to their first measurement for A) sample without the thin layer, B) sample with the layer.

Figure 1

Figure 2a

Figure 2b

Figure 3

Figure 4

Figure 5A

Figure 5B

Figure 6A

Figure 6B

Figure 7

Figure 8

Figure 9

Figure 10A

Figure 10B

Figure 11A

Figure 11B