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The preparation of porous perovskite membranes using $BaTiO_3$ nanopowders

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The aim of this study was to develop a simple and reliable procedure in order to prepare composite membranes through the deposition of thin porous layers of perovskite-like oxides onto ceramic porous supports. $BaTiO_3$ nanopowders with controlled properties were obtained by Low Temperature Aqueous Synthesis (LTAS) and used as starting materials for the thin film deposition. Process parameters were determined in order to obtain a stable suspension of the nanopowder. The nanopowder was then effectively used to realize the layers with controlled properties. The results of characterisation tests indicated that the porosity of the deposited layers was of a mesoporous type and that the starting nanopowder did not undergo structural changes after the deposition process.

1. Introduction

Interest in the development of new ceramic membrane with a high thermal stability, to be used in both inert membrane reactors (IMR) and catalytic membrane reactors (CMR) (as new chemical reactors) has considerably increased in recent years [1, 2].

Catalytic membrane reactors allow both the reaction and separation of the final products to be combined into a single step. By doing so, equilibrium reactions take place with a higher conversion. Higher conversion occurs as a consequence of the preferred permeation of one or more of the reaction products that passes through the membrane. Catalytic membrane reactors also allow the stoichiometry of multiple reactions to be controlled by regulating the addition of one of the reactants, consequently improving the selectivity and/or conversion [3, 4].

Oxides with perovskite-like structures can be applied to many applications in the field of electroceramic materials owing to their particular physical-chemical characteristics [5, 6]. Moreover, the particular transport mechanism (atomic species, for example) of oxygen at a high temperature through the structure of these compounds renders their application suitable for other fields. These could be catalytic reactions, or in particular, partial oxidation reactions (such as those for syngas production) [7–13]. However, the possibility of combining catalytic and membrane properties is related to the capability of depositing thin films with controlled properties onto porous ceramic supports.

Different techniques are generally used to synthesise thin layers of oxides with perovskite like structures, among which the most common are: sputtering [14], pulsed laser deposition [15], metal-organic chemical vapour deposition [16] and sol-gel [17]. The sol-gel technique is most widely used for the preparation of the majority of ceramic composite membranes [18, 19] and particularly to prepare asymmetric mesoporous membranes, such as the γ-Al_2O_3 and TiO_2 based membranes.

This paper is concerned with the preparation and characterisation of new types of composite membranes obtained through the deposition of thin films of $BaTiO_3$ on porous ceramic supports. This type of perovskite was chosen on the basis of previous experience on synthesis [20–23], doping [24, 25] and relevant characterisation of this compound, in particular the addition of various elements to obtain a catalytic effect [26, 27].

The lack of information in literature, along with the difficulties related to the preparation of stable colloidal sols of perovskite oxides from metal-organic compounds, provided the motivation to try a different method to produce the thin layers. This method involved both the synthesis of $BaTiO_3$ nanopowders (which were used as starting materials) by the LTAS procedure [20–23] and research in order to define the

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optimal process parameters, with the aim of obtaining both stable nanopowder dispersion and a suitable coating for the ceramic supports.

2. Experimental procedure

X-ray diffraction was used to characterise the deposited film on two types of porous supports, these characterisations would then help to prepare the perovskite layers. The first type of support was an α-Al_2O_3 flat porous membrane with a thickness of 3 mm and a porosity of 150 nm (supplied by KeraNor, Norway). The second was made up of 2 different types of Alumina tubular module-based commercial membranes. One was a three-channel module-based commercial membrane (supplied by TAMI, external diameter 10 mm, hydraulic diameter of channels 3.6 mm and 150 mm long) with an inner porosity of 140 nm and made up of three different macroporous concentric layers of TiO_2–ZrO_2 over α-Al_2O_3. The other, a single-channel module-based commercial membrane (supplied by SCT-US Filter, external diameter 10 mm, internal diameter of 6 mm and 150 mm long) with an inner porosity of 200 nm and made up of three different macroporous concentric layers of α-Al_2O_3.

Different procedures were employed for the deposition of the thin films onto the porous supports. The first one consisted of the *in situ* synthesis of $BaTiO_3$ from stoichiometric solutions of isopropanol (Aldrich 99%), acetic acid (Aldrich 99.8%) and two metalorganic alkoxide precursors: Ba-isopropoxide (Aldrich tech.) and $Ti^{(VI)}$-isopropoxide (Aldrich 97%). The Alumina tubular support was first dipped into the solution and next thermally treated at 900°C for 2 hours in order to obtain the perovskite structure. This procedure did not lead to satisfactory results as it was impossible to control the growth of the thin films, especially since the perovskite not only formed on the surface of the support but also in the pores.

Problems were encountered with the sol-gel procedure [18] due to the different solubilities of Ti and Ba. Further investigations are therefore needed before it is possible to consider this procedure as an alternative to the use of powder deposition techniques in the preparation of composite membrane.

The procedure therefore developed for depositing $BaTiO_3$ layers began with nanopowders of a ca. $\cong$40 nm average particle size, especially prepared through the LTAS technique [20–23]. This technique is used to

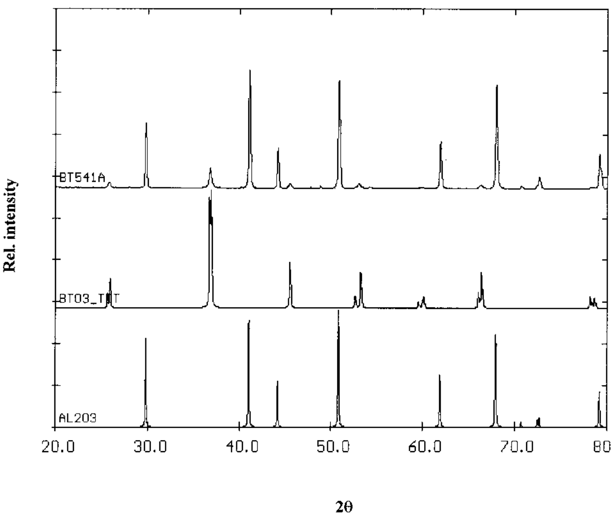
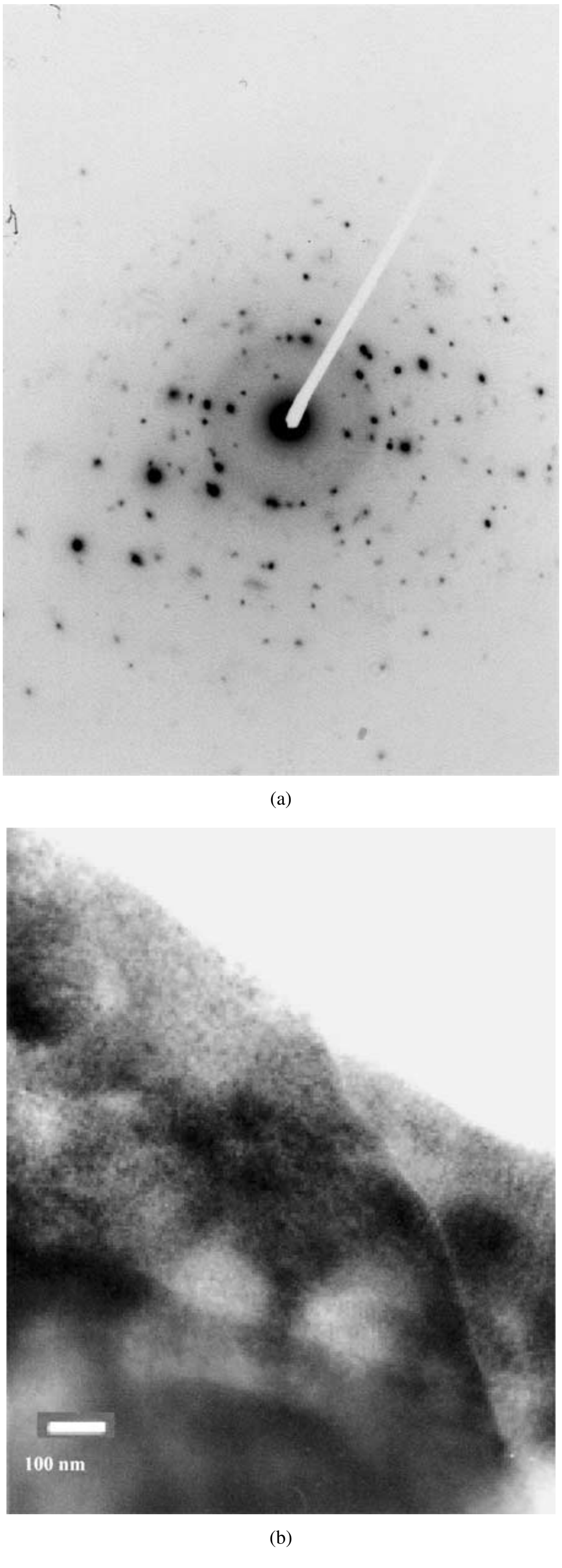


Figure 1 XRD pattern of powdered BT, deposited on a flat α-Al_2O_3 based membrane (BT541A), theoretical $BaTiO_3$(BTO_3—TET) with an Al_2O_3support (Al_2O_3).



(a)

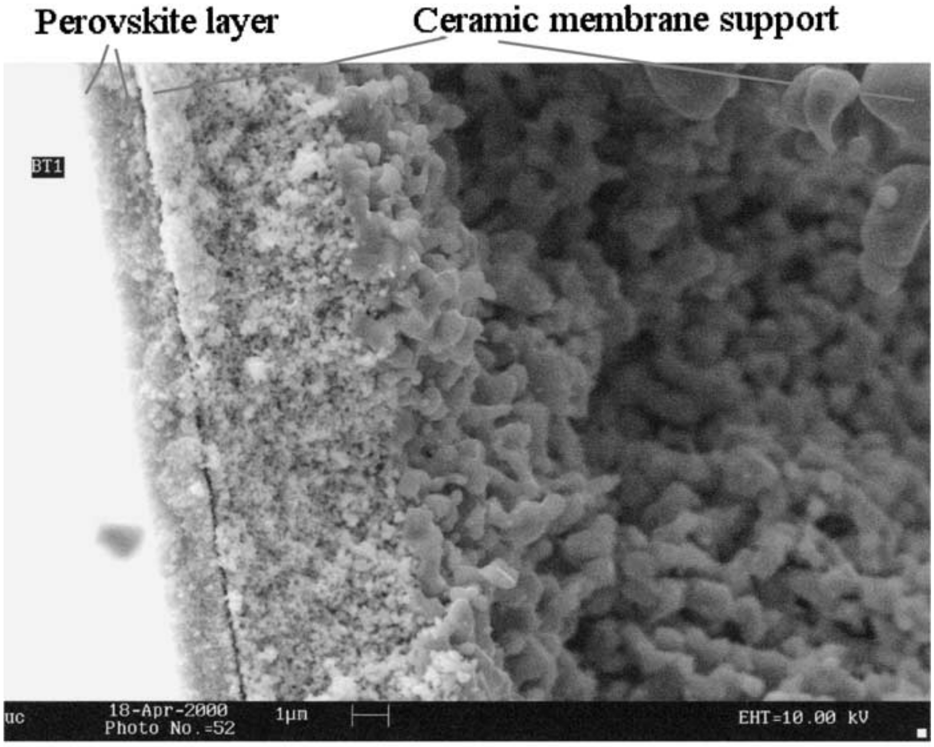
(b)

Figure 2 TEM diffraction (a) and cross-section image (b) of a $BaTiO_3$ layer on a tubular Al_2O_3 mesoporous membrane.

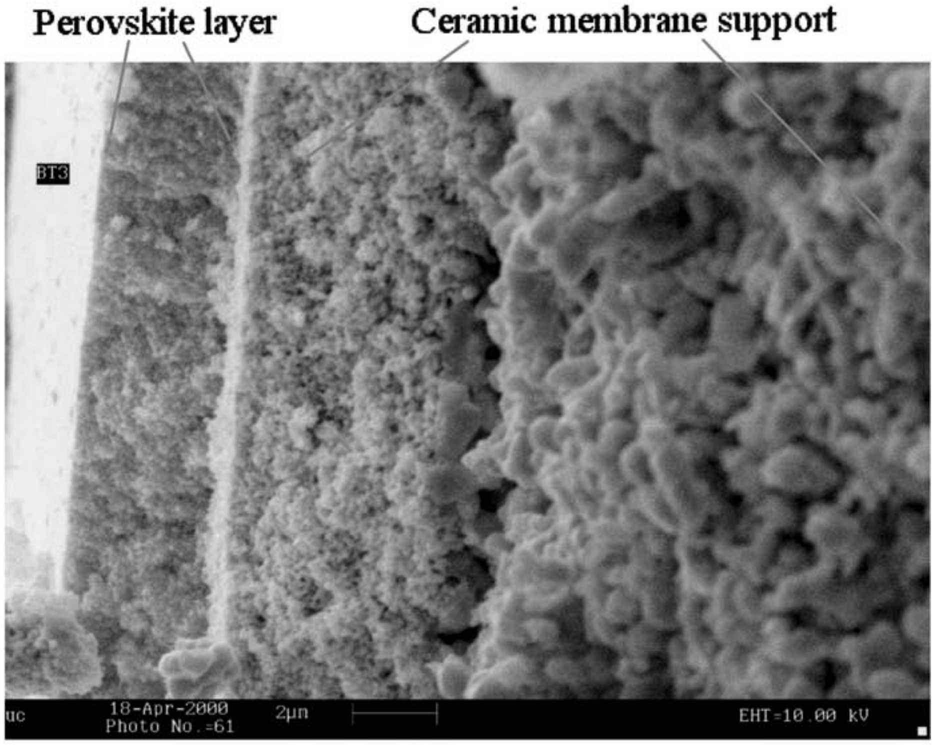
control the average particle size, which was done by first defining the operating conditions.

Various attempts were made in order to create a sol with a suitable viscosity and high stability. The best results were obtained by dispersing the nanopowder in isopropanol, thus forming 0.1 M (2.3 wt%) dispersion, and adding small amounts (0.15 and 0.50 wt%) of hydroxypropylcellulose, (HPC) (Aldrich, 100 kD, average MM). The HPC was found to behave as an excellent DCCA (Drying Control Chemical Additive) since it prevented the formation of cracks and fractures on the sol layer deposited onto the ceramic support during the successive drying and firing processes.

Several efforts were also made in order to find the optimal procedures and operating conditions for the deposited layers with controlled properties. The best results were obtained by dipping the support into the stable sol suspension for 16 seconds and then drying the deposited layer in three steps: first at room temperature for 3 hours, then at 60°C in an oven for



(a) 0.15% HPC



(b) 0.50% HPC

Figure 3 SEM micrographs of a $BaTiO_3$ layer on a tubular Al_2O_3 mesoporous membrane cross-section at 0.15% (a) and 0.50% (b) of HPC.

3 hours and finally a firing at 600°C for 6 hours in order to eliminate the organic additives. By repeating the described procedure several times, layers of the desired increasing thicknesses were obtained. Both starting nanopowders and final perovskite membranes were characterised through: X-ray diffraction (XRD, Philips PW1710 diffratometer) analysis, a scanning electron microscope (SEM, Leo Stereo Scan 440 S with EDS analysis, link-GEM, Oxford) and a transmission electron microscope (TEM, Jeol Jem 2010 with EDS analysis). The porosity of the powder and the mesoporous layer was evaluated by N_2 ads/ des (Asap 2000, Micromeritics) measurements.

Gas permeability measurements of the composite membranes were carried out at a temperature of 25°C and by fixing increasing flows of N_2 and He across the membranes and measuring the corresponding trans-membrane pressure.

3. Results

The XRD analysis on the layers deposited on to the flat Al_2O_3 ceramic porous supports showed that the structure of the deposited film (BT541A) is analogous to that of the theoretical powder (BTO_3-TET) as reported in Fig. 1, where the presence of typical peaks of the Al_2O_3 ceramic support are also observed. The XRD analysis also demonstrated that the final deposited layer was made of perovskite thus confirming the procedure used (since the perovskite layer remained unchanged).

The results of TEM observations and diffraction measurements shown in Fig. 2 and Table I confirm that the composition and crystal structure of the deposited layer are the same as the original starting nanopowder. Fig. 3 shows the results of SEM observations carried out on the composite membranes, prepared by dispersions containing different amounts of HPC. By increasing the HPC concentration, the thickness of the deposited layer increases. The thickness values of the $BaTiO_3$ layer (obtained as an average value from three membranes) as a function of the HPC content in the starting sol are shown in Table II. Observations of the SEM micrographs of Fig. 3 show that the perovskite film is reasonably homogeneous and from further investigations the film was found to adhere well along the whole length of the support. The EDS analysis using SEM and TEM on the cross-sections of Ba and Ti, highlight that with such a procedure the particles of perovskite do not penetrate the porous layer of the ceramic support. Further deposition steps resulted in membranes with different perovskite layer thicknesses; these layers were about a third thinner than the first deposited layer.

TABLE I The results of TEM electron diffraction (ED) measurements of a $BaTiO_3$ layer on an Al_2O_3mesoporous membrane and XRD on a $BaTiO_3$ powder

Theoretical value [28]			Experimental data	
Miller index (*hkl*)	Relative intensity (I/I_0)	*d*	*d* by ED TEM on the film	*d* by XRD on the powder
101	100	2.838	2.86	2.85
110		2.825		
111	12	2.019	2.02	2.01
002	35	1.634	1.61	1.64
211	46	2.314	2.33	2.33

TABLE II Thickness values of the $BaTiO_3$ layer as a function of the HPC content in the starting dispersion solution

Sample	HPC (wt%)	Thickness of perovskite layer (μm)
BT54_1–5	0.15	1.8
BT54_2–30	0.30	2.6
BT54_3–40	0.40	3.0
BT54_4–50	0.50	3.6

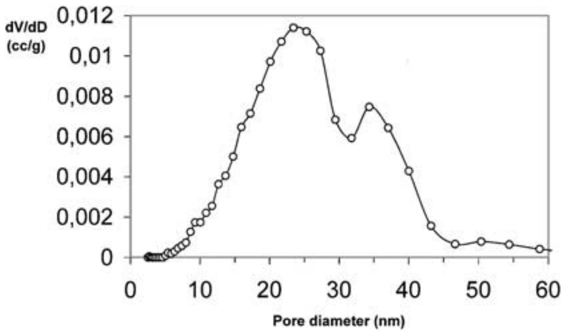


Figure 4 Distribution of the pore-size diameter of $BaTiO_3$layer deposited over tubular macroporous membranes.

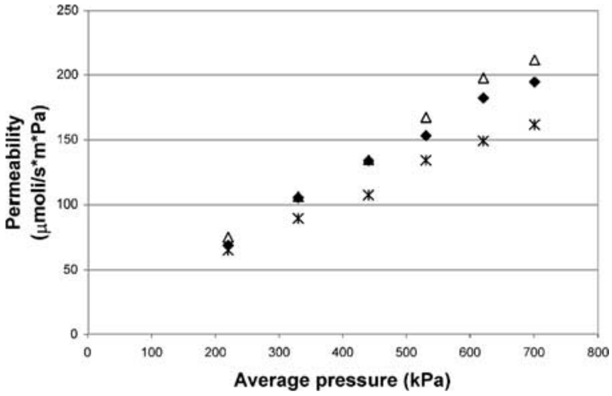


Figure 5 Comparison with the permeability of the tubular macroporous support (Δ), after one deposition of $BaTiO_3$(◆) and of two consecutive depositions (✱).

The results of N_2 ads/des measurements are reported in Fig. 4. The pore diameter distribution is bimodal and rather broad in the mesoporous range, from a few nanometers up to more than 60 nm. The surface area is 38 m^2/g and decreases to 21 m^2/g after the firing step at 600°C. Fig. 5 compares the nitrogen permeability of the support with that of the composite membranes with different thickness layers. As the layer thicknesses increase, the permeability decreases. However, the permeability does not seem to be affected by the average pressure, thus indicating a substantial viscous transport regime.

4. Conclusions

New composite membranes made of thin layers deposited on to porous ceramic supports were prepared by first dipping the support into a $BaTiO_3$

nanoparticle dispersion in an isopronanol and hydroxypropylcellulose solution, then firing them at high temperatures.

The XRD measurements showed that the starting materials retain their original perovskite-like structure even after thermal treatment. The results of both N_2 ads/des and permeability measurements indicated the presence of large pores in the deposited layer that could obviously have a detrimental effect on the gas selectivity of the membranes. Optimum porous membrane were obtained that could be used in many different separation processes (micro and ultrafiltration, membrane contactors, catalytic membrane reactors, etc.). In order for these membrane to be used in gas separation processes, however, their porosity would have to be noticeably less (lower than 4 nm). This could be achieved by using the membrane as a support and adding more depositions (eventually of different materials, too) or by thermal treatment in order to further compact the perovskite layer. Some preliminary results of the thermal treatment indicate that the membrane should be fired at the increased temperatures of 800–1000°C.

Acknowledgments

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