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Hafnia Colloidal Solution from Hydrothermal Synthesis and Membrane Preparation

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Abstract

Hydrothermal synthesis was used for preparation of stable sols of monoclinic hafnia. The preparation conditions were defined by controlling the pressure, the temperature, the time of the reaction and the concentration of the salt precursor. The colloidal solutions and particles were characterized using turbidity, granulometry or dilatometry. Electrophoresis measurements allow the determination of particle charge as a function of nature of electrolyte and pH value. Ultrafiltration membranes were prepared from the hafnia sols. The pore diameters of the membranes depend on the hydrothermal synthesis time. © 1996 Elsevier Science Limited.

La synthèse hydrothermale a été utilisée pour l'obtention de solutions colloïdales stables d'oxyde d'hafnium. La pression, la température, le temps de réaction et la concentration du sel précurseur définissent les conditions de préparation. Les solutions et les particules colloïdales ont été caractérisées par des mesures de turbidité, de granulométrie ou de dilatométrie. Les mesures électrophorétiques, en présence de différents électrolytes, ont permis de définir la charge des particules en fonction du pH. Des membranes d'ultrafiltration ont été élaborées à partir des solutions colloïdales; les diamétres de pore dépendent de la taille des particules et donc du temps de réaction de la synthèse hydrothermale.

1 Introduction

Chemical properties of hafnia[1] present a great similarity with those of zirconia. The first crystalline phase of hafnia is the monoclinic, stable up to 1850°C, the second one, which exists above this temperature, is tetragonal. By stabilization with Y_2O_3 or CaO, a cubic crystalline phase appears and avoids the reversible transformation monoclinic to tetragonal. If hafnia is used as ultrafiltration membrane, it is more interesting than zirconia, because of the larger range of the existence of a monoclinic phase. For zirconia, the transition temperature is about 800–1000°C. During this transition, the increase of volume is smaller for hafnia (3·4%) than for zirconia (7·5%). The melting point of hafnia is 2758°C and the linear thermal expansion coefficient is $5{\cdot}80 \times 10^{-6}\ {}^{\circ}C^{-1}$ between 250 and 1300°C. The chemical resistance is excellent in the whole pH range, except for hydrofluoric acid with which it reacts at 500°C. In contact with graphite, carburation occurs at 1700°C.

In the literature, several methods describe hafnia powder preparation such as the sol–gel process,[2] the precipitation method[3] and hydrothermal synthesis.[4] For preparation of ultrafiltration membranes, sol–gel processes are used; in this case, crystallization occurs during the thermal treatment. Crystallization is an important step which must be controlled to avoid the formation of cracks. By using crystallized powder prepared by hydrothermal synthesis, this can be avoided.

For all these reasons, monoclinic hafnia, prepared from hydrothermal synthesis is a good candidate for ultrafiltration membranes. In this work, we shall describe the preparation and the characterization of hafnia colloidal solutions and powders and the preparation of ultrafiltration membranes.

2 Hafnia Powder Preparation

2.1 Principle

The use of hydrothermal synthesis is very convenient, at low temperature, and for submicron sized and crystallized powders. The precursor of hafnia powder is hafnium oxychloride $HfOCl_2{\cdot}8H_2O$ in aqueous solution. When hafnium oxychloride is dissolved in water, forced hydrolysis occurs rapidly[5] producing hydroxylated sites which conduce to soluble tetrameric species having a defined stoichiometry: $[Hf(OH)_2.4H_2O]_4^{8+}$. These species

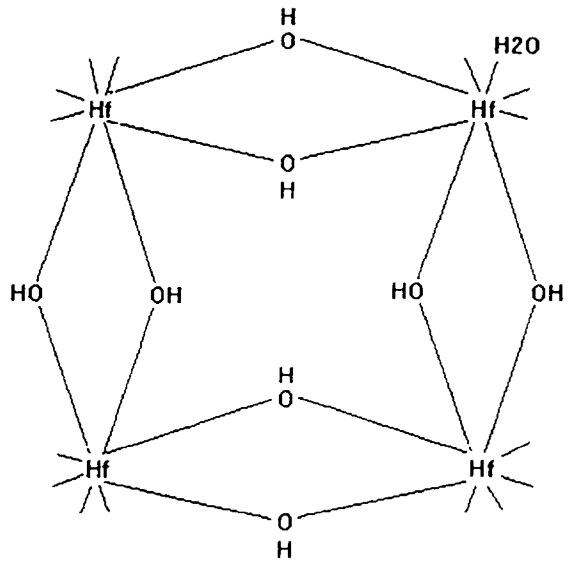

Fig. 1. Planar structure of tetrameric species in aqueous medium.

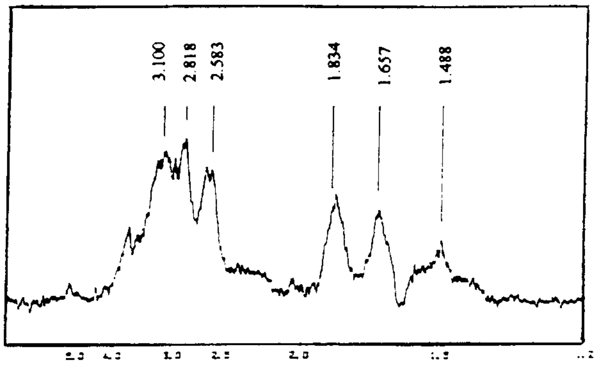

Fig. 3. X-ray diffraction pattern of powder after hydrothermal synthesis.

have a planar structure based on a square of hafnium atoms,[6] as shown in Fig. 1. The coordination number of hafnium atoms is equal to 8: four OH groups and four H_2O molecules. The tetramers can be associated in oligomers which react between themselves; a tridimensional structure is obtained by eliminating water molecules between adjacent hydroxylated sites. Under appropriate conditions, crystalline structures can be prepared.[7]

Usually, the parameters influencing the hydrothermal synthesis, performed in an autoclave, are the pressure, the temperature, the time of synthesis and the concentration of the salt in solution. In these experiments the temperature is fixed at 180°C, the pressure, which depends on the filling

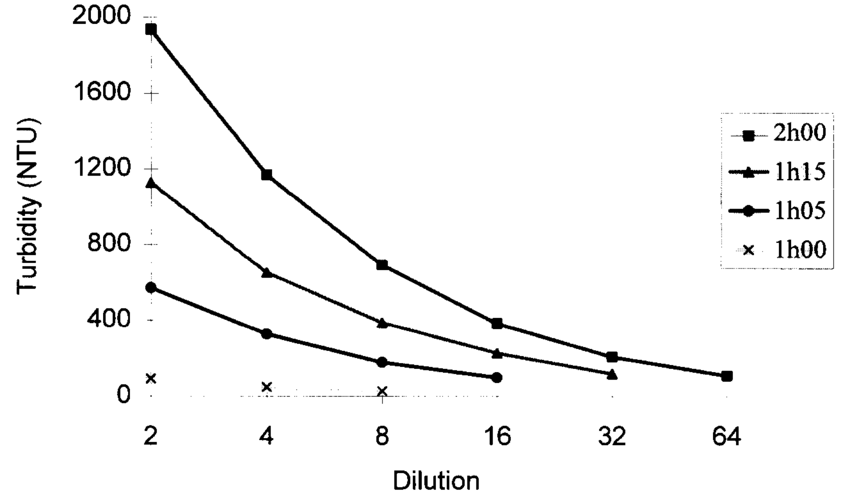

Fig. 2. Turbidity versus autoclaving time.

Table 1. Aspect of the solutions after hydrothermal reaction

Reaction time (min)	*→50*	*55 →60*	*65*	*70→*
Aspect of the solution	Transparent solution	Stable colloidal sol	Slight settling	Settling

Table 2. Turbidity as a function of reaction time for twice-diluted solution

Reaction time (min)	*60*	*65*	*75*	*120*
Turbidity (NTU)	94	570	1130	1940

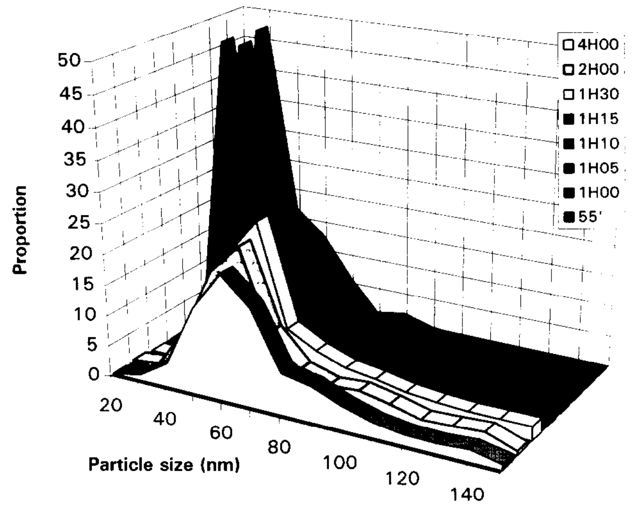

Fig. 4. Particle size distribution as a function of synthesis time.

rate, is equal to 10 bars (filling rate = 70%), the concentration is equal to 150 g/litre by equivalent oxide. Only the time of autoclaving is variable, from 50 min to 4 h.

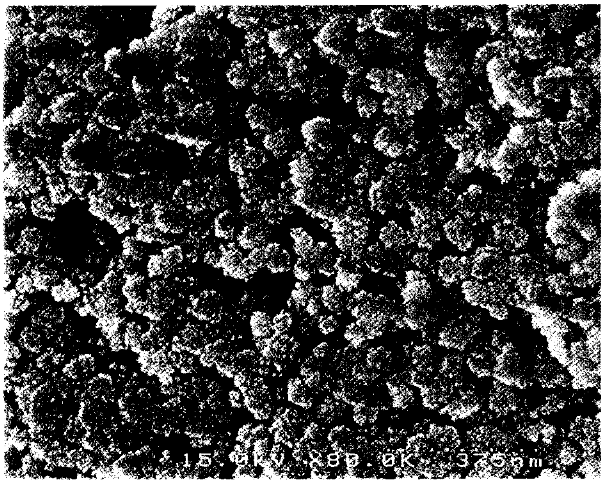

Fig. 5. Powder micrograph after 70 min autoclaving time.

2.2 Results

For these experiments, the results of hydrothermal synthesis are dependent only on the autoclaving time. For 50 min, crystallization did not occur and a transparent solution was obtained. From 55 min, the resulting sols became more and more turbid. That means that the size of the particles increases with autoclaving time and from 65 min a slight settling occured. To obtain stable sols, a dilution by a factor of 2 is sufficient. Table 1 gives the autoclaving solutions. It is noted that the settling rate increases with the reaction time.

The turbidities of the solutions were measured after dilution from a factor of 2 to a factor of 64 (Fig. 2). The turbidity values of the diluted solutions by a factor of 2, are reported in Table 2. To obtain stable sols, a dilution by a factor of 2 is sufficient. The concentration of hydrochloric acid, formed during the synthesis reaction, changes from 1·4 to 0·7 M; peptization occurs at this step. An increase of the turbidity with the autoclaving time may be observed; that means that the particle size is varying with the reaction time and this confirms the results for the solutions obtained after the hydrothermal synthesis.

The X-ray diffraction patterns (Fig. 3) from powders dried at 50°C, were identified as monoclinic hafnia, whatever the autoclaving time.

Figure 4 gives the results of the particle size measurement versus reaction time. Solutions diluted by a factor of 4, as for membrane preparation, were used. Particle size and particle size distribution increase with the reaction time. A Horiba Capa 700 granulometer was used. Measurements are based on the principle of liquid-phase sedimentation, using the optical transmission method.

A scanning electron micrograph of powder after 70 min autoclaving time is reported in Fig. 5. Each grain is formed by agglomeration of very small

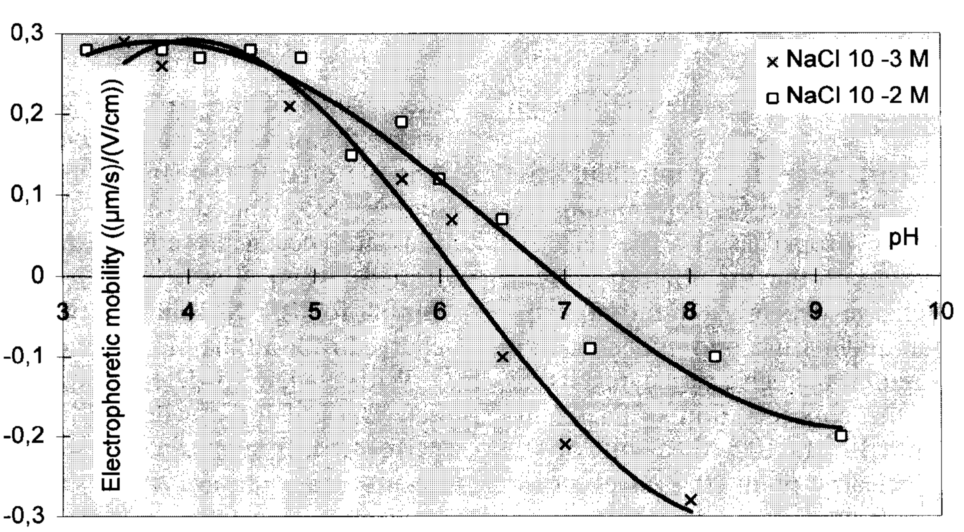

Fig. 6. Mobility versus pH in aqueous NaCl solutions.

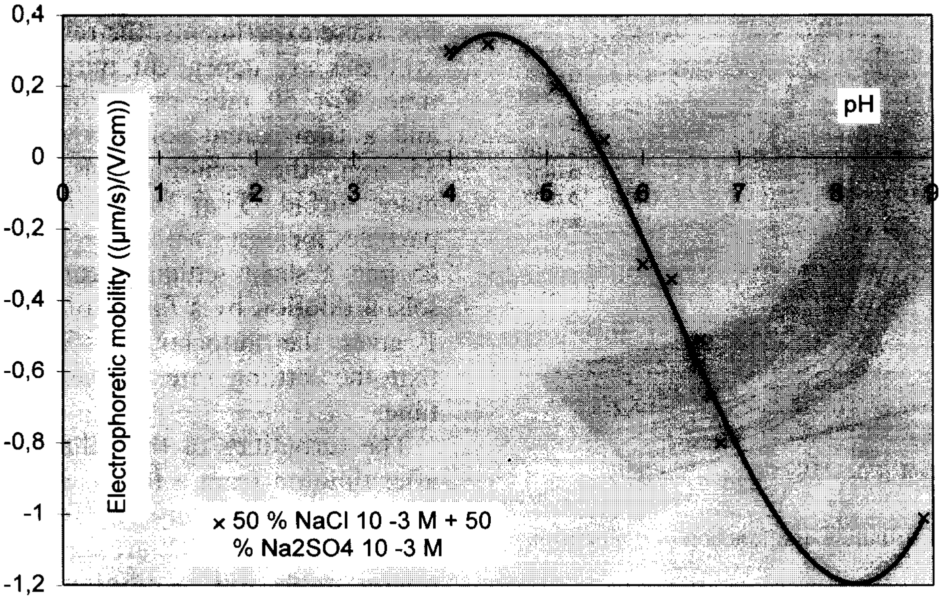

Fig. 7. Mobility versus pH in aqueous NaCl/Na_2SO_4 mixture solution.

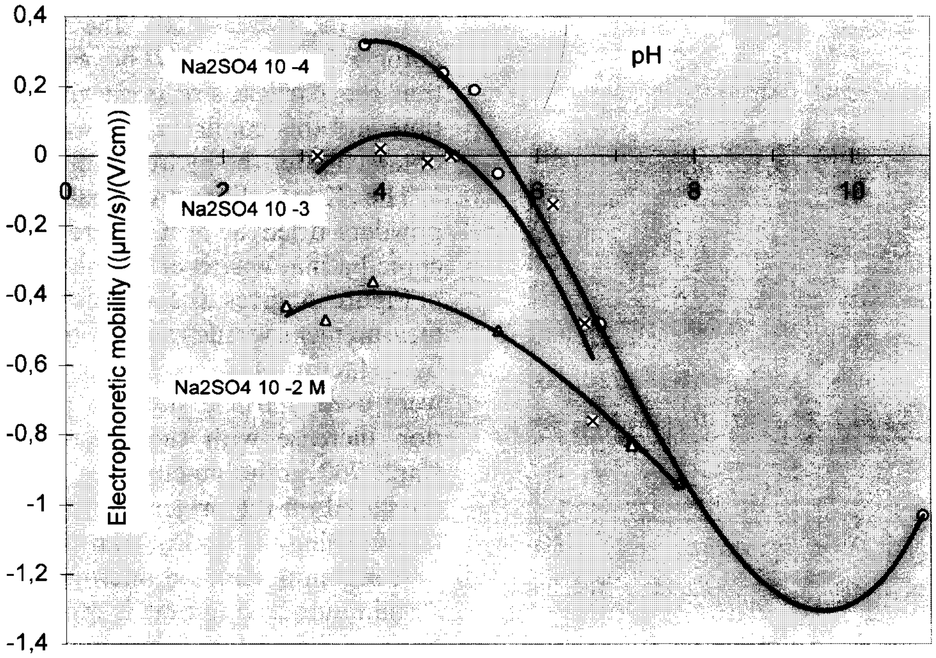

Fig. 8. Mobility versus pH in aqueous Na_2SO_4 solutions.

crystallites, but grains are not sintered between themselves.

An important parameter for controlling the agglomeration of particles and for determining the filtration membrane properties is the electric charge at the surface of the material. It is well known that the charge depends on the aqueous medium, pH value and nature and concentration of electrolytes. Figures 6–8 give some results of this study. When the concentration of NaCl increases (Fig. 6) from 10^{-3} to 10^{-2} M, a shift of the pH value of the isoelectric point (IEP) is observed to the high values, from 6·2 to 6·9; which corresponds to a specific adsorption of sodium ions at the surface of the particles and the range of pH where the particles are positively charged is larger. The pH of IEP decreases when a mixture of NaCl and Na_2SO_4 is used (Fig. 7). In this case, sulphate ions are specifically adsorbed. This fact was confirmed when the Na_2SO_4 concentration was varied; for 10^{-2} M solution, particles are negatively charged over all the pH range (Fig. 8).

With a view to determining the sintering characteristics of the powder, a dilatometry study was performed. Figure 9 shows that the shrinkage occurs from about 450°C and is higher with longer reaction time; respectively 17 and 24% for 55 and 120 min autoclaving time.

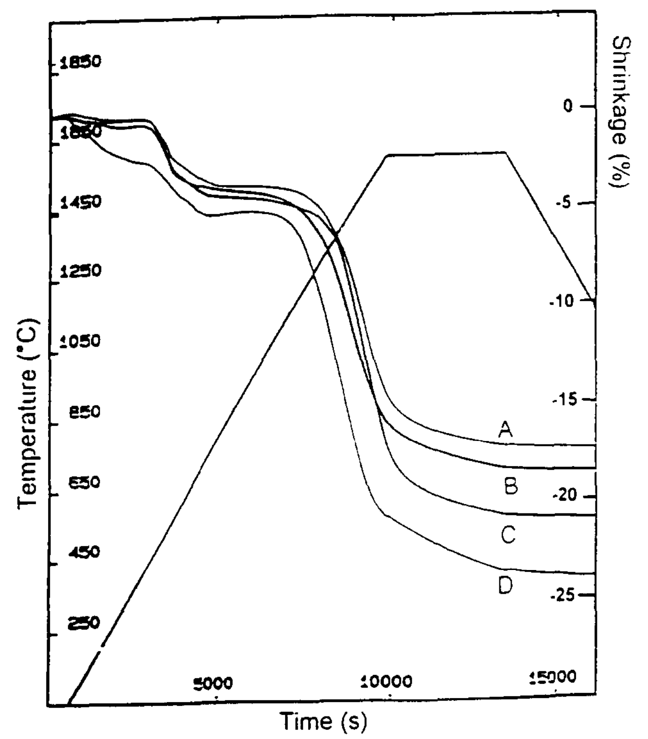

Fig. 9. Dilatometry measurements of hafnia powders.

Fig. 10. Cross-section of 30 nm pore diameter membrane coated on 55 nm pore diameter membrane coated on 0·2 μm support.

3 Membrane Preparation

The classical process of membrane preparation[8] from colloidal solutions was used. Hafnia ultrafiltration membranes were prepared from the four times diluted solutions. Distilled water was added to the hydrothermal suspensions to obtain stable sols by peptization. An organic binder, polyvinyl alcohol, was added to the sol to adjust the viscosity. The sol was then coated on a support, 0·2 μm in pore diameter. A tubular configuration was used and the coating was performed on the internal surface by slip casting. After emptying the sol, the sol layer was dried at room temperature for at least 12 h. The gel layer was then sintered at 550°C to obtain a good mechanical resistance of the layer; this latter was characterized. The same procedure was used for other membrane preparation. The cross-sections of two membranes successively coated on the 0·2 μm support are reported in Fig. 10. The pore diameters are, respectively, equal to 55 and 30 nm for the two membranes of powder autoclaved for 75 and 70 min. The permeability, measured using distilled water at 25°C, is about 170 litre h^{-1} m^{-2} bar^{-1} for the 55 nm pore diameter membrane and about 105 litre h^{-1} m^{-2} bar^{-1} for the 30 nm pore diameter membrane.

4 Conclusion

Monoclinic hafnia powders prepared by hydrothermal synthesis are very interesting materials as precursors for membrane preparation. Submicron-sized powders are formed by unagglomerated grains having a narrow grain size distribution and permit a very low sintering temperature. The grain size of powders and pore diameter of ultrafiltration membranes depend on the autoclaving time. At present, work is in progress to prepare membranes having lower pore diameters, acting in the nanofiltration field.

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