

## Analysis of the oxygen reduction process on SOFC composite electrodes

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### Abstract

The electrochemical characteristics of composite cathodes consisting of Lanthanum Strontium Manganite (LSM) and Yttria Stabilised Zirconia (YSZ) have been analysed in order to emphasise the opportunity offered by these electrodes in the attempt to reduce the temperature of solid oxide fuel cells. Impedance analysis and potentiodynamic polarisation have been used as tools to evaluate the main electrochemical parameters and the results show that a volume ratio between LSM and YSZ close to 1 gives the best electrochemical activity because of the extension of the three phase boundary (TPB) in the electrode. Electrodes of this composition were subjected to high current load to verify the stability of the electrochemical performance and the results confirmed good cathode reliability.

### 1. Introduction

The technology of Solid Oxide Fuel Cells (SOFCs) is in an advanced stage of development, and several demonstration units are successfully operating in the world. However some issues still have to be resolved to improve SOFC performance and reduce the complexity. SOFCs are intended to operate in hybrid systems, in which exhaust gases from the electrochemical reactor are exploited by a turbo gas power unit and, further, by cogeneration. The lowering of the operating temperature of SOFCs is a very important target for the development of such systems. A reduction in the temperature could overcome some of the problems caused by the interconnections and thermal stresses and allow the use of cheaper materials. At the moment, temperatures as high as 1173 K are commonly needed to make the ionic conductivity of the solid electrolyte effective, given that the ionic conductivity drop of Yttria Stabilised Zirconia (YSZ) when the temperature is reduced from 1173 K to 973 K is remarkable. However, the anode-supported cell design [1, 2] reduces the thickness of the electrolyte to a few micrometers, and will permit the ohmic drop in the electrolyte to be reduced. A temperature reduction also influences the kinetic of the electrodic reactions and therefore suitable electrocatalytic materials are required.

The results obtained with the use of Lanthanum Strontium Manganite (LSM) cathodes in SOFCs with cermet anode (Ni/YSZ) and YSZ electrolyte show that it is a remarkably reliable system. The use of other

materials has not yet provided the same good and long-lasting properties. Hence, the increase in the active site for the electrodic reactions is important for the development of intermediate- and low-temperature SOFCs. Some pioneering work [3–5] have already paved the way in cermet and composite electrodes and interesting contributions on composite cathodes of the type LSM/YSZ, (La,Sr)FeO<sub>3</sub> (LSF)/gadolinium doped ceria (GDC) and (La,Sr)(Co,Fe)O<sub>3</sub> (LSCF)/GDC are available [6–8]. However, our opinion is that further studies need to be carried out on this topic. In fact, the difficulty to obtain reliable results is often encountered since correct experimental conditions are not easily met. This last consideration prompted us to carry on a simple approach to obtain reliable experimental data that can emphasize the main electrochemical characteristics of composite electrodes of the LSM/YSZ type.

### 2. Experimental

Typical three-electrode cells were used to perform electrochemical measurements on composite cathodes in air. Only the half-cell characteristics of the cathodes were investigated. The electrolyte pellet was made by pressing 2.5 g of 8 mol% Y<sub>2</sub>O<sub>3</sub> + 92 mol% ZrO<sub>2</sub> powder (TZ-8YS Tosoh powder with 0.3 μm particles assembled in 40 μm agglomerates) at 12 tons and sintering at 1773 K for 5 h. The final result was a ceramic disk 2 cm in diameter and about 2 mm thick. The cathodes were prepared by mixing controlled

amounts of YSZ and LSM ( $\text{La}_{1-x}\text{Sr}_x$ ) $_y\text{MnO}_{3\pm\delta}$  with  $x = 0.25$  and  $y = 0.95$  (Praxair, about  $0.3\ \mu\text{m}$ ). Ball-milling of the powders was performed to obtain a homogenous mixture. The mixture was diluted in  $\alpha$ -Terpineol (Aldrich) to obtain a paste easily applicable to the pellet surface by slurry coating. The electrode was then sintered at 1373 K for 2 h. By changing the relative amounts of YSZ and LSM, a wide range of electrode compositions was investigated. The cathodes had an area of about  $0.3\ \text{cm}^2$  and a thickness of around  $50\ \mu\text{m}$ . In order to reach equipotential conditions (i.e. homogeneous distribution of current lines), a thin layer of current collector made up of large-size, high-conductive particles, prepared by mixing the coarse LSM with terpineol, was applied to the working electrode surface. A Pt reference (Pt ink 6926 Engelhard) electrode was painted on the same side as the working electrode, and care was taken to leave as large a distance as possible between the reference and working electrodes in order to prevent systematic errors in the measurements of the electrochemical characteristics [9]. A Pt counter-electrode, having the same shape and position as the working electrode, was painted on the opposite side of the electrolyte pellet. Reference and counter electrodes were fixed to the pellet using a sintering treatment at 1173 K for about 1 h. The arrangement of the electrodes in the cell is shown in Figure 1.

The cells were placed in a tubular furnace with a PID (proportional, integral, derivative) temperature control. Measurements were carried out between 623 and 1173 K. The connections of the cell to the electrochemical instruments were made with platinum wires which were shielded to reduce noise. The electrochemical techniques applied were electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry. The EIS analyses were performed using a 1186 Solartron electrochemical interface and a 1260 Solartron Frequency Response Analyzer. Potentiodynamic measurements were performed using a potentiostat/galvanostat Amel 2051 with a Softassist software. Ohmic resistance correction of the polarisation curves was made by the extrapolation of the electrolyte resistance from the EIS analysis. The impedance measurements were carried out over a frequency range of 0.1 Hz to 1 MHz with a 20 mV A.C. signal amplitude at equilibrium potential.

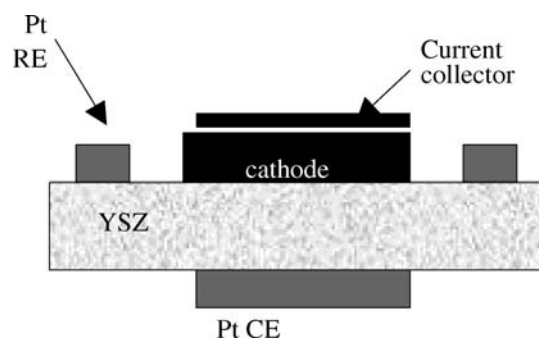


Fig. 1. Arrangement of the electrodes in the three-electrodes cells.

The cell was left at the highest temperature for 24 h before the measurements were taken.

### 3. Results

The impedance spectra obtained are generally composed of a high frequency inductive tail ( $f > 50\ \text{kHz}$ ) and a medium-low frequency capacitive depressed loop. This depression is especially observed in composite cathodes rather than in pure LSM. At a frequency lower than 10 Hz the data are scattered around a maximum impedance with a negligible imaginary component. The high-frequency tail is due to the inductance of the wires used in the connections. In this work stress has been put on the capacitive part of the spectra, which reflects the impedance of the cathodic system whether it arises from a purely kinetic activated control or a mass transport phenomena control in the overall oxygen reduction process. The understanding of the oxygen reduction path and the recognition of the rate determining step represent a very important issue from both a scientific and technological point of view. Many studies have already been carried out in this context but the complete interpretation of the EIS spectra and the understanding of oxygen reduction is still under debate. Our analysis considered the intercept at low and high frequency with the real axis of the Nyquist plot for determination of the so-called polarisation resistance,  $R_p$ . Figure 2 presents an overlap of the Nyquist plots for the different cathodes studied and Figure 3 plots the inverse of the  $R_p$  determined using these results at 1173 K as a function of the percentage of volumetric content of the LSM in the cathode,  $\xi$ .

Even though LSM cannot be considered as a pure electronic conductor, Figure 3 resembles the dome-shaped curve predicted by the theoretical analysis based on cermet electrode performance in several studies [3, 5]. These results are in good agreement with recent papers dealing with similar electrodes [6, 10]. The larger expansion of the three phase boundary (TPB) in the electrode thickness is achieved for a composition having a volumetric ratio between LSM and YSZ close to 1. This cathode composition shows an enhancement of the process rate more than 15 times higher than the pure

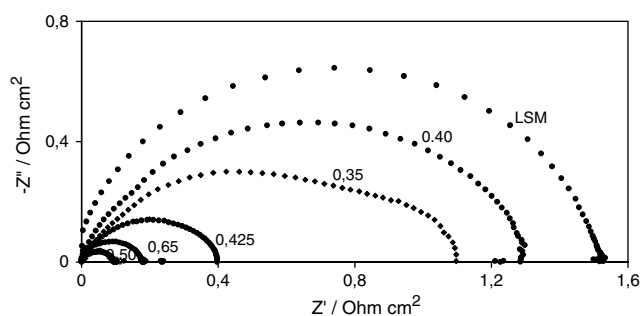


Fig. 2. Nyquist plots of composite cathodes at 1173 K. The volumetric content of the LSM in the cathode is indicated.

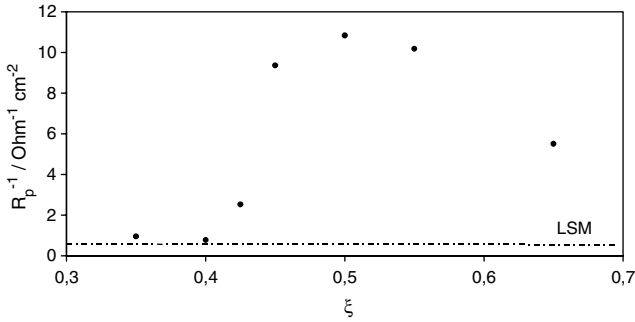


Fig. 3. Diagram of the inverse of the polarisation resistance as a function of the volumetric content of the LSM in the cathode.

LSM at 1173 K. With this type of cathode it is also observed that the polarisation resistance of the LSM at 1173 K is already reached at a temperature of 983 K (Figure 4). The Arrhenius plot for the different cathode composition shows a good linear relationship between  $1/T$  and  $\log(R_p)$ : according to Equation (1), typical for activation controlled processes. An apparent activation energy,  $E_a$ , related to the controlling step of the process, equal to  $120 \text{ kJ mol}^{-1} \pm 5$  is extrapolated for the composite cathodes (except for the cathode with  $\xi = 0.40$  that shows an apparent  $E_a = 110 \text{ kJ mol}^{-1}$ ) while a higher value, close to  $140 \text{ kJ mol}^{-1}$ , was found for the pure LSM cathode (Figure 5).

$$\ln R_p = \ln \frac{1}{k_0} + \frac{E_a}{RT} \quad (1)$$

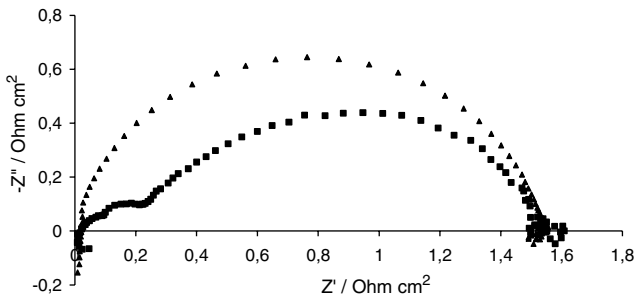


Fig. 4. Nyquist plots of: pure LSM cathode at 1173 K ( $\blacktriangle$ ) and composite cathode ( $\xi = 50$ ) at 983 K ( $\blacksquare$ ).

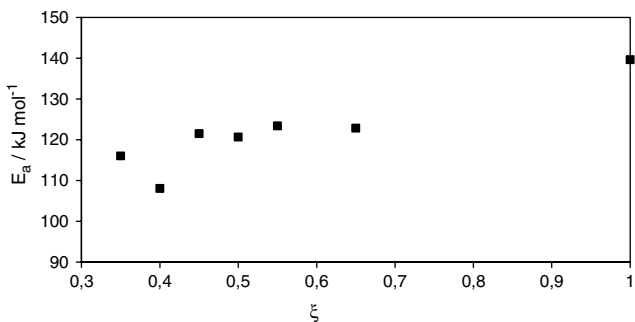


Fig. 5. Apparent activation energy for different composite cathodes and pure LSM.

These values of activation energy depend on the way the polarisation resistance is evaluated and this is probably the reason for some discrepancy encountered in the bibliography. However, the change in activation energy between the pure LSM cathode and the composites suggests that not only does an enlargement of the TPB occur in the composite cathodes but a different controlling step is involved in the overall oxygen reduction.

Figure 6 shows the microstructure of a cathode which highlights a typical non-homogeneity frequently encountered. The cathodic mixture presents agglomerates of ionic and/or electronic conductors which have not been sufficiently dispersed in the composite matrix during preparation. This means that further improvement in the electrochemical activity of the electrode is still possible.

In order to confirm the results obtained by impedance analysis some potentiodynamic measurements were carried out. In Figure 7 the Tafel curves at different temperatures are reported for a cathode composition of LSM/YSZ with volume ratio equal to 1. These curves were fitted into the high field overpotential region using the reduced form of the Butler-Volmer Equation (2) to obtain the exchange current density and compare with that determined from the same equation, reduced for the low field approximation (Equation 3), considering that the  $R_p$  values of the Nyquist plots are the charge transfer resistances  $R_{ct}$ :

$$i = i_0 \exp\left(\frac{\alpha 2F\eta}{RT}\right) \cong i_a \quad (2a)$$

$$i = -i_0 \exp\left(-\frac{(1-\alpha)2F\eta}{RT}\right) \cong i_c \quad (2b)$$

$$i_0 = \frac{RT}{2FR_{ct}} \quad (3)$$

In Table 1 the  $i_0$  and  $R_p$  are reported for both experimental approaches and a reasonable agreement of the data is observed. This confirms that the data reported are properly extrapolated. The  $R_p$  extrapolated from the linear part of the potentiodynamic  $\eta/i$  curves has also been included in the table.

The stability of the electrochemical characteristics of the cathodes with  $\xi = 50$  was verified applying a procedure in which the cell was heated at 1173 K and left under a current load of  $-500 \text{ mA cm}^{-2}$  for 100 h. During the cathodic current passage 4 current load peaks of  $-1000 \text{ mA cm}^{-2}$  were applied for 1 h. Several impedance measurements at open circuit potential were performed during the ageing procedure. The impedance results showed no relevant variation of the polarisation resistance before and after this procedure, as demonstrated by the typical Nyquist plots reported in Figure 8.

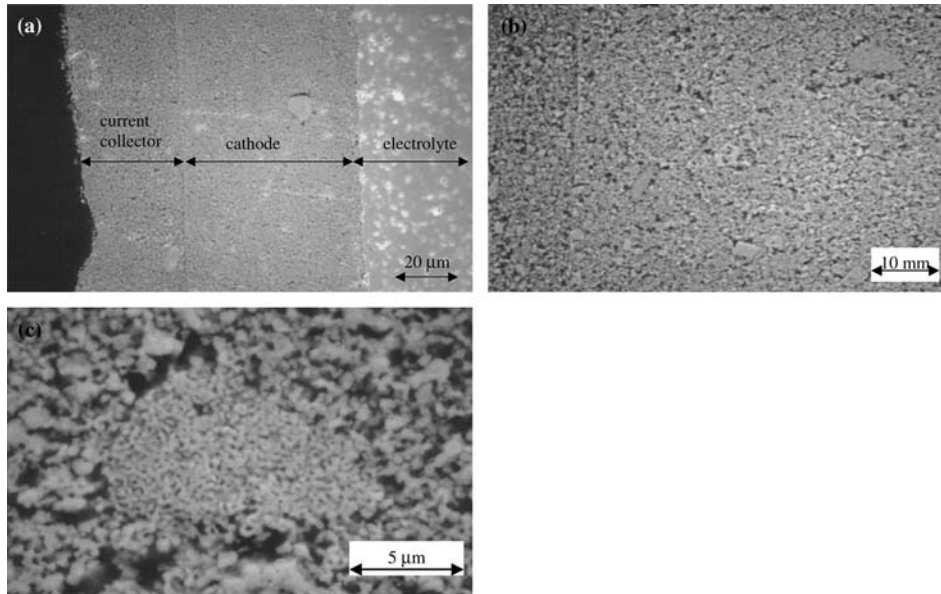


Fig. 6. Microstructure of the cathode ( $\xi = 50$ ), section of one of the samples used in the electrochemical measurements: view of the interfaces (a), magnification which highlights the presence of particle agglomerates (b) and the detail of a YSZ agglomerate (c).

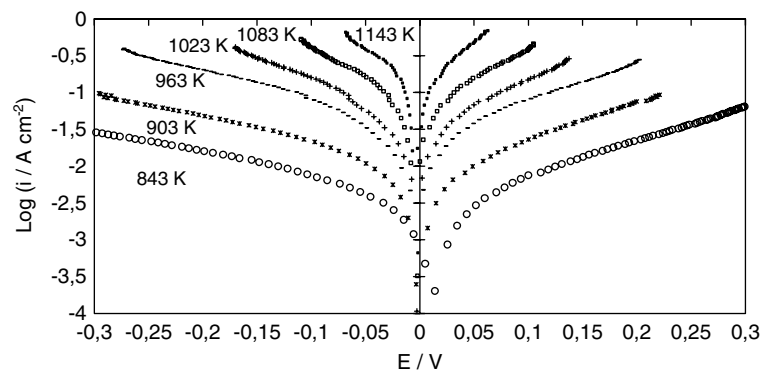


Fig. 7. Tafel plot (IR-free) obtained at different temperatures (sample  $\xi = 50$ ).

Table 1. Electrochemical parameters for several temperatures obtained by: EIS measurements ( $R_p$  and  $i_0$  Equation 3), potentiodynamic measurement ( $R_p'$ ,  $i_0'$  by Equation 2).

T/K	E.I.S.		Potentiodynamic	
	$R_p/\Omega \text{ cm}^2$	$i_0/\text{A cm}^{-2}$	$R_p'/\Omega \text{ cm}^2$	$i_0'/\text{A cm}^{-2}$
1143	0.11	0.47	0.11	0.13
1083	0.24	0.19	0.31	0.08
1023	0.64	0.069	0.82	0.047
963	1.76	0.024	1.8	0.024
903	4.78	0.008	4.7	0.009
843	15	0.0024	14.5	0.004

#### 4. Conclusions

The development of a composite cathode allows lowering of the operating temperature of SOFCs without loss of electrode performance. The best results were obtained for a LSM/YSZ volume ratio close to 1 ( $\xi = 50$ ). The microstructure of the cathode shows that it may be possible to obtain improvements by improving the homogeneity of the composite mixture. Impedance measurements show a good agreement

with potentiodynamic measurements. The reliability of the cathodes has been verified under a heavy current load.

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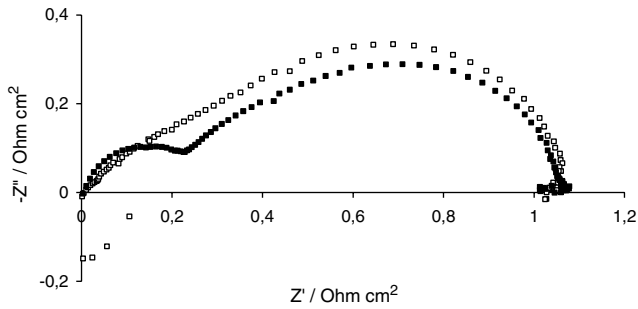


Fig. 8. Nyquist plots for the composite cathode ( $\xi = 50$ ) (■) before and (□) after ageing.

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