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# A sedimentation process for the fabrication of solid oxide fuel cell cathodes with graded composition

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**Abstract**

Materials with graded composition can be obtained by a sedimentation process during which particles of a powder mixture within a suspension fall by gravity upon a substrate. This process has been used to fabricate bulk SOFC cathodes by sedimentation of lanthanum strontium manganate (LSM) and yttria stabilised zirconia (YSZ) powder mixture upon a dense YSZ substrate and subsequent firing. A numerical simulation of sedimentation based on Stokes' law has been developed to control material and process parameters. Two cathodes with different composition gradients have been obtained by changing the initial conditions of the sedimentation. Their compositions estimated by electron dispersive spectrometry (EDS) have been found to be in reasonably good agreement with the prediction of the numerical model.


*Keyword:* Fuel cells; Composites; Sintering; Suspensions; Functionnaly graded materials

## 1. Introduction

The progress of fuel cell technology is nowadays a major project for sustainable development. Concerning solid oxide fuel cells (SOFC), a critical point is decreasing the operating temperature (from 1000 °C in present systems to 700/800 °C) while keeping suitable electrochemical properties. This objective can be achieved by optimising the microstructure of each element of the cell. A standard SOFC architecture is planar, anode-supported cell. It is a stack of various sintered layers: the few hundred micron thick anode, which supports the structure, the electrolyte, whose thickness must be reduced to a few microns to improve ionic conduction, and the cathode.[1] The cathode is typically a few tens of microns thick and comprises two layers, one with a mixed conductor in contact with the electrolyte and one with pure electronic conductor to enhance the current collection.[2] This composition allows increasing the number of triple points (coincidence of gas, ionic conductor and electronic conductor), where the reaction of reduction of oxygen takes place.[3] The materials classically used are: for the anode, a porous cermet of nickel and yttria stabilised zirconia (YSZ); for the electrolyte, dense YSZ; for the cathode, a composite with YSZ as an ionic conductor and lanthanum strontium manganate (LSM), as an electronic conductor. A electrochemical model[4] of composite cathode has shown that a graded structure with LSM in a larger proportion close by the surface, where the collecting of the current is dominating, and YSZ in a larger proportion near the electrolyte, where the ionic conduction is preponderant, should enhance the electrochemical properties. Also it is expected that the composition gradient improves the mechanical properties of the cell under thermal cycling: since there will be no marked interface between LSM and YSZ layers, the stresses induced by thermal expansion coefficient mismatch will be reduced.

Research programmes on the development of functionally graded materials (FGM) have been conducted in various fields since the eighties.[5] Numerous fabrication techniques have been proposed: physical and chemical vapour deposition,[6] slip casting,[7] plasma spraying,[8] multilayer pressing,[9–11] colloidal processing such as electrophoretic deposition[12] and sedimentation.[7,13] This last method consists in the settlement of powders dispersed in a suspension upon a substrate under gravity and leads to a continuous composition variation. It has been chosen for the fabrication of composite LSM–YSZ cathode with graded composition as explained in this paper. A numerical model allowing a better control of the sedimentation process is also described. Two cathodes with different composition have

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been fabricated by changing the initial conditions of sedimentation. Their compositions are analysed after sintering by electron dispersive spectrometry under scanning electron microscopy and compared between each other and with the prediction of the sedimentation model.

## 2. Experiments and modelling

Assuming that each particle has no interaction with its neighbours, the sedimentation regime is controlled by Stokes' law. According to this law, a spherical particle of diameter $D$ placed at a distance $h$ from the substrate reaches it in a time $t$ expressed as:

$$t = \frac{18\eta h}{D^2(\rho_p - \rho_0)g} \quad (1)$$

where $\rho_0$ is the mass density of the liquid, $\rho_p$ is the bulk density of the particle, $\eta$ is the viscosity of the liquid and $g$ is the gravity's acceleration.

During sedimentation, differences in falling rate may arise from differences in particle size and bulk density. Since the bulk densities of YSZ and LSM are close ($\rho_{YSZ} = 5.9\,g\,cm^{-3}$ and $\rho_{LSM} = 6.1\,g\,cm^{-3}$), a composition gradient will mainly result from the difference in size distribution. YSZ powder provided by Praxair contains particles with a size between 0.4 and 10 μm. The coarsest particles (above 6 μm) have been removed through a preliminary sedimentation procedure because they were found to be poorly reactive. The as provided and final particle size distributions are shown in Fig. 1. LSM powder, also provided by Praxair, includes particles between 0.3 and 7 μm (Fig. 1). Although the smallest and largest sizes of YSZ and LSM powders were very close, the difference in size distribution was sufficient to obtain distinct sedimentation rates.

To optimise the parameters of the sedimentation process, such as the proportion of powders and the time of sedimentation, a numerical simulation of the process has been developed. The model of sedimentation predicts the composition of the deposited layer knowing the proportion of powder introduced and the deposition duration. The total volume of powder is divided in 1000 equal volumes, part of them containing LSM particles and the other ones YSZ particles, in accordance with the mixture composition. A diameter is associated to every elementary volume so that the particle size distributions of both powders are enforced. A height is next selected at random between 0 and the sedimentation column height, $H$, and the time required for a particle of this diameter to fall from this height to the substrate is calculated using Stoke's law Eq. (1). The position of each elementary volume in the deposit is then found. The obtained results are averaged after simulating 100 sedimentations in the same conditions. They allow calculating:

- the sedimentation curve (percentage of deposited powder versus time);
- the particle size distribution in the deposited layer;
- the composition gradient along the thickness of the deposit.

This simulation process has been run using the parameters of YSZ and LSM powders in order to predict the composition of deposits obtained with different initial conditions. Two cases are described below. In case A the starting material is a mixture of 50 vol.% of YSZ and 50 vol.% of LSM whose particles are randomly dispersed along the height of the column, $H$. In case B both materials are initially separated: YSZ particles are supposed to be located at a distance between 0 and $H/2$ from the substrate and LSM particles are at a distance between $H/2$ and $H$ from the substrate. The composition of the deposit is obtained for each time increment.

The experiences matching the simulations described above have been realised. The sedimentation liquid was obtained by adding 1 wt.% of polyvinylic acid and 0.1 wt.% of sodium polyacrylate in deionised water, which made the dispersion of aggregates easier. This mixture had a viscosity of 2 centipoises measured by the capillary flow method. In case A, 0.1 g of powder mixture (50 vol.% YSZ and 50 vol.% LSM) has been introduced in 50 g of liquid. The suspension was dispersed by mechanical agitation and ultrasounds before introduction in the sedimentation column. The particles settled upon a 30 mm diameter dense substrate of YSZ. After 22 h sedimentation, the liquid was poured out of the column. This liquid contained less than 20 vol.% of the particles initially in the suspension. The particles that did not settle were mainly the smallest ones. The deposit was dried at 30 °C during 2 days and next sintered, still upon the substrate, during 2 h at 1200 °C in air. In case B, two suspensions were prepared. Each one contained 0.05 g of powder (either LSM or YSZ) in 25 g of liquid. These preparations were introduced in a column comprising two chambers separated by a gate with LSM suspension in the upper chamber and YSZ suspension in the lower one. The gate was immediately opened to start the deposition. The sedimentation time and the drying and sintering conditions were the same as in case A. The deposits have been observed after sintering by scanning electron microscopy (SEM).

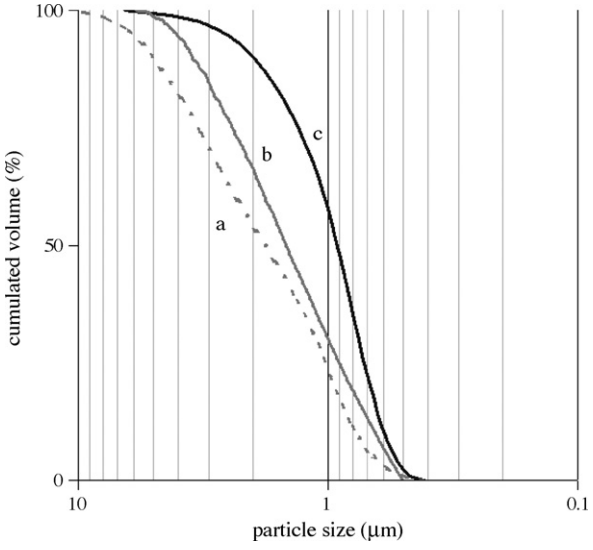


Fig. 1. Particle size distribution of powders: (a) YSZ as provided, (b) YSZ after preliminary sedimentation and (c) LSM as provided.

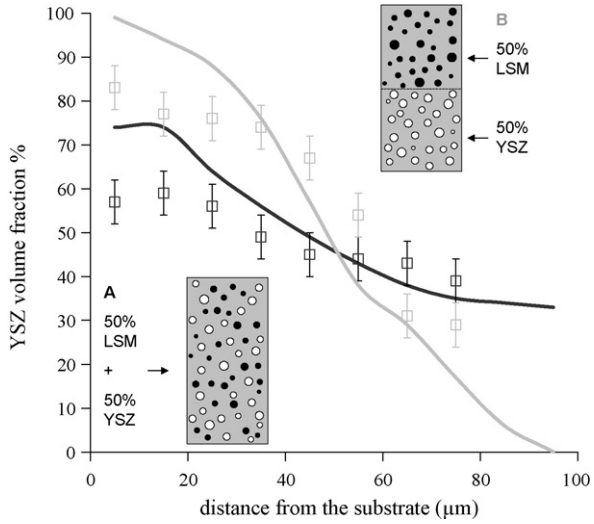


Fig. 2. Composition of simulated and fabricated deposits. The lines show simulation data and the marks show experimental data drawn from EDS analysis. The drawings illustrate the initial conditions of A and B sedimentation processes.

## 3. Results and discussion

For both simulations described in paragraph 2 the variation of the volume fraction of settled YSZ particles along the thickness of the deposit after an infinite sedimentation time appears in Fig. 2. The simulation predicts a composition in YSZ between 33 vol.% at the top of the deposit and 74 vol.% at the bottom in deposit A and between 0 and 100 vol.% in deposit B.

Fig. 3 shows micrographs of A and B deposits. The thickness is about 80 μm thick for A deposit and 65 μm for B deposit. It is uniform all over the substrate. The porosity of the deposited layers have been estimated at 45 ± 5% by image analysis. SEM micrographs do not exhibit significant differences in microstructure between both materials. In particular, differences in composition cannot be detected.

To get a quantitative estimate of the composition gradient, electron dispersive spectrometry (EDS, Silicon–Lithium diode, X numeric analyser PGT) technique has been used. EDS identifies the elemental composition of materials imaged by SEM (Philips XL30 apparatus) for all elements with an atomic number greater than boron. Associated with numerical algorithms it provides the precise composition of bulk materials. For porous materials it does not directly give quantitative information. A prior work is necessary to calibrate the data. Thus five samples with uniform controlled composition in YSZ and LSM – 0, 25, 50, 75, 100 vol.% YSZ – and 45% of porosity have been prepared. EDS analysis of these samples has been performed in stationary conditions (unchanged spot size, acceleration voltage, magnification and counting rate). The ratio of the counts per second of Zr element to the total counts per second for each composition has been plotted as function of YSZ volume fraction in Fig. 4. An analytical relation has been fitted to the experimental points. The difference between the data and the fitted relation is smaller than 5%. This value will be considered as the error of the measure.

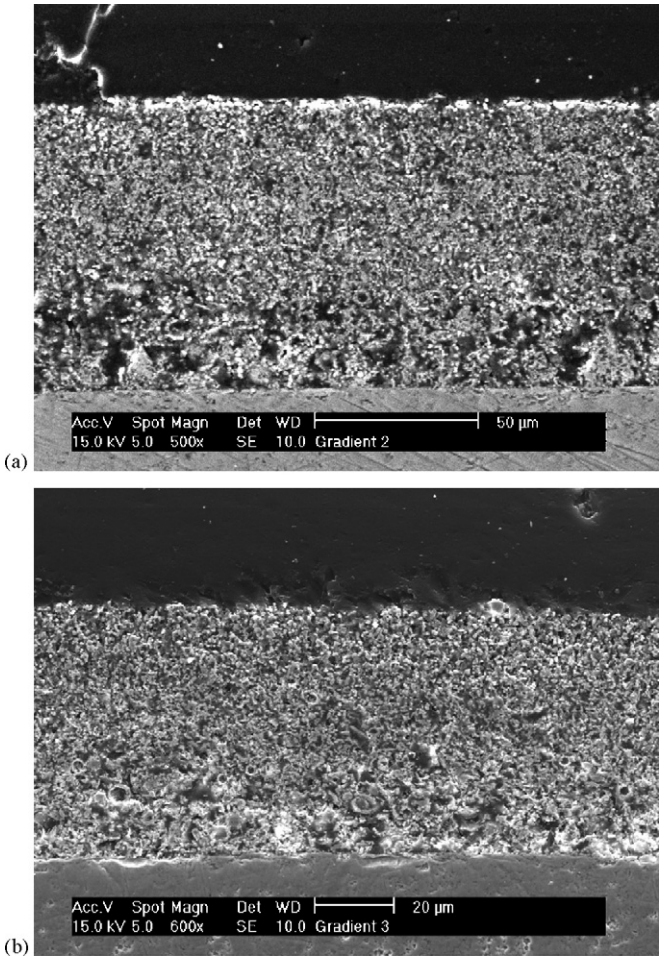


Fig. 3. SEM pictures of A (a) and B (b) deposits after sintering.

Eight layers of fabricated graded cathodes, which correspond to the layers calculated with the simulation program, have been analysed by EDS with the same conditions as in calibration. For each one, the YSZ volume fraction has been

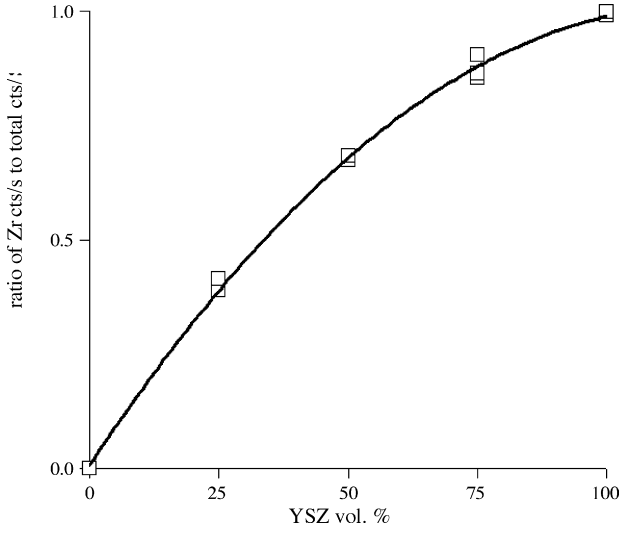


Fig. 4. EDS analysis of LSM/YSZ composites with prescribed compositions. Each mark corresponds to a zone of a specimen and the line shows an analytical fitting.

estimated from the count ratio through the fitted relation. To investigate the reproducibility and homogeneity of the sedimentation process, the compositions found in two A deposits and in two zones of a same deposit have been measured. The differences have been found to be within the 5% uncertainty range.

Fig. 2 compares the composition of deposits A and B between each other and with the prediction of the simulation. The volume fraction of YSZ varies from about 80 to 30% in deposit A and from about 60 to 40% in deposit B. Experimental data do not perfectly stick to the results of the simulation but the trends are consistent. As predicted by the model, the composition variation in deposit B is much larger than the one in deposit A. However in both cases the volume fraction of YSZ close by the substrate is lower than expected. This discrepancy should be due to the formation of LSM particle agglomerates in the suspension, which are not taken into account in the simulation. Note that the deposits should also exhibit a gradient in particle size. This gradient, which may affect the sintering behaviour, has not been investigated so far.

## 4. Conclusion

Powder sedimentation thus appears to be a suitable technique to fabricate composite ceramic structures with controlled composition gradient. This technique, associated with a numerical simulation of the sedimentation process, has been successfully applied to the fabrication of composite SOFC cathodes from YSZ and LSM powders. The parameters that have been adjusted to control the composition are the particle size distributions of the powder and the relative position of each powder at the beginning of the sedimentation process. Two deposits have been obtained, one with a composition from 60 to 40 vol.% YSZ and the other one with a composition from 80 to 30 vol.% YSZ. The mechanical and electro-chemical properties of these deposits should next be measured in order to analyse the benefit of a composition gradient with a view to improving cathode performance. Electrochemical features will also be used to validate the numerical simulation of SOFC electrodes based on a discrete element method,[14] which will help optimising electrode microstructure.

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