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İ. Erdem



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Sol-gel Applications for Ceramic Membrane Preparation

İ. Erdem

*Abdullah Gül University, Engineering Faculty, Material Science & Nanotechnology Engineering Department, Kayseri, Turkey, Phone: +90 352 2248800 (7222)
Corresponding author: ilker.erdem@agu.edu.tr*

Abstract. Ceramic membranes possessing superior properties compared to polymeric membranes are more durable under severe working conditions and therefore their service life is longer. The ceramic membranes are composed of some layers. The support is the layer composed of coarser ceramic structure and responsible for mechanical durability under filtration pressure and it is prepared by consolidation of ceramic powders. The top layer is composed of a finer ceramic micro-structure mainly responsible for the separation of components present in the fluid to be filtered and sol-gel method is a versatile tool to prepare such a tailor-made ceramic filtration structure with finer pores. Depending on the type of filtration (e.g. micro-filtration, ultra-filtration, nano-filtration) aiming separation of components with different sizes, sols with different particulate sizes should be prepared and consolidated with varying precursors and preparation conditions. The coating of sol on the support layer and heat treatment application to have a stable ceramic micro-structure are also important steps determining the final properties of the top layer. Sol-gel method with various controllable parameters (e.g. precursor type, sol formation kinetics, heat treatment conditions) is a practical tool for the preparation of top layers of ceramic composite membranes with desired physicochemical properties.

Keywords: Ceramic membrane; Sol-gel; Zirconia; Pressure-driven filtration; Top layer.

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CERAMIC MEMBRANES

Ceramic membranes possess superior properties when compared to polymer membranes. They are chemically, physically, microbiologically, thermally more durable ensuring them to have a longer service life. The main disadvantage of them is their brittleness that they should be handled carefully. Other drawback for their utilization may be relatively higher cost for the first installation. But the longer service life of them overcomes this drawback.

UTILIZATION of CERAMIC MEMBRANES in PRESSURE-DRIVEN FILTRATION

Filtration is a widely used unit operation for different purposes like separation, clarification, concentration. Utilization of filtration, instead of heat applied techniques like evaporation, is inevitable for separation/concentration of heat-sensitive organic molecules like proteins, antibiotics, etc.

The driving force for filtration may be concentration difference (dialysis), electrical charge difference (electro-dialysis), partial pressure (pervaporation), pressure (micro-, ultra-, nano-filtration and reverse osmosis) [1, 2]. The pressure driven filtration applications are widely used in industrial applications handling great quantities of matter to be filtered. The pressure driven filtration types are classified with respect to the size of the material to be separated from the liquid media. For example separation of microorganisms like bacteria micro-filtration (MF) is used. For smaller particulates like proteins or viruses ultra-filtration (UF), for even smaller particulates like sugar molecules or pesticides nano-filtration (NF) is used. The tiniest species, salt ions, can be removed via reverse osmosis (RO). With decreasing size of the target material the pore size of the membrane (top layer) is decreasing. Therefore, the necessary pressure for the application to make the liquid pass through the multilayer membrane increases. A pressure difference of a couple of bars may be sufficient for MF while higher pressures (e.g. 5-20 bars) may be necessary for NF. The share of pressure driven membrane processes in the market was 1.8 billion USD at the very beginning of this century [2]. Ceramic membranes for MF, UF, and currently for NF, are present in the market.

STRUCTURE of CERAMIC MEMBRANES

Ceramic membranes have a multilayer structure. In general there is a *support* layer, which is mainly responsible for the mechanical stability of the membrane. The second main layer is the relatively thinner *top* layer, which is responsible for separation having smaller pores than the support. There may be another layer between these two main layers for regulating the structural fitting of them. This layer with pore size among the sizes for the former two main layers is called as *intermediate* layer. These possible layers are illustrated in Fig. 1. This multilayer structure is called *asymmetrical structure* with relatively larger pores within the support getting narrower through the membrane to the top layer which has the finest pores in contact with the media containing materials to be separated.

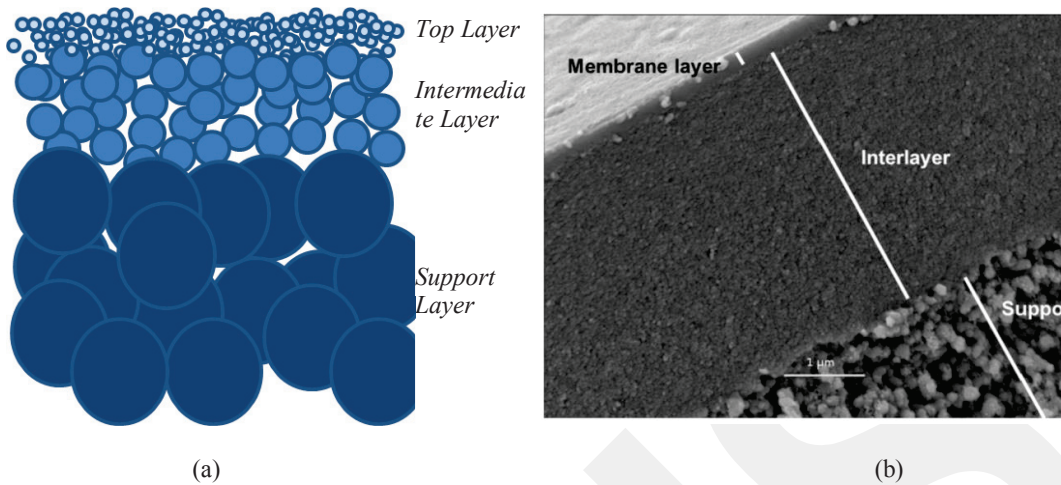


Figure 1. The possible layers of a ceramic membrane with asymmetrical structure: a) Schematic, b) SEM (scanning electron microscope) micrograph of the cross-section showing these layers [3].

PREPARATION of CERAMIC MEMBRANES

Ceramic membranes with asymmetric multilayer structure should be prepared layer by layer. The first layer to be prepared is the support. The support may be prepared by shaping the slip, a suspension of ceramic powders and some additives for controlling the viscosity and drying behavior of the slip. The ceramic powders may be pure ceramic powders (e.g. alumina (Al_2O_3), titania (TiO_2)) or some clay like ground ceramic powders can be utilized. The shaping can be performed via classical methods like molding or extrusion. The shaped green bodies are heat treated after drying. The heat treatment helps the solidification of the green body and results in a mechanically strong but porous structure. The resulting porosity of the support is mainly related with the particle size distribution of the ceramic powders in the slip and heat treatment conditions like heating rate and duration. The ceramic powders go through a semi-sintering process during the heat treatment forming some necks among the particles. The sintering process will be excess if the heating duration is elongated and the final porosity will be lower. The porosity is decreasing the resistance against the fluid flow through the membrane (support) which helps getting a higher flux by using lower energy for pumping the fluid. Therefore, a high inter-connected (open) porosity is preferable and some pore forming additives (e.g. starch) can be added to the slip before shaping [4]. Partial-sintering at lower temperature and addition of pore forming additives (i.e. starch) results in higher porosity in the alumina (Al_2O_3) support as shown in Fig.2. The increasing porosity of the support also increases the fluid (i.e. water) flux through the support.

Intermediate layer can be either prepared by consolidation of a slip on the support and heat treatment for stabilization or by sol-gel method. Ceramic powders finer than the powders used in support preparation are used for preparation of intermediate layer. The slip for forming the intermediate layer can also contain some drying control additives and/or viscosity modifiers. The SEM micrograph of the cross-section of an intermediate layer with a thickness of around 10 micrometer, formed via dip-coating

of 1.5 volume % zirconia (ZrO_2) suspension and heat treatment at $1100^\circ C$ is shown in Fig.3. Different coating methods can be applied for coating the slip on the support to form the intermediate layer (e.g.. dip-coating, spin-coating, etc.). As mentioned above sol-gel method can also be used for intermediate layer formation. The sol prepared with fine particulates in it is coated on the support instead of finer ceramic powder suspension.

Top layer, which is the most important layer for the separation activity of the membrane, can be prepared by using sol-gel method, through which a very fine (microporous) thin layer can be prepared on the intermediate layer.

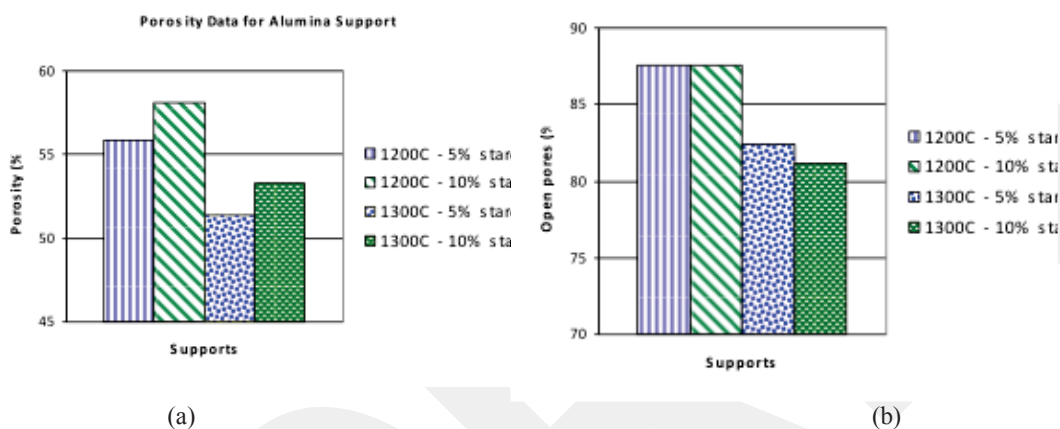


Figure 2. The a) total and b) open (inter-connected) porosity ratios for supports prepared with starch addition as pore forming additive and heat-treated at different temperatures $1200^\circ C$ or $1300^\circ C$ [4].

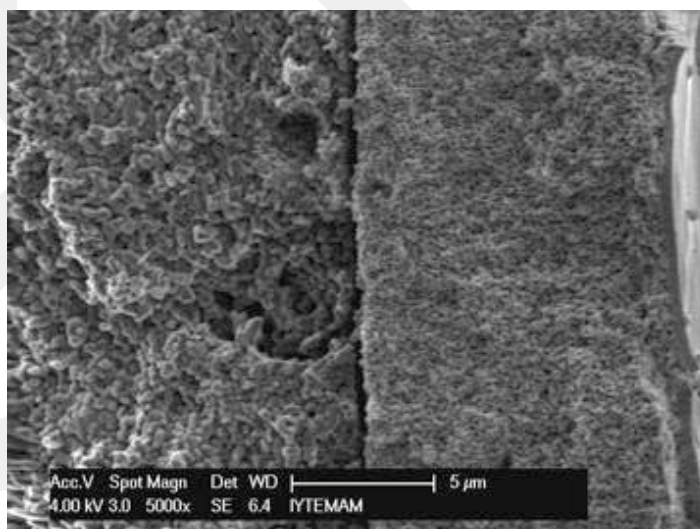


Figure 3. The SEM micrograph showing the cross-section of an intermediate layer formed via dip-coating of 1.5 volume % zirconia suspension and heat treatment at $1100^\circ C$ [4].

SOL-GEL METHOD FOR PREPARATION of CERAMIC MEMBRANES LAYERS

Sol-gel is a method for forming fine particulates in a liquid media and consolidating them after coating/shaping to have homogeneous layers/structures of fine particulates after drying and heat treatment. The starting materials for sol-gel can be metal-organic compounds (alkoxides) or metal salts. Appropriate precursors are reacted through either *polymeric* or *colloidal* routes. The routes contain the formation of polymeric or colloidal particulates in the liquid media (i.e. formation of the sol), establishment of a network among these particulates (i.e. gel formation), drying of the gel and heat treatment. Acidic or basic catalysts may be used in the reaction routes, and finer particulates can be produced via acidic catalysts, which will eventually result in a finer microporous structure at the end of the membrane preparation process [5, 6].

The reactions taking place during the sol formation from alkoxides are *hydrolysis* and *condensation* reactions. In hydrolysis water reacts with the alkoxide ($M(OR)_n$ where M may be Zr, Ti, Al, Si, etc. and R is an alkyl group) and removes/replaces R with H. In condensation reaction alkoxide ($M(OR)_n$) or hydrolyzed alkoxide react with each other and form chains by releasing either H_2O or ROH (alcohol). The rates of these reactions determine the formation speed and size of the particulates in the sol. Therefore, the reaction conditions can be regulated in order to prepare a sol with desired particulate size. Some additives (like acetyl acetone) can be used for slowing the condensation and preventing formation of relatively bigger particulates in the sol [4,7].

Sol-gel method enabling selection of different precursors and additives and formation of homogeneous products of these precursors/additives in elemental level is a very useful method for preparation of *tailor-made* membrane layers. It is not only possible to control the particulate size in the sol (eventually the microstructure of the membrane layer) but also regulate the surface characteristics of the membrane layer by regulating the chemical composition.

CONTROLLING the PARTICULATE SIZE in the SOL

The particulates in the sol forming a network during gel formation will determine the microstructure of the membrane layer after drying and heat treatment. In other words, the porosity and the pore size of the membrane layer is directly affected from the particulate size distribution of the sol. (The other important parameter on the fine microstructure of the membrane layer is the heat treatment conditions i.e. heating rate and duration, which can still be controlled). Having finer particulates in the sol may help formation of a finer microporous structure in the membrane layer. Adjusting the rates of the hydrolysis and condensation reactions can help regulating the particulate size in the sol. Some additives like acetyl acetone can be used for preventing the condensation or formation of big particulates in the sol as mentioned above. The amount of catalyst can be adjusted to regulate the particulate size. The particulate size in the sol was adjusted by using different ratios of acid catalyst (nitric acid) as shown in the Table 1. The increased amount of acid catalyst altering the relative rates of

hydrolysis and condensation reactions resulted in formation of smaller particulates in the sol.

Table 1. The mean particle sizes of zirconia sols with different acid contents [6].

Nitric Acid (mmol / mL propanol)	Mean Particle Size (nm)
0.826	5.7
0.926	4.7
1.026	3.1

It is possible to form the top and intermediate membrane layers via sol-gel method. While in general finer microstructure is necessary for top layers relatively coarser microstructures can be needed for intermediate layer. Then the particulate size in the sol should be larger. The particulate size in the sol can be adjusted by adjusting the water ratio in the recipe as shown in Fig 4. The sol can be *aged* to have a larger average particulate size, too. Aging is keeping the sol at a temperature equal to or higher than the room temperature, which results in increasing of the average particulate size. A growth rate of 0.8 nm per hour was observed for a zirconia sol, resulting in a 10-fold growth in the particulate size in 48 hours at room temperature which may be used for intermediate layer formation [4].

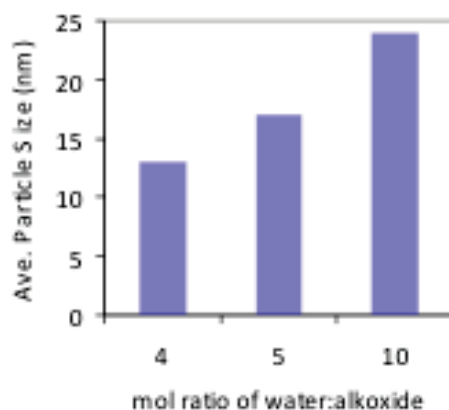


Figure 4. The change of average particulate size in the zirconia sol with water: alkoxide ratio [4].

CONTROLLING the SURFACE CHARACTERISTICS of the MEMBRANE LAYER by ADJUSTING SOL-GEL METHOD PARAMETERS

The separation of components in the feed stream is the target of filtration. For pressure driven filtration applications like MF, UF, NF there are two main separation mechanisms. First one is the *size exclusion*, in which the separation is performed with respect to the sizes of the components and the sizes of the membrane pores. If the

component size is larger than the membrane pore size it will be retained and vice versa. The second mechanism for the separation is called the *Donnan exclusion*, in which the separation occurs with respect to the surface electrical charge of the membrane and the components to be separated. In Donnan exclusion mechanism the components with similar charge with the membrane surface are repelled from the membrane surface (i.e. retained). The retention of these components will increase with increasing magnitude of the membrane surface charge and component's charge. The surface charge (also called *zeta potential*) of the membrane and components are gained and vary with respect to the pH of the liquid media. In general at acidic pH values the zeta potential of ceramic materials (oxides) are positive (i.e. the surface of the material is positively charged) and it decreases with increasing pH and reaches zero value at a pH value which is called *isoelectric point* (iep). If the pH increases above the iep the material gains negative surface charge. The change of surface charge (zeta potential) is somehow characteristic to the material. The chemical composition and physicochemical properties of the material affect the surface characteristics of the material. The types and concentration of ions in the liquid media is also effective on the surface charge of amphoteric materials. The magnitudes of the surface charge decrease by increasing ionic strength. [4]

The most common materials used in ceramic membranes are alumina (Al_2O_3), silica (SiO_2), zirconia (ZrO_2) and titania (TiO_2). Among these chemical durability of zirconia and titania are superior at both acidic and basic pH values which makes them more preferable for membrane applications in liquid media [8]. Changing the sol-gel parameters may alter the surface charge of the resulting top layer of the membrane, which will affect on separation efficiency of the membrane for charged species by Donnan exclusion mechanism. Addition of some elements in the sol recipe may change the chemical composition of the oxide layer homogeneously which will result in having different surface characteristics. Iron (Fe) and Boron (B) were added to the zirconia sol during preparation and the sols were dried and heat-treated at similar conditions (at 500°C). The surface charge (zeta potential) of these oxides with varying chemical composition were measured in 10^{-3} M KCl solution at pH 7.9. There was a considerable difference (40%) in the magnitudes of zeta potential (surface charge) of pure zirconia and 0.2 mol Fe-added zirconia and no significant difference among pure and 0.2 mol B-added zirconia, as shown in Fig 5. Further analysis showed that the isoelectric point (iep) of pure zirconia synthesized was 6.9 and it was decreased to 5.3 and 5.7 by addition of 0.2 mols of Fe and B, respectively [9].

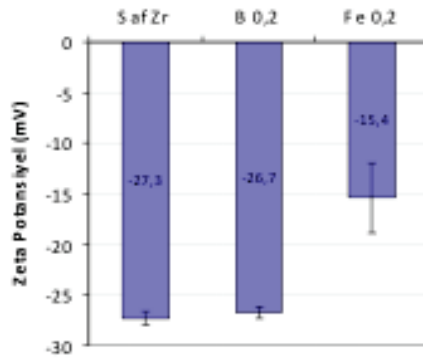


Figure 5. The change of zeta potential (surface charge) of zirconia with addition of other elements (Fe and B) during the sol preparation, measured in 10^{-3} M KCl solution at initial pH of 7.9 [9].

The drying and heat treatment conditions also may affect the surface characteristics of the oxide membrane layer prepared via sol-gel method. Zirconia samples were prepared by using a sol having average particulate size of $4.9 (\pm 0.4)$ nm by drying and calcination (heat treatment) at different temperatures (400° C, 450° C and 500° C). The resulting oxide layer was uniform networking structure with particles of 15-40 nm in size. The surface charge of these zirconia samples were determined in 10^{-3} M KCl solution at pH 7.9 as shown in Fig. 6. There is almost a linear change in the magnitude of zeta potential with increasing heat treatment (calcination) temperature with a difference of around 32 %. It was concluded that this change might be related with the crystal phase transformation in zirconia from tetragonal to monoclinic phase [10].

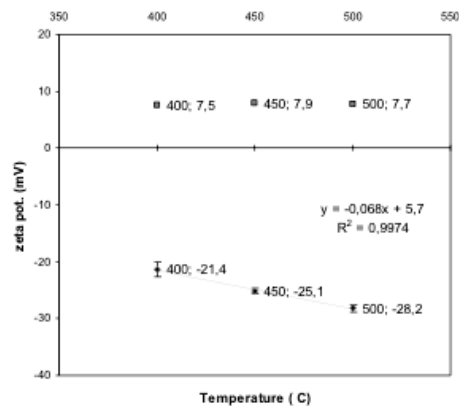


Figure 6. The change of zeta potential (surface charge) of zirconia with varying calcination (heat treatment) temperature, measured in 10^{-3} M KCl at initial pH 7.4 (The upper values on the figure next to the temperatures are final pH values for the samples) [10].

CONCLUSION

Ceramic membranes are better choices for pressure driven filtration applications where harsh conditions are present, since they possess superior chemical, thermal, microbiological durability compared to polymeric membranes. Sol-gel method can be a very preferable method for the formation of membrane layers of an asymmetric ceramic composite membrane. Among these layers especially the top layer is mainly responsible for the filtration/separation efficiency. The separation takes place with two main mechanisms; size exclusion and Donnan exclusion. Tailor-made top layers with specific characteristics can be prepared via sol-gel method by adjusting the parameters during preparation of top layer via sol-gel method.

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