Synthesis and characterization of a magnetite (Fe$_3$O$_4$) nanofiltration membrane

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Abstract. Meso- porous magnetite membranes have been synthesized by dip-coating iron oxide dispersion on ~2 mm thick α-Al$_2$O$_3$ supports, followed by nitrogen-environment thermal processing. Both gas and water permeabilities of magnetite membranes were investigated. At room temperature, the nitrogen permeance was $3 \times 10^{-8}$, which increased to $3 \times 10^{-7}$ at 400°C, but decreased to $9 \times 10^{-8}$ at 500°C (still higher than room temperature). The argon permeance at corresponding temperature was slightly lower than nitrogen permeance. 0.001 mol/L NaCl was used as feed solution for dead-end filtration test. Experimental result indicated the mechanical permeance of magnetite membrane was $5.5 \times 10^{-16}$ m, and the maximum salt rejection was 44% at transmembrane pressure of 0.35 MPa. From the perspective of thermal stability, a magnetite membrane was immersed in 60°C deionized (DI) water for a week, and there was no change in thickness according to ellipsometry analysis. Meanwhile, it was found that the membrane was chemically stable in base solution, which is expected for Fe$_3$O$_4$. However, the membrane thickness increased in nitric acid solution at pH 5.0, which was tentatively ascribed to oxidation of Fe$_3$O$_4$ to Fe$_2$O$_3$.

1. Introduction

The use of nanofiltration (NF) membranes is rapidly expanding since late 80’s, especially for water purification, desalinization, pharmaceutical and biotechnological applications. Compared with organic NF membranes, inorganic NF membranes have numerous potential benefits, such as good chemical and thermal stabilities, wide pressure/temperature/pH operation range, compatibility with organic solvent system and regeneration ability[1].

Sol-gel method is the mostly adopted route for the synthesis of inorganic NF membranes. Alumina is the first material that has been used for inorganic membrane preparation due to its well-known colloidal behavior[2]. According to M. Schillo, defect-free γ-alumina membranes could produce nearly 100% rejection of Ca$^{2+}$ ions[3]. Titania membranes show excellent chemical resistance and can be used in wider pH range than γ-alumina membranes[4]. Besides predominant research effort on Al$_2$O$_3$ and TiO$_2$ membranes, many new inorganic materials have been investigated. Uhlhorn et al.[5] reported the properties of microporous ceria membranes compared with their work of titania membranes. They found sintering of single phase CeO$_2$ membranes at higher temperature always resulted in denser coatings and the overall porosity of CeO$_2$ is much lower than TiO$_2$ membranes.

Recently we discovered the synthesis of meso-porous magnetite membranes accidentally, and explored several properties, among which we found the nanofiltration properties were the most
interesting. The present study focuses on preparing a thin, defect-free magnetite membrane on α-Al₂O₃ support by colloidal deposition, rapid thermal processing (RTP), and gas reduction procedures. The gas and water permeabilities of magnetite membranes were investigated. The second objective of this work was to study the thermal and chemical stabilities of magnetite membranes by putting them in aqueous solutions at various pH values and measured the change of membrane thickness.

2. Experimental

2.1. Synthesis of iron oxide dispersion
In sonochemical syntheses, ultrasonic waves are utilized in a liquid medium to achieve the reaction from dissolved precursor salts into nano-particle oxides. This is possible due to the localized energy released when the ultrasound wave created micro-voids collapse. In this work, Fe(NO₃)₃ was dissolved in deionized (DI) water, and the solution was sonified in a chilled reactor vessel with tetramethylammonium hydroxide at 10 °C for 20 min. After that the dispersion was filtered using a 0.45 µm nylon filter to remove agglomerates and contaminants, followed by dialysis for 4 hours in nitric acid. The dialysis step removed unreacted precursor ions, as the initial formulation ideally would yield 4 wt% iron oxide dispersion.

2.2. Preparation of supported magnetite membrane
Before membrane deposition, polyvinyl alcohol was added to iron oxide dispersion to alter the rheology and form dipping dispersion with 1:1 weight ratio. To form a highly uniform membrane, the dipping dispersion was applied on a α-alumina support by dip-coating process, followed by drying in an oven at 110°C for 1h. The dried sample was then treated by rapid thermal processing (RTP) in nitrogen environment at 600°C for 3 min with ramping rate of 20 °C/s. After drying and RTP treatments, the membrane was reduced in forming gas (5% H₂ balanced in N₂) at 400 °C with heating and cooling rates of 2 °C/s. The color of magnetite membrane changed from earthy yellow to dark brown after gas reduction and remained stable when exposed to air at room temperature, indicating the membrane does not contain iron.

2.3. Characterization
The thickness of magnetite membrane was analyzed by Ellipsometry (Woollam). Nitrogen and argon permeances at various temperatures were measured by single-gas permeance setup[6]. The water permeability was characterized by using a dead-end filtration apparatus. 3,000 mL feed solution (0.001 mol/L NaCl) were added to the chamber and the stirrer located ~2 mm above the membrane was set at 2000 rpm. The mechanical permeance (fᵢ) was calculated according to equation (1),

$$ f_i = \frac{j_i \cdot \eta}{\Delta p} \quad (1) $$

where \( j_i \) is flow rate (m/s), \( \eta \) is dynamic viscosity (Pa·s), and \( \Delta p \) is transmembrane pressure (TMP).

Salt rejection properties of magnetite membranes were determined under TMP in the range of 0.1…0.35 MPa. The salt rejection (R) was calculated using equation (2).

$$ R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2) $$

where \( C_p \) and \( C_f \) were ionic concentrations of permeate and feed solutions, respectively.

3. Results and discussion

3.1. Membrane morphology and thickness
Finished magnetite membrane had shiny and smooth surface, dark brown in color, and did not contain visible defects. Thermodynamically, since the chemical potential of Fe and Fe₃O₄ mixture is lower...
than that of Fe$_3$O$_4$ and Fe$_7$O$_4$ mixture at 400°C, it is highly possible that Fe$_7$O$_4$ was formed during forming gas reduction[7]. Fe$_7$O$_4$ is a very stable compound and its presence was consistent with all experimental observations. Based on Ellipsometry analysis, the membrane thickness was 1190 nm after RTP, and reduced to 411 nm after gas reduction.

3.2. Single gas permeance
The nitrogen permeance of magnetite membrane at room temperature (25°C) was 3×10$^{-8}$, which increased to 3×10$^{-7}$ at 400°C, but decreased to 9×10$^{-8}$ at 500°C. The argon permeance at corresponding temperature was slight lower than nitrogen. After permeance test, the membrane looked completely oxidized when removed from test cell. Table 1 summarizes the nitrogen and argon permeances of magnetite membrane at different temperatures.

| Temperature | N$_2$ permeance | Ar permeance |
|-------------|-----------------|--------------|
| 25°C        | 2.98×10$^{-8}$  | 2.61×10$^{-8}$ |
| 400°C       | 2.78×10$^{-7}$  | 2.28×10$^{-7}$ |
| 500°C       | 9.19×10$^{-8}$  | 7.00×10$^{-7}$ |

3.3. Mechanical permeance and salt rejection
The feed solution used for dead-end filtration test was 0.001mol/L NaCl solution at pH 9 by adding ammonia. The magnetite membrane was tested using an increasing sequence of TMP. Table 2 presents the mechanical permeance and salt rejection at various TMP. Overall, the salt rejection increased with pressure difference, and reached a maximum value (44%) at a TMP of 0.35 MPa. The mechanical permeance of magnetite membrane was 8.3×10$^{-16}$ m at the beginning, which gradually decreased, and finally stabilized around 5.5×10$^{-16}$ m. This could be caused by membrane wettability [8]. Due to the low permeance, the experiment was performed for 672 hours to collect data.

| Temperature | N$_2$ permeance | Ar permeance |
|-------------|-----------------|--------------|
| 25°C        | 2.98×10$^{-8}$  | 2.61×10$^{-8}$ |
| 400°C       | 2.78×10$^{-7}$  | 2.28×10$^{-7}$ |
| 500°C       | 9.19×10$^{-8}$  | 7.00×10$^{-7}$ |

Table 2. Mechanical permeance and salt rejection of magnetite membrane.

| TMP (MPa) | 103 | 138 | 172 | 207 | 276 | 345 |
|-----------|-----|-----|-----|-----|-----|-----|
| f$_r$ (m) | 8.3×10$^{-16}$ | 6.2×10$^{-16}$ | 5.9×10$^{-16}$ | 5.7×10$^{-16}$ | 5.5×10$^{-16}$ | 5.5×10$^{-16}$ |
| R (%)     | 17  | 19  | 27  | 34  | 42  | 44  |

3.4. Thermal and chemical stabilities
From the perspective of thermal stability, a magnetite membrane was place in deionized (DI) water at 60°C for 168 hours. Ellipsometry analysis showed that both membrane thickness and refractive index did not change during the test, indicating the membrane was chemically stable in water for a week. To further analysis the chemical stability, the membrane was immersed in base and acid solutions at various pH for 168 hours. As shown in table 3, magnetite membrane was chemically stable in NaOH solution at pH 11, which is expected. However, the membrane thickness increased by 9 nm in nitric acid at pH 5 after a week. The increase in thickness was tentatively ascribed to oxidation of Fe$_7$O$_4$ to Fe$_3$O$_4$. The reduction of thickness in nitric acid at pH 3 and 4 was due to gradual dissolution. The surface of magnetite membrane remained shiny and uniform before and after each test.

| Solution | pH | Thickness (nm) | Refractive index |
|----------|----|----------------|-----------------|
| Before test | -  | 258            | 2.1             |
| NaOH      | 11 | 254            | 2.1             |
| HNO$_3$   | 5  | 265            | 2.0             |
| HNO$_3$   | 4  | 217            | 2.1             |
| HNO$_3$   | 3  | 197            | 2.2             |
4. Conclusion
Iron oxide dispersion was successfully synthesized from iron nitrate solution and tetramethylammonium hydroxide by sonochemical precipitation. Uniform magnetite membrane was formed by deposition of iron oxide dispersion on AKP30 support, followed by nitrogen-environment RTP and gas reduction. Results of gas permeance experiment indicated the nitrogen permeance for magnetite membrane was $3 \times 10^8$ at 25°C, and increased to $3 \times 10^7$ at 400°C. The increase in permeance was due to the formation of Fe$_2$O$_3$. However, the nitrogen permeance decreased to $9 \times 10^8$ at 500°C, which might be caused by gas leaking. The argon permeance at corresponding temperature was slightly lower than nitrogen permeance. To investigate the performance of water purification, dead-end filtration test was performed on magnetite membrane. The salt rejection increased with pressure difference, and reached the maximum value (44%) under 0.35 MPa. The mechanical permeance of the membrane was $8.3 \times 10^{-16}$ m at the beginning of test, and gradually decreased and stabilized at $5.5 \times 10^{-16}$ m. To analyze the thermal and chemical stability, a magnetite membrane was immersed in DI water, base and acid solutions at various pH for 168 hours. Ellipsometry analysis showed the membrane was chemically stable in 60 °C DI water and base solution, which is expected. However, the thickness increased in nitric acid solution at pH 5. This was tentatively ascribed to oxidation of Fe$_3$O$_4$ to Fe$_2$O$_3$. The reduction of thickness at pH 3 and 4 was due to chemical dissolution. In the future, stability studies will be continued at various circumstances, and specific selectivity for certain ions such as arsenate will be studied through filtration experiments. The reduction reaction of magnetite membrane could be used to obtain robust structures on polymers.

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