Sol–gel synthesis of yttria stabilized zirconia membranes through controlled hydrolysis of zirconium alkoxide

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Abstract

Yttria stabilized zirconia (YSZ) polymeric sols were synthesized by controlled hydrolysis and condensation of zirconium tetra-n-propoxide. Yttrium nitrate was added before hydrolysis as the source of yttria. Acetylacetone was used as chelating ligand to modify the reaction rate of zirconium alkoxide. The dependence of YSZ sol formation as well as gelation time was investigated experimentally on the contents of acetylacetone, n-propanol (solvent) and water for hydrolysis. With a stable sol, YSZ membranes were prepared on porous α-alumina supports by a dip-coating process. The membranes were characterized by scanning electron microscopy and gas permeability testing. Unsupported YSZ membranes were also prepared with the same sol, and were investigated with isothermal nitrogen adsorption/desorption porosimetry and X-ray diffraction. The results show that YSZ membranes with nanosize pores were successfully prepared by the sol–gel technique with the polymeric sols.

Keywords: YSZ; Sol–gel; Ceramic membrane; YSZ sol; Controlled hydrolysis

1. Introduction

The sol–gel technique is considered to be the most practical method for fabrication of porous ceramic membranes. In addition to ultrafiltration applications, these membranes offer potential applications for high temperature catalytic reactions and gas separation as well as nanofiltration [1]. Much work has been done on the preparation of alumina, titania and zirconia membranes by the sol–gel technique. These three mesoporous ceramic membranes are now produced at the commercial level. Zirconia and yttria stabilized zirconia (YSZ) membranes are known to be chemically more stable than titania and alumina membranes, and therefore are more suitable for liquid phase application under harsh conditions. For higher temperature applications such as membrane reactors and gas separation by Knudsen diffusion, YSZ membranes are more practical than zirconia ones, since zirconia membranes form cracks due to the stress developed associated with phase transformation from metastable tetragonal to stable monoclinic phase [2]. In addition to chemical and phase stability, YSZ membranes exhibit considerable oxygen ionic conductivity at high temperature. Dense YSZ layers can be used as the electrolyte for solid oxide fuel cells, oxygen sensors and oxygen pumps. Normally, a dense YSZ layer should be fabricated on a porous support to achieve...
a high oxygen flux and mechanical strength [3]. So mesoporous YSZ membranes will find more applications as supports for ultra-thin dense YSZ and other ceramic or metallic membranes.

However, compared with the alumina and titania membranes, less research has been performed on sol–gel derived YSZ membranes. Recently, the sol–gel synthesis of YSZ membranes have been reported [4–6]. Due to expense of yttrium alkoxide, a mixture of zirconia sol and yttrium nitrate is used to synthesis YSZ membranes. This process is sometime referred to as a sol–solution method. The first step of this method is to obtain a stable sol (sol–solution), which consists of zirconia sol and yttrium nitrate. In the reported studies, zirconia sols were firstly prepared and yttrium nitrate was then mixed with these sols. Kim et al. [4] reported the synthesis of porous YSZ membranes with a particulate zirconia sol, which was obtained by hydrolysis and peptization of zirconium \( n \)-propoxide. The zirconia sol used by Okubo [5] et al. to synthesis YSZ membranes was a mixture of particulate sol and polymeric sol. The polymeric sol was prepared by controlled hydrolysis and condensation of zirconium tetra-\( n \)-butoxide. With zirconium alkoxides as precursors, the controlled synthesis of zirconia sol was studied as early as in 1985 [7]. However, no systematic data on the practical preparation of zirconia sol via controlled hydrolysis was available until the present time.

In this work, polymeric zirconia sol was synthesis by controlled hydrolysis and condensation of zirconium tetra-\( n \)-propoxide. The dependence of sol formation and gelation time was investigated systematically on the concentration of chelating reagent, solvent and water for hydrolysis. Yttrium nitrate was added before hydrolysis, which is different from the previous work. With a selected sol, crack-free YSZ membranes were fabricated by the sol–gel procedure. And the membranes were characterized by permeation tests and scanning electron microscopy.

2. Experimental

2.1. Preparation of polymeric sol

The procedure of preparing polymeric YSZ sol is shown in Fig. 1. Zirconium tetra-\( n \)-propoxide (Zr(\( \text{OPr}^n \))\(_4\), Fluka Chemie) and yttria (\( \text{Y}_2\text{O}_3\), 99.95%) were used as starting materials for YSZ, whereas acetylacetone (AcAc) was used as a chelating agent to Zr(\( \text{OPr}^n \))\(_4\) and \( n \)-propanol as solvent. AcAc was also used as a drying control chemical agent here. Yttrium nitrate was synthesized by dissolving yttria in nitric acid. It was then crystallized and dried. The actual yttria contents in yttrium nitrate was standardized thermogravimetrically. Yttrium nitrate and Zr(\( \text{OPr}^n \))\(_4\) were carefully weighted in the defined molar ratio to get 8–10 mol\% yttria stabilized zirconia. The YSZ concentration was in the range from 2.79 to 3.95 wt\%. To get more information about the preparation conditions, the molar ratios of AcAc, \( n \)-propanol and water to zirconium in the final solutions (sols) were varied. Thus three series of study have been done. In each series, the molar ratio of AcAc, \( n \)-propanol or water was changed, while the others were fixed. A typical molar ratio was as follows: \( n \)-propanol:H\(_2\)O:AcAc:Zr=50:10:0.3:1, resulting in a YSZ sol whose concentration was 3.76 wt\%.

In three separate beakers, yttrium nitrate, Zr(\( \text{OPr}^n \))\(_4\) and AcAc were dissolved in \( n \)-propanol and stirred for 10 min to get three clear solutions. AcAc solution was then dripped to Zr(\( \text{OPr}^n \))\(_4\) solution to form complex compound by the reaction of AcAc with Zr(\( \text{OPr}^n \))\(_4\). This reaction can be used to control the
The sol–gel process of zirconium alkoxides [7,8]. After stirring the two solutions with a magnetic stirrer for half-an-hour, yttrium nitrate solution was added. This resulted in a mixed solution, the solvent was \( n \)-propanol, whereas the solutes were yttrium nitrate, complex of \( \text{Zr(OPr}_n^4 \text{)} \) and \( \text{AcAc} \), and maybe some \( \text{Zr(OPr}_n^4 \text{)} \) and \( \text{AcAc} \). Subsequently, deionized water was dripped into the mixed solution for hydrolysis and condensation. The final solution was stirred until a clear sol or a precipitate was formed. Otherwise, the stirring time was 2 days. The color of the sols was different if the composition varied. With time some sols became gels. The gelation point is extremely difficult to measure analytically but easy to observe qualitatively [9]. In this work, the gelation point was defined qualitatively as that, at this point, the sol did not change its shape immediately when the container was inclined.

As the hydrolysis reaction can take place even in an atmosphere of low humidity, the moisture and conditions of hydrolysis were strictly controlled in order to prepare homogenous sol. Therefore all of the procedures shown in Fig. 1 were carried out in a glove box under drying air flow. The glass containers, which were used to contain solutions were covered with plastic wraps to prevent evaporation. The solutions were transferred and dripped with syringes of different types. It should be mentioned that the synthesis route was processed at a temperature range of 10–14°C.

2.2. Synthesis of YSZ membranes

Supported YSZ membranes were prepared by a dip-coating procedure. The content of YSZ in the dipping sol was 3.76 wt%. The YSZ layers were supported on a home-made porous \( \alpha \)-alumina disks (diameter: 12 mm, thickness: 2 mm, pore diameter: 0.2 \( \mu \)m, porosity: 40%). After 25 s dipping in the sol, the coated \( \alpha \)-alumina disks were dried at room temperature and 70% RH (relative humidity) for 48 h. In a programmed oven, they were calcined in two steps. At a rate of 10°/h, they were firstly heated to 300°C and kept for 2 h. And then they were heated to 650°C at a rate of 60°/h and kept for 3 h. The heating program was set according to thermal gravimetry (TG) and differential thermal analysis (DTA) curves in a nitrogen stream (Fig. 2). The dipcoating-drying-calcination procedure was repeated three times to get fine YSZ membranes.

Unsupported membranes were obtained by casting the dipping sol in glass petridishes, drying at 100°C for 24 h and heating at 350–900°C for 3 h.

The pore size and its distribution of the unsupported YSZ membrane was obtained from nitrogen adsorption/desorption isotherms measured by using a porosimeter (Micrometrics, ASAP 2000). The phase structures of the unsupported YSZ membranes were identified by X-ray diffractometer (D/Max-\( \gamma \) A, Cu \( \text{K}_\alpha \)). Thickness and morphology of the supported film were investigated by a scanning electron microscope (HITACHI, X-650), and argon and hydrogen permeation properties were measured by a home-made gas permeation system.

3. Results and discussions

3.1. Sol synthesis

The preparation of YSZ sol via a controlled hydrolysis and condensation of zirconium alkoxides has been previously reported [5]. However, this study followed a procedure of titania sol preparation with titanium alkoxides and limited information on the controlled synthesis was reported. The greater reactivity of zirconium tetra-\( n \)-propoxide (\( \text{Zr(OPr}_n^4 \text{)} \)) requires that it must be processed with strict control of moisture and conditions of hydrolysis in order to prepare homogeneous sol rather than precipitates. The most important conditions for preparing a stable sol via controlled hydrolysis include:

1. the dilution degree of \( \text{Zr(OPr}_n^4 \text{)} \) with \( n \)-propanol,
2. the amount and type of chelating ligands used to modify reaction rate,
3. the amount of water used for hydrolysis of the alkoxide, and
4. temperature and catalytic agent.
In this work, these conditions were investigated experimentally. The dependence of gelation time as well as color and state of the resulted solution has been studied experimentally on the molar ratio of AcAc to zirconium. The results are summarized briefly in Table 1. The synthesis procedure has already been described above. In this series experiments, YSZ concentration changed only a little with AcAc content since the amount of other substances was fixed. The molar ratios of water and \( n \)-propanol to zirconium were set to be 10 and 50, respectively. When no AcAc was added, as reported in literature, a white precipitate was observed as a result of hydrolysis. The precipitate is considered as the molecular aggregate of hydrated zirconium oxide alkoxides which is caused by the much faster hydrolysis rather than condensation [7].

An equimolar reaction of AcAc and Zr(OPr\(n\))\(_4\) is believed to prevent precipitation or gelation [8]. However, it can be seen from Table 1 that a molar ratio AcAc/Zr between 0.06 and 0.24 can partially stabilize Zr(OPr\(n\))\(_4\) and thus prevent immediate precipitation, whereas a molar ratio of around 1.0 can stabilize the sol for a period of 100 days. Similar results were observed by Debsikdar [7], who found that zirconium alkoxide can be stabilized by less than one mole of AcAc per mole of the alkoxide when he prepared pure zirconia sols. Unfortunately, no further data was reported. As shown in Table 1, too much AcAc leads to formation of clear solutions rather than sols under the conditions investigated.

Gelation time is very important for the preparation of a YSZ membrane by a sol–gel process. In this process, sol viscosity must be carefully controlled in order to produce a fine membrane. If it is too viscous, a sol cannot be applied to a support homogeneously, let alone to form a fine membrane. Thus a sol cannot be used for membrane fabrication in the case that the sol is either over condensed or becomes a gel. The gelation time, which is observed qualitatively is listed in Table 1 as a function of AcAc content. It increases with AcAc/Zr and increases sharply when AcAc/Zr reaches 0.30, as also shown in Fig. 3. The mechanism for synthesis of a zirconia sol via a polymeric route can be simplified as two steps, the hydrolysis and the condensation. If the hydrolysis reaction is much faster than the condensation reaction, a precipitate is obtained. On the contrary, if condensation exceeds hydrolysis rate, a clear sol or gel is formed. The use of AcAc is to decrease the hydrolysis rate by a way of forming a chelate with Zr(OPr\(n\))\(_4\). Our results show that, firstly, more than 0.30 mole AcAc per mole Zr(OPr\(n\))\(_4\) can modify the hydrolysis and poly-condensation rates to form a clear sol which is stable for a period long enough for the membrane fabrication.

<table>
<thead>
<tr>
<th>Molar ratio AcAc/Zr</th>
<th>YSZ concentration % (wt)</th>
<th>Solution description</th>
<th>Gelation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>3.49</td>
<td>Yellow solution</td>
<td>–</td>
</tr>
<tr>
<td>1.8</td>
<td>3.61</td>
<td>Yellow solution</td>
<td>–</td>
</tr>
<tr>
<td>1.2</td>
<td>3.67</td>
<td>Yellow sol</td>
<td>More than 120 days</td>
</tr>
<tr>
<td>0.60</td>
<td>3.73</td>
<td>Yellow sol</td>
<td>109 days</td>
</tr>
<tr>
<td>0.30</td>
<td>3.76</td>
<td>Yellow sol</td>
<td>100 days</td>
</tr>
<tr>
<td>0.24</td>
<td>3.77</td>
<td>White sol</td>
<td>1 h</td>
</tr>
<tr>
<td>0.18</td>
<td>3.78</td>
<td>White sol</td>
<td>30 min</td>
</tr>
<tr>
<td>0.12</td>
<td>3.78</td>
<td>White sol</td>
<td>20–25 min</td>
</tr>
<tr>
<td>0.06</td>
<td>3.79</td>
<td>White sol</td>
<td>20–25 min</td>
</tr>
<tr>
<td>0</td>
<td>3.79</td>
<td>White precipitates</td>
<td>–</td>
</tr>
</tbody>
</table>

The molar ratio of \( n \)-propanol and water to Zr(OPr\(n\))\(_4\) were set to be 50 and 10, respectively.

Fig. 3. Gelation time (h) as a function of AcAc content.
Secondly, too much AcAc (AcAc/Zr>1.8) completely stops the hydrolysis reaction. This causes the formation of a clear solution rather than a sol or precipitate. Finally, a content smaller than 0.24 mole AcAc per mole Zr(OPrₙ)₄ cannot decrease the hydrolysis rate to an extent which results in a sol stable for more than 1 h.

A well modified zirconium alkoxide causes a stable YSZ sol and an expected gelation time. However, gelation time depends not only on the amount of chelating ligands, but also on the amount of solvents and water used for hydrolysis reaction, and further more, on the temperature and catalytic agent. No catalytic agent was used in this work and room temperatures of 10–14°C are applied when the mixed solution was prepared. The gelation time as a function of the amount of n-propanol was investigated. The results are shown in Fig. 4, where the dependence of gelation time and YSZ concentration on the mole ratio of n-propanol to Zr(OPrₙ)₄ is plotted. It can be seen that, larger quantities of n-propanol correspond to longer gelation times. Actually, it took several seconds to become a gel for a ratio PrOH/Zr of 30, whereas 5 days for a ratio of 60. It is clear that the lower the YSZ concentration, the longer the gelation time.

Table 2
Dependence of sol formation and gelation time on molar ratio of H₂O to Zr(OPrₙ)₄

<table>
<thead>
<tr>
<th>Molar ratio of H₂O/Zr</th>
<th>YSZ concentration % (wt)</th>
<th>Solution description</th>
<th>Gelation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.95</td>
<td>Light yellow sol</td>
<td>58 days</td>
</tr>
<tr>
<td>4</td>
<td>3.89</td>
<td>Light yellow sol</td>
<td>2 days</td>
</tr>
<tr>
<td>10</td>
<td>3.77</td>
<td>White sol</td>
<td>1 h</td>
</tr>
<tr>
<td>50</td>
<td>3.55</td>
<td>Blue sol</td>
<td>12 h</td>
</tr>
<tr>
<td>100</td>
<td>2.59</td>
<td>Blue sol</td>
<td>100 days</td>
</tr>
</tbody>
</table>

The molar ratio of n-propanol and AcAc to Zr(OPrₙ)₄ were set to be 50 and 0.24, respectively.

Water used for hydrolysis also affects gelation time. The gelation time together with YSZ concentration and sol color are listed in Table 2 as a function of the amount of water. For ratio H₂O/Zr less than 10, an increase of the amount of hydrolysis water decreases the gelation time dramatically, although there is a dilution effect. On the other hand, for ratio of H₂O/Zr higher than 10, the gelation time increases with the quantity of water greatly due to the dilution effect.

It should be noted that at a temperature of 28°C, the mixed solution became a gel in a few seconds after adding of water when molar ratio of AcAc/Zr≤0.3 regardless of the content of water and propanol. It was also observed that a stable YSZ sol could be obtained by adding yttrium nitrate to a polymeric zirconia sol. So whether one adds yttrium nitrate before or after hydrolysis one is able to produce a stable YSZ sol by the controlled synthesis of zirconium alkoxides.

3.2. Characterization of unsupported membranes

Fig. 5 shows XRD patterns of unsupported yttria doped zirconia after calcination. It was observed that the membranes dried at 100°C for 2 h had an amorphous structure before further heat treatment. After being calcined to 350°C for 3 h, the membrane transforms to a fluorite cubic structure, which is the typical structure of YSZ. Further heat treatment at much higher temperature makes the membrane even more crystallized. However, it maintains the same diffraction patterns of cubic phase structure. Crystallite size calculated from the Sherrer equation is given in Table 3. Sintering results in a considerable growth of the grains (crystallites).

The grain size of the YSZ membrane is compared with those prepared by Lin and co-workers [4] in Table 3. After calcination at 450°C and 700°C for 3 h.
in this work, the crystallite sizes are 4.6 and 8.2 nm, respectively. These values are about 1/4–1/5 as those reported by Lin at the same temperatures. The difference between the two works are that in this work unsupported membranes are obtained from a polymeric sol, and in Lin’s work from a particulate sol. The polymeric sol is prepared by controlled hydrolysis of $\text{Zr(OPr}_n\text{)}_4$ in organic media, whereas the particulate sol is obtained by hydrolysis and peptization of $\text{Zr(OPr}_n\text{)}_4$ in aqueous media. It therefore seems to be that, in a sol–gel process using zirconium alkoxide as a precursor, grain size of YSZ membrane from polymeric sols is of the order of a nanoscale, and therefore is much smaller than that of those prepared from particulate sols. The grain size is further affected by preparation conditions. For an example, grain size of unsupported YSZ membranes from particulate sols reported by Okubo and co-workers [10] is much bigger compared to those from polymeric sols in this work (Table 3). And it is much smaller than those from particulate sols reported in [4]. These sols were synthesized via hydrolysis and peptization of zirconium tetra-$n$-butoxide with diluted nitric acid in 2-propanol, which was later replaced with water. Okubo and co-workers [5] have also prepared both polymeric sols of YSZ, and XRD patterns have been reported of samples derived from the two type sols and further calcined at 600°C. Unfortunately, no data on crystallite size from Sherrer formula were given. However, the particle size from polymeric sol is much smaller compared to that from particulate one, since the XRD peaks of the polymeric sample are much broader than that of the particulate sample as can be seen in the reported XRD patterns [5].

The pore morphology of the unsupported YSZ membrane was studied from its nitrogen adsorption–desorption isotherm. The pore size distribution computed from the adsorption isotherm by BJH method is shown in Fig. 6. However, pore size lower than 1.7 nm cannot be detected with the porosimeter. The curve shape in Fig. 6 suggests that there should be some pores having size smaller than 1.7 nm, since a pore size distribution curve normally has one or more peaks. Furthermore the pore size distribution curve obtained from the desorption isotherm is similar to that of Fig. 6. The mean pore size from adsorption isotherm is 2.9 nm, and 2.2 nm from desorption. It should be noted that the actual pore size is smaller than the BJH size as mentioned above.

### 3.3. Characterization of supported membranes

The most important parameters in the dip-coating process were sol concentration, dipping time, pore size and porosity of the support and temperature [1,11,12]. The YSZ content in the dipping sol was 3.76 wt% and the dipping time was 15 s in this work. It was observed that the coated YSZ layers prepared from a over-condensed sol (thicker sol) cracked during drying or calcination process. Thus, the sol which was

![XRD patterns of unsupported yttria doped zirconia membranes calcined at different temperature for 3 h.](http://www.paper.edu.cn)
later tested to be stable for a period of 100 days was used in the dip-coating process. It was observed with SEM that there were pinholes in the coated YSZ layer after the first coating. In the case of the γ-alumina membranes prepared by a sol–gel technique, pinholes and defects could be self-repairing by way of repeating the dipping-drying-heating procedure [12]. Therefore, in this work the self-repairing procedure was repeated three times to get a crack-free YSZ membrane. The resulting YSZ membrane was tested for the presence of pinholes or defects by gas permeability experiments. Fig. 7 presents the permeability for hydrogen and argon as a function of mean pressure for the membrane. It can be seen that argon or hydrogen permeability is independent of average pressure for the membrane. This indicates that the top-layer is governed by Knudsen flow. So it is clear that after three subsequent dip-coating procedures, the membrane appears to contain no pinholes.

Basically the gas phase permeability is represented by [12]

\[ F = \alpha + \beta P_m \]

where the permeance is defined as \( F = Q/S(P_h - P_l) \) with \( Q \) being the molar gas flow rate, \( S \) the permeation area of the membrane, and \( P_h \) and \( P_l \) the pressures upstream and downstream, respectively. The mean pressure is defined as \( P_m = (P_h + P_l)/2 \). The permeability coefficients, \( \alpha \) and \( \beta \) are attributed to Knudsen and viscous flow, respectively. In theory, \( \alpha \) is in inverse proportion to the square root of the molecular weight of the permeation gas. The theoretical Knudsen-flow ratio of hydrogen and argon can be calculated as

\[ \frac{\alpha_{H_2}}{\alpha_{Ar}} = \sqrt{\frac{M_{Ar}}{M_{H_2}}} = 4.47. \]

With linear regression of the permeation data measured as a function of average pressure, the Knudsen flow coefficients of hydrogen and argon are computed to be 3.45 and 0.771 \((10^{-6} \text{ mol/m}^2 \text{ s Pa})\). Their ratio is 4.48, which is approximately equal to the theoretical ratio 4.47. This also shows that the membrane is well fabricated and has pore size in the magnitude of a nanometer.

SEM investigation of the cross-section of YSZ membranes formed on the porous alumina supports having pore diameters of 0.2 \( \mu \text{m} \) showed that no sol was sucked into the support while dipping. The thickness of the membrane obtained by three times dipping was about 3 \( \mu \text{m} \). And it was less than 2 \( \mu \text{m} \) thick for a membrane prepared by only one dipping procedure.

4. Conclusion

Polymeric yttria stabilized zirconia sols can be prepared from the controlled hydrolysis and condensation of zirconia tetra-\( n \)-propoxide. However, the stability and gelation time of these sols are dependent on the concentration of acetylacetone, \( n \)-propanol and water as well as temperature. Typically with the ratio propanol: \( \text{H}_2\text{O} \): AcAc: Zr = 50:10:0.3:1, a yttria stabilized zirconia sol could be obtained at low temperature (10–14°C) and was stable for a period of 100 days. X-ray diffraction measurement showed that the average individual crystal size of the polymeric sol is much smaller than many previously reported particulate sols.

Crack-free supported mesoporous yttria stabilized zirconia membranes can be prepared from a stable polymeric sol by the sol–gel technique. The average
The pore size of unsupported membrane was less than 3 nm measured by nitrogen adsorption/desorption porosimeter. It is necessary to repeat the dip-coating processes several times to get a film without pinholes or cracks. The thickness of the sol–gel derived membrane by three times dip-coating is 3 μm obtained by scanning electron microscopy.

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