

Effect of Cation Demixing on the Electrochemical Performance of LSCFO Cathodes for SOFCs

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The commercialization of Solid oxide fuel cells (SOFCs) is still hindered by their cost and long term degradation. One of the most common degradation mechanisms of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-d}$ (LSCFO) cathodes reported in literature is element demixing. In this work, the degradation of LSCFO cathodes deposited on $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-d}$ electrolytes at 800°C in air for 50 h was investigated by electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). EIS spectra from LSCFO cathodes present two contributions: one at high frequency and another at low frequency. The high frequency contribution remains invariable during the ageing treatment while the low frequency contribution continuously increases. The formation of small segregates was observed after the ageing treatment. Energy dispersive spectroscopy analysis reveals that these segregates were particularly poor in Sr.

Introduction

Hydrogen along with renewable energy resources are planned to replace fossil fuels in the near future. Solid oxide fuel cells (SOFCs) are an attractive solution for the transition period between both energy sources since they can operate by using not only hydrogen but also fossil fuels (1,2). Nevertheless, the commercialization of these devices is still hindered by their cost and long term degradation. Overall cell degradation depends on the degradation mechanisms of its main components: anode, electrolyte and cathode.

The use of mixed conducting cathodes such as $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-d}$ (LSCFO) improves considerably the performance of the cell. However, one of the most common degradation mechanisms of LSCFO cathodes reported in the literature is element demixing and, particularly, Sr segregation. Although Sr segregation is usually reported in literature as a degradation mechanism responsible for the deterioration of the cathode performance, it is rarely seen as precipitates themselves. It is generally detected by an increase in the Sr content in some zones, mostly at the surface of the sample. However, Oh et al. (3) has actually observed Sr-rich precipitates in dense LSCFO samples but they did not report how these precipitates affect the cathode electrochemical performance.

The aim of this work is to study the effect of ageing on the electrochemical performance of LSCFO cathodes. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-d}$ powders were prepared by solid state reaction and deposited on $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-d}$ electrolytes by spin coating. Afterwards,

these cells were heat treated at 800°C in air during 50 h. These conditions would facilitate the formation of Sr segregates, according to literature. The electrochemical properties of the cathodes were monitored by electrochemical impedance spectroscopy (EIS), while the microstructure was characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Energy Dispersive Spectroscopy (EDS).

Experimental

Two $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-d}$ (LSCFO) powder batches (A and B) were prepared by solid state reaction method. Stoichiometric amounts of La_2O_3 , SrCO_3 , Fe_2O_3 and Co_3O_4 were mixed and ball milled for 1h at 400 rpm. The obtained powders were heat treated at 1000°C for 5h. Powder batch A was uniaxially pressed to form a cylindrical pellet. Batch B was dispersed in an ink and deposited onto both sides of a rectified $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-d}$ (CGO) substrate with ~ 1.5 mm thickness by spin coating technique. Afterwards, both the pellet and the LSCFO/CGO/LSCFO cell were sintered at 1250°C for 6 h. Finally, the pellet and the symmetrical cell were heat treated at 800°C in air for 50 h.

Impedance measurements were performed on the LSCFO/CGO/LSCFO symmetrical cell during the ageing treatment at 800°C under air for 50 h. EIS spectra were recorded using a potentiostat/impedance analyzer Autolab (Eco Chemie BV) within the 10^{-3} - 10^6 Hz frequency range. Platinum grids, slightly pressed on electrodes, were used as current collectors. All the impedance spectra were normalized taking into account the cathode geometric area ($= 0.747 \text{ cm}^2$).

The microstructure of the symmetrical cell was characterized by SEM before and after the ageing treatment. Samples were broken into pieces in order to observe their cross-section. The pellet was grinded into powder and its microstructure was investigated by TEM after the ageing treatment.

Results and discussion

Figure 1 show an impedance spectrum corresponding to the LSCFO/CGO/LSCFO cell measured under air at 800°C after 50 h of ageing. Two contributions can be clearly observed: one at high frequency and another at low frequency. All measured spectra present similar shape and were fitted with the equivalent circuit shown in the inset of Figure 1. High frequency contribution was fitted with a Warburg element Z_w (4), while the low frequency contribution was fitted with a parallel sub-circuit composed of resistance (R_{LF}) and a constant phase element (CPE_{LF}).

The evolution of the cathode electrochemical performance as a function of the ageing time can be observed in the Bode plot displayed in Figure 2. It is clearly seen that all the spectra have two contributions. High frequency contribution remains unchanged over the entire ageing treatment, while the low frequency contribution continuously augments. After the ageing treatment, the area specific resistance (ASR) corresponding to the low frequency contribution increases by a factor of ~1.8 (see Table I).

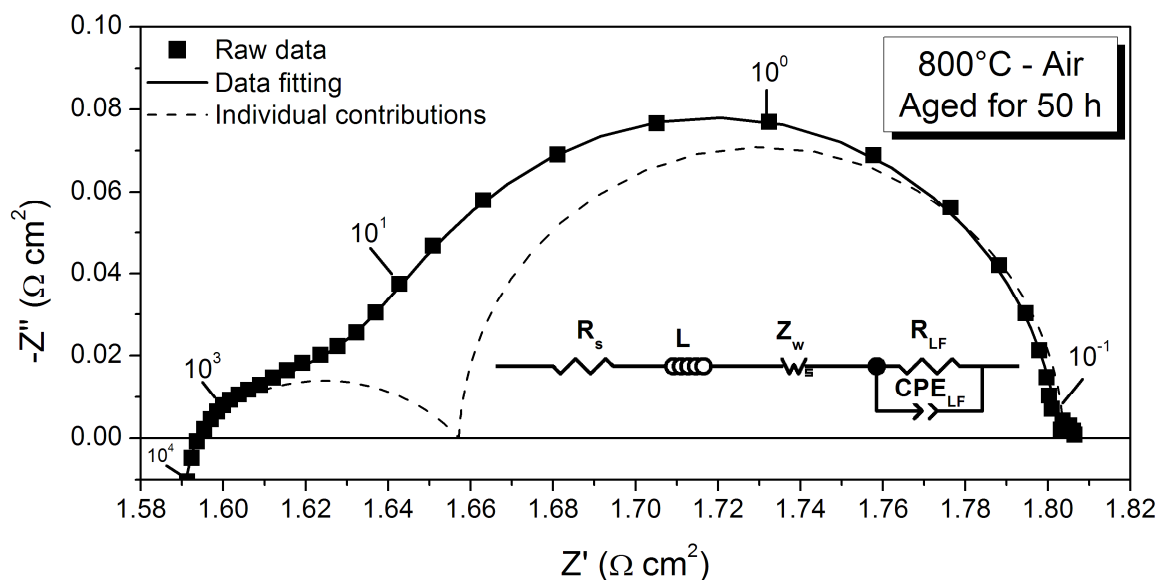


Figure 1. Nyquist plot of the impedance spectrum recorded after 50 h of ageing under air at 800°C for the LSCFO/CGO/LSCFO symmetric cell. The numbers in the Nyquist plots indicates the frequency.

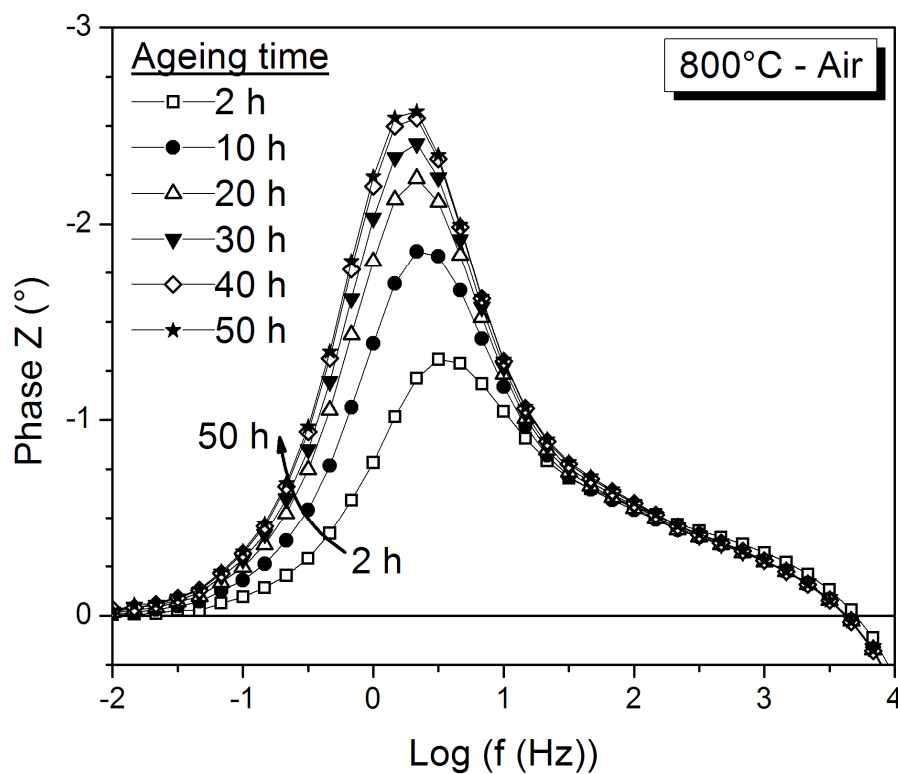


Figure 2. Bode plot of the impedance spectra recorded under air at 800°C after different ageing times for the LSCFO/CGO/LSCFO symmetric cell. The numbers in the Nyquist plots indicates the frequency.

TABLE I. ASR values corresponding to the Warburg and the low frequency contributions as a function of the ageing time.

Ageing time (h)	ASR _w (Ωcm^2)	ASR _{LF} (Ωcm^2)
2	0.08 ± 0.01	0.08 ± 0.01
50	0.077 ± 0.004	0.147 ± 0.003

SEM images at the cathode/electrolyte interphase before the thermal treatment (Figure 3a) show that the electrode grains cover a high percentage of the electrolyte surface forming a smooth and continuous layer of about $5\mu\text{m}$ thickness. An enlarged view at the cathode surface (Figure 3c) show grain sizes in the range of the hundreds of nanometers to one or two micrometers. The grain surfaces seem to be flat, and sharp grain borders are observed between them. Low magnification SEM images after the thermal treatment at 800°C for 50 hours (Figure 3b) show no visible damage or modification of the cathode layer or the electrode/electrolyte interphase. No alteration, delamination or growth of reaction compounds could be observed. However, a close view in the electrode grains detects a modification: some precipitates or wrinkles appear at some grain surfaces in the electrode side (white arrows in Figure 3d).

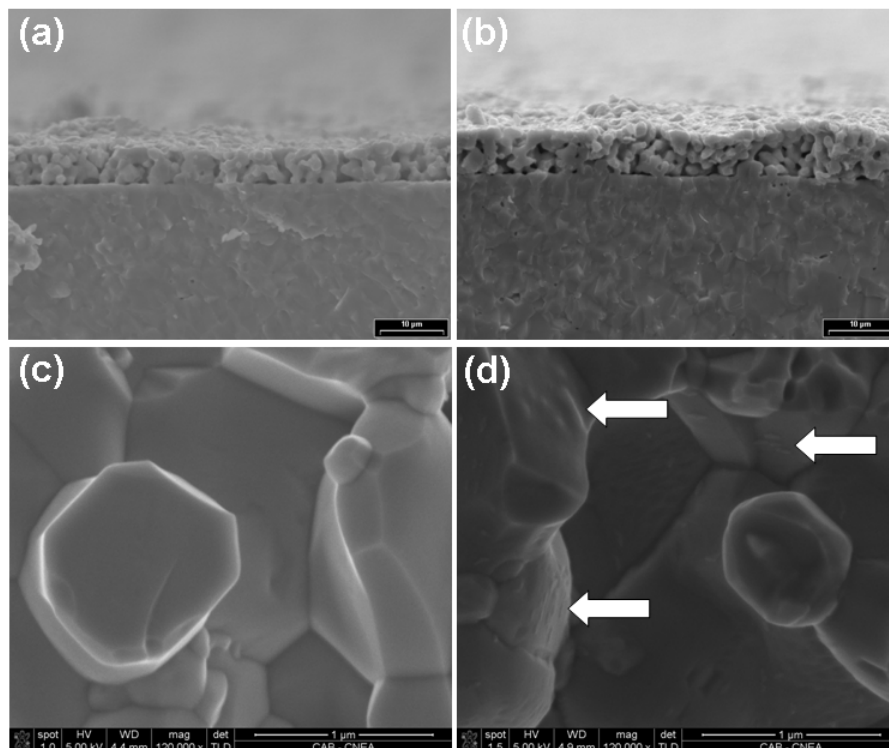


Figure 3. Cross-section SEM images of the (a,b) LSCFO/CGO/LSCFO cell and (c,d) the LSCFO cathode before (a,c) and after (b,d) the ageing treatment.

EDS technique can be used to identify and even quantify the chemical elements present in a sample. However, it is well known that a volume of at least $1\mu\text{m}^3$ is analyzed when EDS technique is used. This is caused by the nature of the interaction between the electron beam and the analyzed material. In view of that, it was not possible to investigate the composition of the precipitates observed in Figure 3d, which were appreciably smaller than $1\mu\text{m}^3$. EDS-TEM technique is instead suitable to accomplish

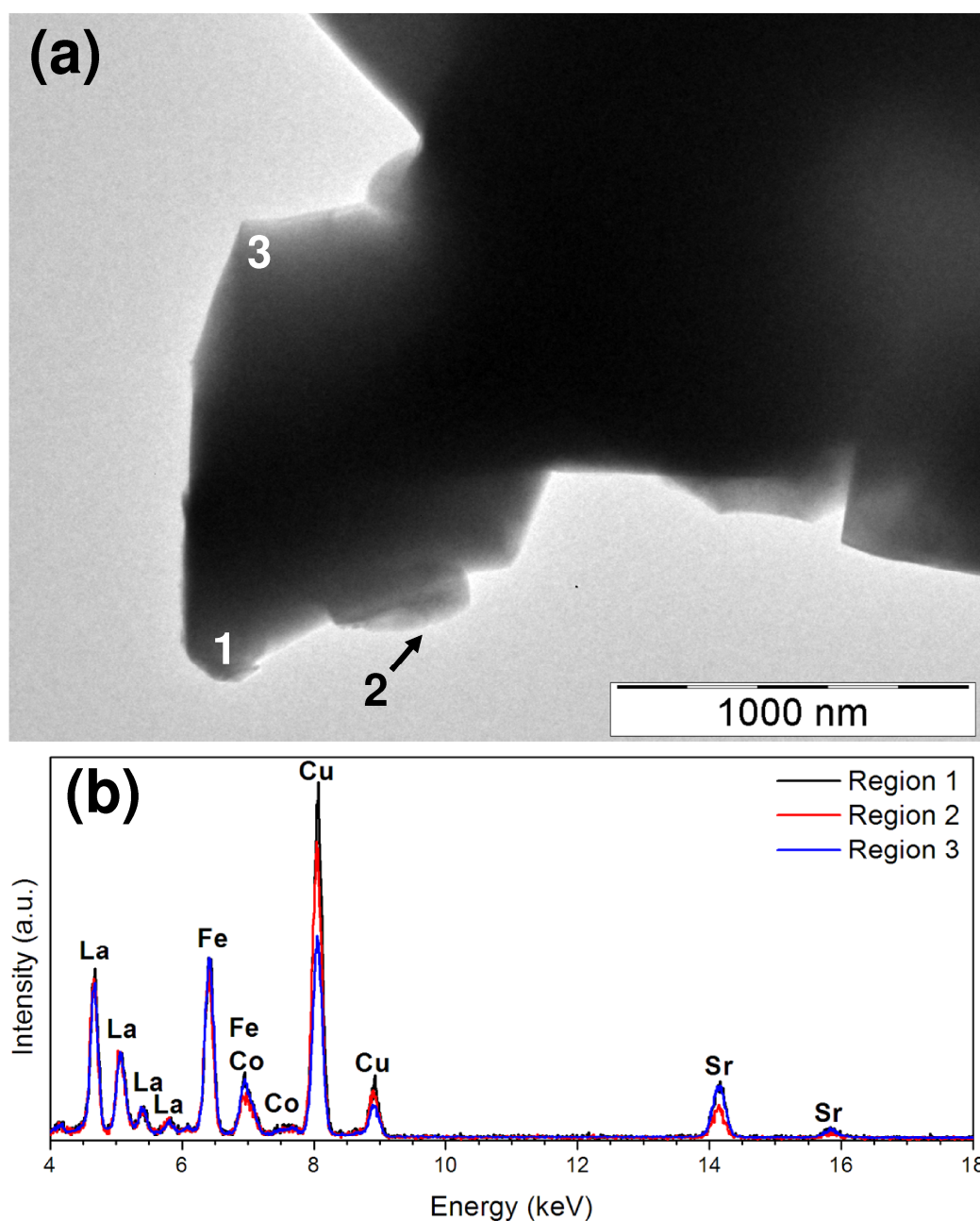


Figure 4. (a) TEM images an LSCFO particle after ageing treatment at 800°C in air for 50 h. (b) EDS spectra acquired in the regions indicated in (a).

TABLE II. Atomic percentages determined by EDS of the selected regions indicated in Figure 4a.

Region	La	Sr	Fe	Co	Sr/La	Co/Fe
1	42.3	19.5	30.0	8.2	0.46	0.27
2	47.8	12.6	32.0	7.6	0.26	0.24
3	40.5	19.2	31.4	8.9	0.47	0.28

this task but a thinner sample is required. Conversely, powder samples were studied by EDS-TEM after the ageing treatment performed at 800°C in air for 50 h. Figure 4 shows one of these LSCFO particles. A small precipitate appears attached at the bottom of the particle (see region denoted as 2 in the image). EDS spectra corresponding to the some

regions of the particle and the precipitate (indicated in Figure 4a) are displayed in Figure 4b. Element quantification is summarized in Table II. Composition in regions 1 and 3 (inside the particle) is similar to the nominal composition. In contrast, region 2 is poor in Sr (i.e. about the half of the nominal composition). Oh et al. (3) has reported the existence of Sr precipitates on dense LSCFO samples treated also at 800°C in air for 50 h. They also observed a subsurface Sr-depleted region between the LSCFO bulk and the Sr precipitate. However, the extension of the subsurface zone and the precipitate is not clearly reported. In our case, the volume analyzed with a beam spot of ~100 nm could include both regions. High resolution scan line EDS-TEM analysis is in progress.

Conclusions

The ageing effect on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-d}$ (LSCFO) cathodes at 800°C in air for 50 h was investigated by electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). EIS spectra from LSCFO cathodes present two contributions: one at high frequency and another at low frequency. The high frequency contribution remains invariable during the ageing treatment while the low frequency contribution continuously increases. The formation of small segregates was observed after the ageing treatment. Energy dispersive spectroscopy analysis reveals that these segregates were particularly poor in Sr. These findings give an valuable insight on the effect of element demixing on the electrochemical performance of LSCFO cathodes.

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