Journal of the European Ceramic Society 22 (2002) 41–48

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Fabrication and performance of advanced multi-layer SOFC cathodes

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Received 30 August 2000; received in revised form 31 January 2001; accepted 16 February 2001

Abstract

Multilayered cathodes for solid oxide fuel cells are presented. The cathodes are composed of strontium doped lanthanum manganate and yttria stabilised zirconia, the ratio of which is increased with increasing distance from a supporting zirconia electrolyte. Some cathodes additionally carry a number of layers with a graded transition from manganite to cobaltite to add an electronically highly efficient current collector. The cathodes were prepared by spray painting and low temperature sintering. Electrochemical measurements revealed a performance up to 0.2 Ω cm^2 at 750°C for the first generation of these cathodes. The electrochemical performance was found to be influenced further by the microstructure at the interface close to the solid electrolyte and the quality of electrical contact thorough the sintered electrode. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cathodes; Electrical properties; Fuel cells; Functionally graded materials; $LaMnO_3$; ZrO_2

1. Introduction

A solid oxide fuel cell (SOFC) is an assembly of different, mostly ceramic materials building up the functional elements air electrode, solid electrolyte and fuel electrode. The air electrode includes at least one electronically conducting oxide, traditionally Sr- doped $LaMnO_3$ for high temperature SOFC's.[1] Single- but also double-layer electrodes have been reported,[2–4] where the functions of an electrode, (i) electrochemical reaction and (ii) current pick up are attributed to regions associated with the interface to the solid electrolyte and to a topping layer, respectively. It has been shown earlier, that it is advantageous to prepare the electrochemically active volume from a composite of LSM and yttria stabilised zirconia (YSZ).[5,6] Results for double-layer cathodes made with $(La_{0.85}Sr_{0.15})_{0.9}MnO_{3\pm\delta}$ (LSM) and ZrO_2 with 3 mol% Y_2O_3 (TZ3Y) in the electrochemically active layer have been reported.[7–9] The polarisation resistance at 850°C in dry air was found to be in the range of 0.3–0.5 Ω cm^2 referring to a non-polarised state (OCV).

It is well known, that the quality of a contact between two materials, different with respect to physical properties, may be enhanced by allowing a gradual change in the composition between the two materials. The grading principle has been used earlier for cobaltite assisted current collection for SOFC cathodes[10] and the previously mentioned double-layer LSM based cathodes may be argued to represent grading principles. General perspectives of grading have been described by Sasaki and Gauckler.[11] With this work we want to describe the fabrication and performance of multi-layer cathodes consisting of up to nine layers and combining three groups of materials, (1) zirconia stabilised with 3 or 8 mol% yttria (TZ3Y, TZ8Y, respectively), (2) $(La_{0.85}Sr_{0.15})_{0.9}MnO_{3-\delta}$ (LSM), and (3) $La_{0.84}Sr_{0.16}CoO_{3\pm\delta}$ (LSCo).

2. The construction of functionally graded cathodes

The advanced cathode is, in principle, composed of a number of individual layers, each with its own characteristics, but with variations between adjacent layers kept below a critical level, which would influence performance adversely.

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[✝] This paper is dedicated to the memory of Carsten Bagger.

PII: S0955-2219(01)00238-2

The construction of the present multi-layer electrodes is illustrated in Fig. 1. The individual layers are graded in a way which allows a smooth and constant transition from one pure material to another. Starting from the electrolyte surface of 100% TZ8Y, the cathode steps up the LSM content from 20% in a first layer to 100% in the 5th layer. In the subsequent four layers, LSCo is graded into the LSM from 25 to 75 wt.% followed by pure LSCo. This grading enables redistribution of TEC-mismatch effects from otherwise planar interfaces between pure materials, electrolyte — traditional cathode or LSM — cobaltite[11] to larger volumes of the cathode. Thus it is presumed to increase the mechanical stability of the cathode.

Grading also allows tailoring of other properties such as microstructural functionality. The electrochemical process in the cathode reaction involves insertion of oxygen ions supplied from gaseous oxygen into the electrolyte phase. The related processes take place in a certain region around the so called triple phase boundary (TPB) where YSZ/LSM and the gas phase are in contact to each other. The length of the TPB is inversely proportional to particle size. A composite YSZ/LSM layer comprises TPB's inside the porous layer and consequently a certain region of the composite layers above the solid electrolyte is expected to be electrochemically active.[9] The general in-plane conductivity of the cathode may be improved by grading the better conducting LSCo into LSM in the current pickup parts of the cathode. Since gas transport limitation inside the porous cathode is indicated for simple double-layer electrodes[8] the individual structures of the current collecting layers may be optimised to allow maximum availability of air and oxygen ions at the triple phase boundaries. Those electrodes combine a graded composition with adjusted functionality in the individual layers, and can be regarded as ''functionally graded cathodes''.

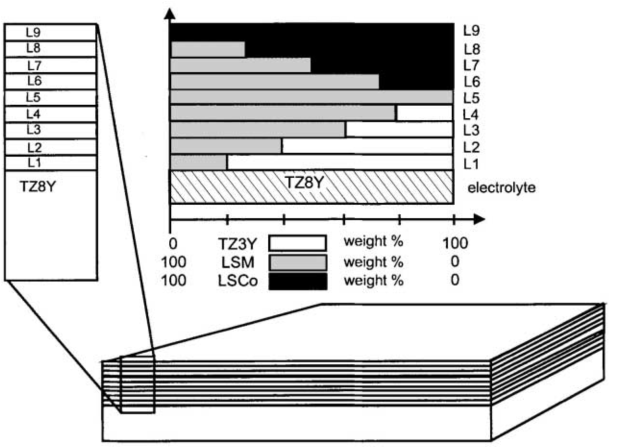

Fig. 1. Construction of advanced multi-layer cathodes with graded composition in YSZ, LSM, and LSCo.

3. Experimental

3.1. Slurry preparation

Spray paint slurries with different ratios of $(La_{0.85}Sr_{0.15})_{0.9}MnO_{3\pm\delta}$ (LSM) and $La_{0.84}Sr_{0.16}CoO_3$ (LSCo), (both Haldor Topsøe A/S) or yttria stabilised zirconia (YSZ) have been prepared. The YSZ is zirconia stabilised either with 3 mol% yttria (TZ3Y) (Tosoh Corp.) or 8 mol% yttria (TZ8Y, Tosoh Corp. or Unitec). The YSZ fraction was non-calcined, whereas both as-prepared and calcined fractions of LSM and LSCo were used. The powder mixtures have been rotary ball-milled with dispersant and ethanol. In Table 1 details are summarised on representative slurry compositions used to fabricate a cathode consisting of nine layers and graded in composition from YSZ to LSM and further from LSM to LSCo.

3.2. Cathode fabrication

The slurries have been applied by spray painting on both sides of a sintered electrolyte foil made from TZ8Y. Two types of electrodes have been prepared: (1) 5-layer cathodes consisting of LSM and YSZ (denoted YSZ/LSM cathodes) and 9-layer cathodes having additional layers made from LSM and LSCo (denoted YSZ/LSM/LSCo cathodes). Starting with the slurry of the lowest LSM content (20 wt.%) (L1) subsequent layers (L2–L9) were graded with respect to YSZ/LSM and LSM/LSCo as shown in Fig. 1. For some samples a tape cast LSM foil formed the layer L5 instead of a spray paint LSM layer.

The preparation of the individual layers and their mutual adhesion was controlled by intermediate sintering. A maximum of three layers have been sprayed on top of each other before sintering the samples for 2 h at 1100°C in air. A low sintering temperature of 1100°C was chosen in order to reduce both the chemical reaction between electrolyte and electrode material during fabrication.[12,13] The cells were either mounted vertically in the furnace or sandwiched horizontally between two porous alumina plates.

3.3. Electrochemical measurements

The as-prepared cathodes were electrochemically characterised as symmetrical cells in a two-terminal setup described in Fig. 2. Fractions of the sintered cells with areas in the range between 0.07 and 0.46 cm^2 were obtained either by breaking the cells by hand or cutting squares of ca. 0.25 cm^2 out of the cell with a diamond saw. The area of the cell fractions tested was determined after the electrochemical tests using (a) an optical microscope with an image analysis system or (b) weighing the corresponding area of paper.

Table 1
Slurry compositions used to prepare a nine layer YSZ/LSM/LSCo cathode (Fig. 4)[b]

Layer	YSZ/LSM/LSCo	YSZ		LSM			LSCo			Milling time (h)
		Kind	Fraction (wt.%)	T_{calc} (°C)	t_{calc} (h)	Fraction (wt.%)	T_{calc} (h)	t_{calc} (h)	Fraction (wt.%)	
L1	80/20/0	TZ3Y	80	600	*[a]	10	–	–	–	21
				1300	2	10				
L2	60/40/0	TZ3Y	60	600	*	20	–	–	–	21
				1300	2	20				
L3	40/60/0	TZ3Y	40	600	*	6	–	–	–	21
				1300	2	56				
L4	20/80/0	TZ3Y	20	600	*	8	–	–	–	21
				1300	2	72				
L5	0/100/0	–	–	1000	2	25	–	–	–	L6
				1300	2	75				
L6	0/75/25	–	–	1300	2	75	1400	2	25	24
L7	0/50/50	–	–	1300	2	50	1400	2	50	24
L8	0/25/75	–	–	1300	2	25	1400	2	75	24
L9	0/0/100	–	–	–	–	–	1400	2	100	24

[a] *"As-prepared", calcinations in air at given temperature and time.

[b] Additives: 2% PVP-MEK [polyvinylpyrrholidone M10.000 + ethanol–methy-ethyl ketone (2:1)], solvent: ethanol.

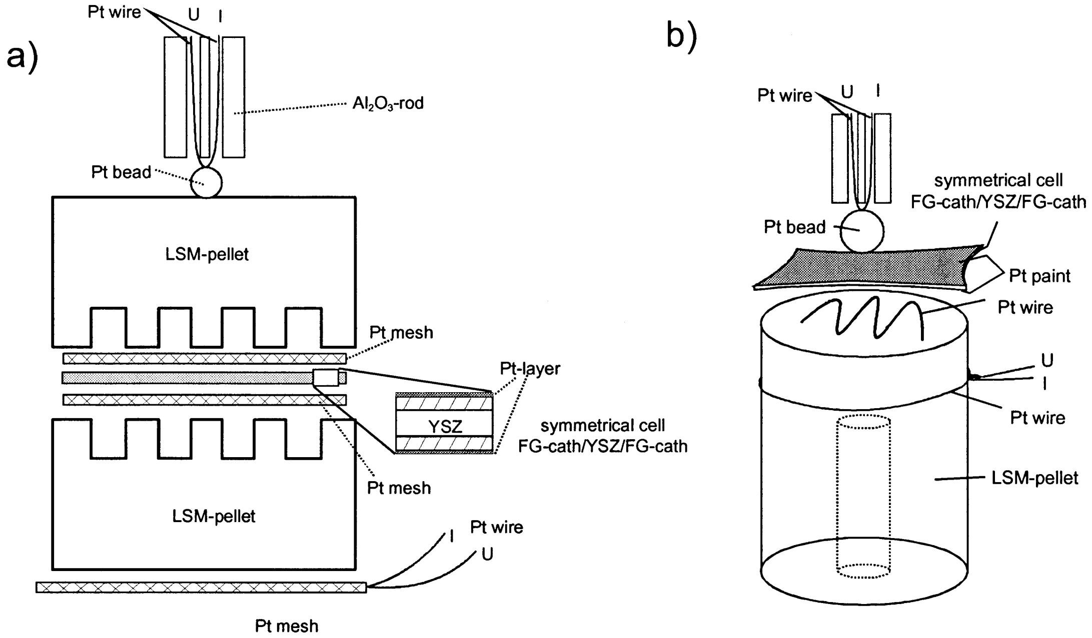

Fig. 2. Set-up for electrochemical measurements on symmetrical cells of type (YSZ/LSM)/YSZ/(YSZ/LSM) and (YSZ/LSM/LSCo)/YSZ/(YSZ/LSM/LSCo).

Proper contacting to the electrodes and appropriate in-plane conductivity of the current pickup system were realised to be critical points for electrochemical measurements of the high performance cathodes. The most reproducible results have been obtained in a symmetrical set-up described in Fig. 2(a). The samples were sandwiched between a painted Pt layer, a Pt-mesh and a sintered LSM-pellet with channels ground in one side. The Pt-layers were either painted Pt-paste (Demetron 328 A) or screen printed Pt-paste (ESL Europe).

Additional measurements have been performed in a slightly different and nonsymmetrical set-up shown in Fig. 2(b).

Electrochemical measurements have been performed in a pseudo-four terminal configuration by using separate Pt-leads to probe the current and the potential from one electrode. The cell compartment was flushed with pressurised air during the measurements.

Impedance spectroscopy at the open circuit voltage (OCV) was performed by using a Solartron 1287 Electrochemical Interface in combination with a 1260 frequency response analyser. The applied amplitude was 14 mV RMS, which gives an electrode perturbation well inside the linear i–η range. The frequency was 100 kHz to 0.1 Hz.

The impedance spectra are analysed in terms of equivalent circuits using the EQUIVCRT software.[14]

3.4. Microstructural investigations

The microstructure of the cathodes was investigated using a low vacuum scanning electron microscope (LVSEM). Pictures were obtained from unpolished cross sections of the samples. Several pictures have been combined in order to get a high resolution image covering the full width of an electrode.

4. Results

4.1. Microstructural investigations

Fig. 3 shows the microstructure of a graded YSZ/LSM cathode consisting of five sprayed layers. Different microstructures are distinguished and correlated to the layers L1–L5. The thicknesses determined from the micrograph are: L1 (20 wt.% LSM): 5–6 μm; L2(40 wt.% LSM): 5–7 μm; L3 (60 wt.% LSM): 15 μm; L4 (80 wt.% LSM): 15 μm; L5 (100% LSM): 40 μm. A homogeneous packing of particles (grey areas) with pores (black areas) is observed in each layer. The particle and pore sizes increase from L1 to L5.

The microstructure of a YSZ/LSM/LSCo-cell with 9 layers in total is shown in Fig. 4. The overall thickness of the graded cathode is approximately 95 μm. The individual layers are difficult to distinguish. Only the sections with and without LSCo are indicated each covering half of the electrode thickness. Homogeneous distribution of particles and pores is to see over the whole electrode thickness with an increase similar for particle size and pore size over the distance from the solid electrolyte interface to the top of the cathode. As expected samples show a much coarser structures in the first 30 μm attached to the solid electrolyte interface when the Tosoh YSZ is exchanged by Unitec YSZ in the first layers L1–L3. This correlates well with a higher fraction of particles with grains sizes above 1 μm arising from factory calcination of the Unitec powder.

4.2. Electrochemical performance

A typical impedance curve measured at 750°C for symmetrical cells of nine layer YSZ/LSM/LSCo cathode sintered freely suspended three times at 1100°C is given in Fig. 5. An ohmic resistance, R_{Ω}, (intercept between the impedance at high frequencies and the real axis) and a complex contribution (difference between high frequency and low frequency intercept with the real axis) can be distinguished. Two semicircles are resolved: a small one with a summit frequency of 10 kHz and a large but unsymmetrical one with a summit frequency of 40 Hz. Neither the presence of LSCO-layers nor the kind of Pt-Paste has an influence on the frequency distribution of the impedance. The dominating contribution shows close resemblance to a Gerischer impedance which has been observed for two-layer cathodes as well.[8]

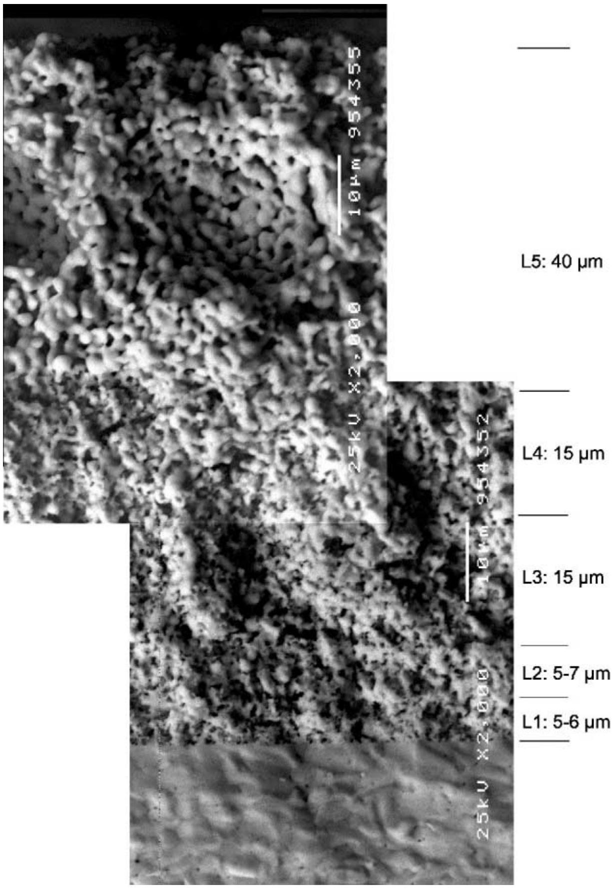

Fig. 3. Unpolished cross-section of a 5-layer YSZ/LSM cathode sintered 3 times at 1100°C in air.

In the ‘two electrode configuration’, the real part of the impedance corresponds to the sum of the voltage losses arising from the electrochemical processes in both electrodes that is twice that of the single electrode polarisation resistance and denoted $2R_{\mathrm{P}}$. In an ideal symmetrical cell the contribution of each electrode is the half of the total impedance. For some electrodes different thickness of the cathode layers on the two sides of the electrolyte are observed. Therefore different losses on each side of the cell can not be excluded.[9] Nevertheless half of the measured $2R_{\mathrm{P}}$ is used as an average value $R_{\mathrm{P,av}}$ in order to estimate the single cathode performance. The ohmic resistance in the test circuit, the difference between the origin and the high frequency intercept of the impedance with the real axis is determined by residual losses in the test circuit e.g. the ionic conductivity of the electrolyte structure, the electronic conductivity of the cathodes and the electrical contact between the cell and the measurement system.

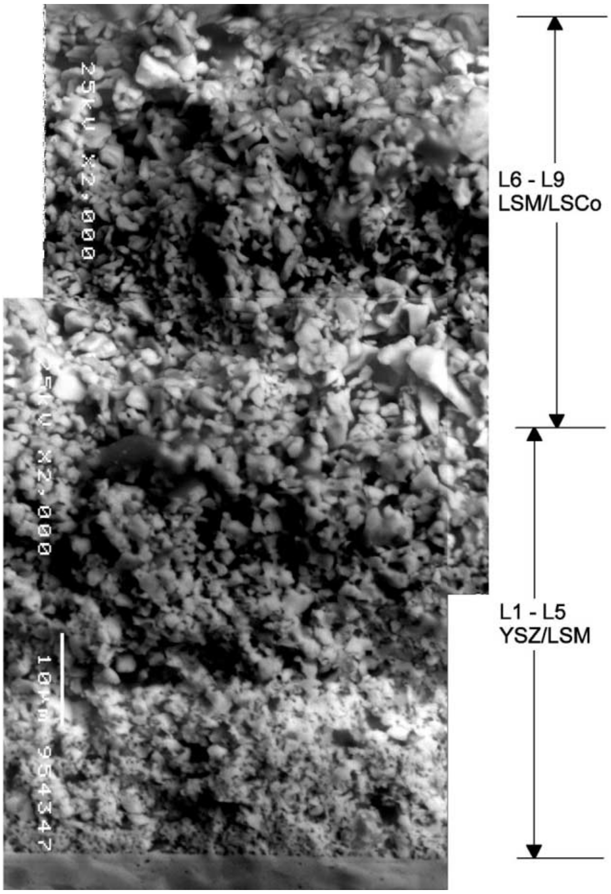

Fig. 4. Unpolished cross-section of a nine-layer YSZ/LSM/LSCo cathode sintered 3 times at 1100°C in air. The layers L1–L9 correspond to Fig. 1. Total thickness is around 95 μm.

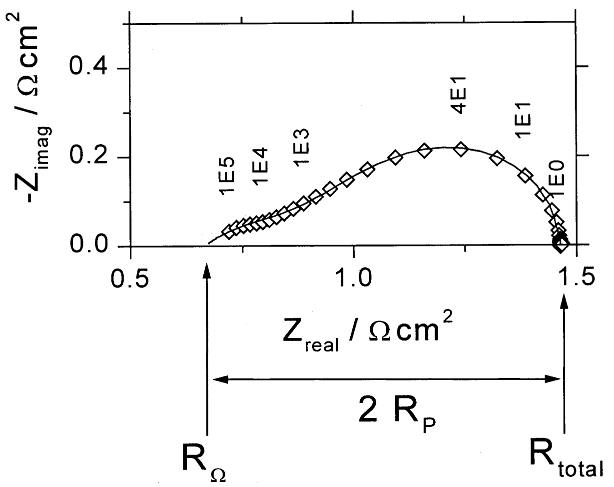

Fig. 5. Impedance curve (symbols) and simulation (line) for a nine-layer YSZ/LSM/LSCo cell measured at 750°C in air and OCV, the numbers indicate the frequencies in Hz.

The reliability of the measurement set-up was verified with five-layer YSZ/LSM cathodes by applying different weight loads to the electrical contacts. The impact of the weight load on R_{Ω} and $R_{P,av}$ is described in Fig. 6. Variation of the contact pressure from 77 to 828 g/cm^2 had no influence on the measured $R_{P,av}$. Only R_{Ω} decreases with increasing contact pressure. This corresponds to the situation, that the electrochemical performance of the cathode remains constant, as it should be expected for a properly contacted electrode.

The polarisation resistance $R_{P,av}$ is given in Fig. 7 for different electrodes. For a five-layer YSZ/LSM cathode sintered between alumina plates $R_{P,av}$-values of 0.07 and 0.076 Ω cm^2 at 850°C are obtained. At 750°C one sample has been measured giving $R_{P,av} = 0.234$ Ω cm^2. These are the lowest $R_{P,av}$-values achieved for the first generation of the advanced graded cathodes in the Risø-development.

Differences between multi-layer cathodes are most pronounced at the lowest measured temperature of 750°C. Samples with a fine structure towards the solid electrolyte, sintered vertically, and measured with a painted Pt layer show $R_{P,av}$ values between 0.328 cm^2 and 0.526 Ω cm^2. This holds for both five layer YSZ/LSM and nine layer YSZ/LSM/LSCo cathodes. Samples made from Tosoh YSZ, TZ3Y or TZ8Y, in the first layer L1 perform similarly within the observed scatter.

Replacing the painted Pt layer by a screen printed Pt layer decreases the measured electrochemical performance at 750°C. The poorest performance measured at this temperature was 1.62 and 2.08 Ω cm^2 and obtained for nine-layer YSZ/LSM/LSCo cathodes with a very coarse electrode structure in the first 30 μm towards the solid electrolyte.

The differences in the electrochemical performance are not reflected in the temperature dependence of $R_{P,av}$. Although not more than three temperatures are

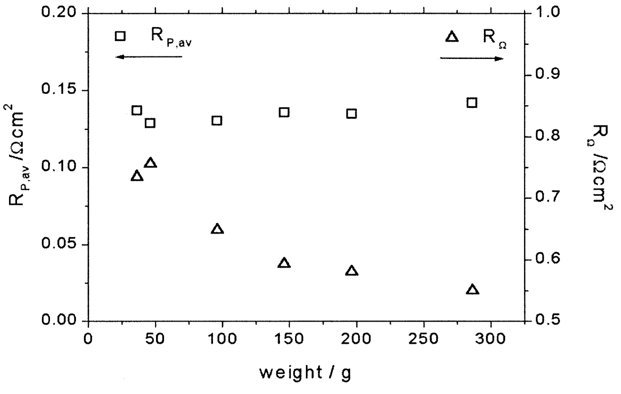

Fig. 6. Impact of weight load on $R_{P,av}$ (□) and R_{Ω} (△) for a 5-layer YSZ/LSM cathode at 850°C in air at OCV.

investigated the $R_{P,av}$-values show an apparent Arrhenius behaviour which would correspond to apparent activation enthalpies of 1.3–1.4 eV for all kind of multi-layer cathodes. Similar activation enthalpies are presented for conventional double-layer electrodes made from the same LSM and YSZ.[8]

Further modification within the first generation of multi-layer cathodes have been the thickness of the intermediate layers, the packing of particles and the pore sizes, and the use of a tape cast LSM foil in L5. Those samples have been tested in the non-symmetrical set-up [Fig. 2(b)]. The $R_{P,av}$-values scatter between 0.5 and 1.8 Ω cm^2 at 750°C without clear correlation to the sample variations. Furthermore, the results for identically prepared samples show up to 100% deviation in this particular setup. However, the best measured values coincide well with the range of $R_{P,av}$-values obtained by using the symmetrical measurement configuration. Assuming that the observed differences arise mostly from the uncertainty of the results in the unsymmetrical setup, the variations in the electrochemical performance are considered less important.

5. Discussion

The micrographs in Figs 3 and 4 show clearly that adhering porous structures consisting of up to nine individual layers can be realised by using conventional ceramic application techniques. In those layers, the composition changes smoothly from one pure material to another. The concept allows a smooth transition between three materials with different functions. Thus it is possible to combine the good electro catalytic properties of composite YSZ/LSM layers with the high electrical conductivity of LSCo as current collector, while a direct contact between YSZ and LSCo with possible associated unfortunate solid state reactions can be avoided. Although the number of layers is increased, the number of sintering was easily kept to 3 or 4 and further reduction seems possible.

The setup for the electrochemical measurements was considered important to qualify the advanced multi-layer cathodes. Both the reproducibility of the electrochemical performance and stability under various weight loads onto the cell indicate that the measurement set-up was suitable for measuring high performance symmetrical cells. The $R_{P,av}$-values of 0.2–0.5 Ω cm^2 correspond to voltage losses between 60 and 150 mV at a current density of 300 mA cm^{-2} and at 750°C. A similar performance of conventional two-layer cathodes requires a 100°C higher operating temperature of 850°C. The improved electrochemical performance together with derived activation enthalpies significantly lower than 2 eV are promising for using the advanced multi-layer cathodes in SOFC systems at reduced temperatures.

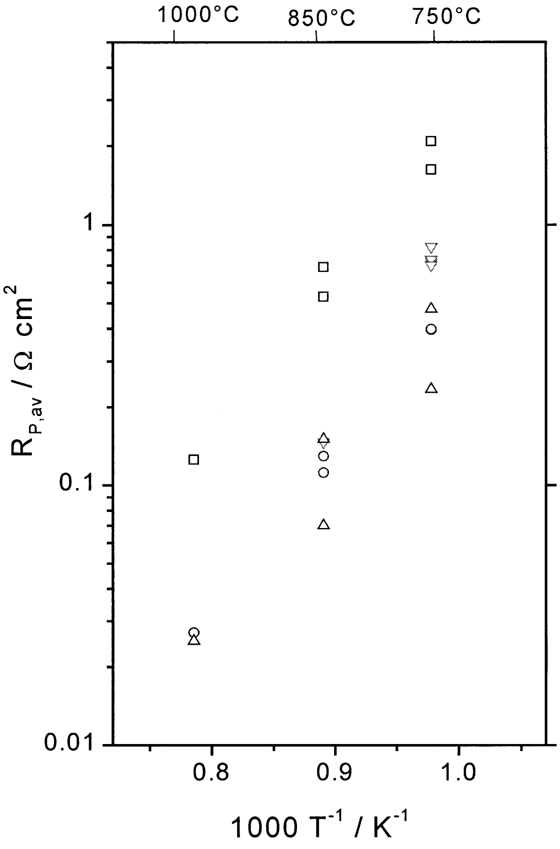

Fig. 7. Temperature dependent values of $R_{P,av}$ for various multi-layer cathodes in air at OCV. □: 9-layer YSZ(coarse)/LSM/LSCo cathodes with painted Pt layer on top; ▽: 9-layer YSZ(fine)/LSM/LSCo cathodes with screen printed Pt-layer on top; ○: 9-layer YSZ(fine)/LSM/LSCo cathodes with painted Pt layer on top; △: 5-layer YSZ(fine)/LSM cathodes with painted Pt layer (Demetron) on top.

At the measured high performance level we observed characteristic differences in the electrochemical measurements by varying certain preparation or measurement procedures. Understanding these differences may lead to further improvements and consequently will be discussed in the following.

5.1. Impact on the electrochemically active layer

In the multi-layer cathodes we assume that the electrochemically active area is extended over not more than a 10 μm thick region extending from the solid electrolyte, i.e. within layer L1, L2 and L3. Changing from a fine to a coarser structures of these layers by using different kinds of YSZ decreases the electrochemical performance significantly. This behaviour is in accordance with a decreased length of the TPB in a coarse structure due to the larger average particle size. Similar dynamic behaviour e.g. the shape and summit frequencies in the impedance and similar activation enthalpies are strong indications that the assumed active area is affected by these structural changes.

5.2. Impact on the intermediate layer

Only those TPL areas electrically connected to the top of the porous current collecting layer can be used during operation of the electrode. Pores needed to supply the oxygen gas to the electrochemically active layer and-more severe- micro-cracks may electronically disconnect parts of the geometric area at the interface to the solid electrolyte as discussed by Sasaki et al.[3] Those isolated domains may range from micron scale to larger dimensions leading to smaller active areas compared to the geometrical electrode area.

Undesired micro-cracks may be introduced by mechanical stresses under thermal cycling during electrode fabrication and SOFC operation. Suppression of micro cracks should lead to improved electrical contract throughout the electrode. Sintering of samples between alumina plates instead of freely suspended might affect the packing of particles and micro-cracking in intermediate layers. Although difficult to quantify, the advantage of such a sintering procedure might, therefore, be an improved electrical contact in intermediate layers. Therefore, the improvement of the advanced cathodes compared to conventional ones prepared from the same materials could be attributed to an improved interface structure combined with improved current pickup in layers adjacent to the electrochemically active layers. Similar impedance behaviour and temperature dependence of the electrode performance of both conventional and advanced multilayer cathodes support this interpretation.

5.3. Impact on the LSCo-layer and Pt-layer

Both LSCo and the Pt-layer are introduced to help the current collection within the volume of the porous electrode. Their functions are solely current pick up since there is no ionic conducting YSZ in direct contact with or reasonably close to these topping layers. No difference in performance between samples with and without LSCo layer could be observed indicating that the in-plane conductivity in the intermediate layers of the cathodes can be considered optimised for the measurement setup in Fig. 2(a) Additional LSCo-layers might be of importance in other SOFC designs.[15]

In the set-up of Fig. 2(a), only, the Pt-layer had a significant impact upon $R_{P,av}$. Although not clearly understood whether this results from the kind of paste or the type of application (painting or screen printing), the result indicates that the overall electrical contact to the sintered cathode is still of importance. The explanation might be related to an observed lower in-plane conductivity of screen printed Pt-paste with sub-micron size particles, which has not seen the correct curing temperature for such pastes of 1300–1500°C, as this would destroy the 1100°C cathodes.

A number of modification have been made to vary the thickness and porosity of the intermediate layers. The effects are generally weaker than the uncertainty arising from to the non-optimised measurement set-up. We assume that the optimisation of the current collection dominates residual losses e.g. gas transport limitations in the porous structure.[8]

5.4. Residual contributions from the test circuit

The above discussion was concerned with the $R_{P,av}$ value which is related to the electrochemical processes. The ohmic part, R_{Ω}, is determined by the electrolyte structure, resistance in the current pickup parts of the cathode and residual losses in the test circuit, mainly contributions from Pt-wires and contact points. Due to the high conductivity of LSM the contribution of a porous, percolating LSM phase with a thickness of 100 μm to R_{Ω} is assumed negligible. We are aware of the fact that at least the first layer of the cathode may not contain a percolating LSM network and consequently behaves as an electrolyte component. This means, that part of the electrode may contribute to R_{Ω} what would influence the overall cell performance negatively.

In the following, a rough estimate is made in order to distinguish the individual contribution to R_{Ω}. The electrical contact between the sample and the measurement system may be affected by the weight load applied to the Pt bead on top of the LSM pellet. Since $R_{P,av}$ remains constant under various weight loads these contributions are not related to the faradaic electrode reaction but may still be a significant part of R_{Ω}. The change in R_{Ω} with the applied weight load indicates that this contribution is indeed significant although its exact value has not been determined separately. Therefore extra contributions of the first layer to R_{Ω} can hardly be resolved for the examples described here, but may have to be discussed for other multi-layer electrodes.[16]

6. Conclusions

We have demonstrated five- and nine-layer cathodes made out of three traditional cathode materials to give improved electrochemical performances compared to that of conventional double layer cathodes. The improvement is attributed to a grading of composition and microstructure leading to an improved functionality of the individual layers. The first generation of the functionally graded cathodes show promising perspectives for SOFC applications and advanced mechanical properties are to be expected.

Acknowledgements

This work was performed as part of the European programme "Low-cost fabrication and improved performance of SOFC Stack components" (contract no. BRPR-CT97-0413). We wish to thank Birgit H. Nygaard for sample preparation and microstructural investigations.

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