Fundamental characteristics study of anion-exchange PVDF–SiO₂ membranes
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ABSTRACT
A new type of poly(vinylidene fluoride)(PVDF)–SiO₂ hybrid anion-exchange membrane was prepared by blending method. The anion-exchange groups were introduced by the reaction of epoxy groups with trimethylamine (TMA). Contact angle between water and the membrane surface was measured to characterize the hydrophilicity change of the membrane surface. The effects of nano-sized SiO₂ particles in the membrane-forming materials on the membrane mechanical properties and conductivity were also investigated. The experimental results indicated that PVDF–SiO₂ anion-exchange membranes exhibited better water content, ion-exchange capacity, conductivity and mechanic properties, and so may find potential applications in alkaline membrane fuel cells and water treatment processes.

Key words | anion-exchange membrane, PVDF–SiO₂, physical–chemical properties

INTRODUCTION
Ion-exchange membranes are receiving multidiscipline attention in both theoretical investigations and industrial application nowadays. Ion-exchange membranes with better selectivity, lower electrical resistance and improved electrochemical and chemical properties have been developed for a number of potential applications in a variety of fields, such as food, drug, chemical process industries as well as biotechnology and wastewater treatment (Matos et al. 2008; Strathmann 2010).

The ion-exchange membranes prepared from monomer, styrene and divinylbenzene are most common as basic materials for a traditional use ion-exchange membrane. Compared with the cation-exchange membrane, the preparation of anion-exchange membrane seems to be more complicated involving chloromethylation, in which, the traditionally used chloromethyl methylether is a carcinogen and harmful to human health (Lin & Takai 1994). The preparation process of anion-exchange membranes avoiding chloromethylizing reagents is increasingly important and has received remarkable attention in recent years. An alternative way to avoid the use of chloromethyl methylether may be: (i) copolymerization to form copolymer films that can be converted to anion-exchange membranes by quaternary amination (Herman et al. 2003; Liu et al. 2012); (ii) anion-exchange membranes prepared by directly grafting 4-vinpyridine onto polymeric membranes, such as polyethylene (PE), polypropylene (PP) and polystyrene chloride (PVC) followed by quaternization (Richardson et al. 2005); (iii) anion-exchange membranes prepared directly from engineering polymer poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) by bromination instead of chloromethylation with chloromethyl methylether (Wang et al. 2003); and (iv) epoxy acrylate (glycidyl acrylate or glycidyl ethacrylate) copolymerized with divinylbenzene and followed by a simple amination reaction, which can serve as a way to prepare anion-exchange membranes (Xu et al. 2010). As described above, making full use of the methyl group in available polymers in the chloromethylation may be the best choice to avoid the use of chloromethyl methylether.

A great deal of work has been dedicated to preparing ion-exchange membranes from polymer, such as hydrocarbon PE and PP or fluorocarbon origin. Besides the polymeric ion-exchange membranes, ion-exchange membranes can also be prepared from inorganic material, such as Fe(OH)₃ and Fe₂O₃ (Kang et al. 2004) and Li₁.₃₃Mn₁.₆₇O₄ (Ohya et al. 1998). However, due to their
high cost and other disadvantages in terms of relatively bad electrochemical properties and permeability, the inorganic membranes are less important, even though they can undergo higher temperatures than organic membranes (Ohya et al. 1995). It has been reported that inorganic–organic composite materials are important owing to their extraordinary properties, such as mechanical, thermal, and electrical compared with pure organic polymers or inorganic materials (Thayumanasundaram et al. 2010).

Poly(vinylidene fluoride) (PVDF) was chosen as the polymeric material for the preparation of ion-exchange membrane because of PVDF-based membranes exhibiting outstanding oxidative, thermal and hydrolytic stability as well as good mechanical and film-forming properties (Qiu et al. 2013; Salehi et al. 2012). In this work, a new type of organic–inorganic (hybrid) anion-exchange membrane was prepared from PVDF and inorganic SiO2 nanoparticles. And the anion-exchange groups were introduced by the reaction of epoxy groups of glycidyl methacrylate (GMA) with trimethylamine (TMA) at 25 °C. The aim of this research was to characterize the PVDF–SiO2 anion-exchange membrane. The effects of SiO2 particle concentration in the casting solution on membrane hydrophilicity, mechanical and transport properties were investigated.

**MATERIALS AND METHODS**

**Materials**

PVDF used was a commercial product (FR904) (Shanghai 3F New Materials CO., Ltd). Silica particles with a nano-size of 30 nm were used as additives for PVDF solutions (Zhejian Mingri Chemicals Co., China). GMA and divinyl benzene (DVB, >55%) were used as received (Shanghai Yuanji Chemical Ltd, China). Dimethylacetamide (DMAC, >99%, reagent) used as the solvent, TMA (33%), benzoyl peroxide (BPO), fuming sulfuric acid, NaOH, HCl, and NaCl were of analytical grade and used without further purification (Tianjin Chemical Reagents Plant, China). Double distilled water was used for the preparation of all the solutions.

**Membrane preparation**

Casting solution was prepared by dissolving PVDF in DMAC at room temperature and then adding SiO2 nanoparticles with ultrasonic vibration for at least 24 h. Other additives such as BPO, DVB, and GMA were also added to the mixture under stirring. Casting solution was deposited in a no sunlight place for one day to remove air bubbles from it and to obtain gels. An appropriate amount of the resulting gel was dispersed uniformly on a glass plate by using a doctor blade and dried at 80 °C to obtain a film. The film was heated immediately for 12 h at 100 °C and then immersed in TMA for 3 h at 25 °C to introduce the quaternary ammonium groups by the reaction of the epoxy groups of GMA with TMA. The obtained membranes were conditioned in 1 mol/L HCl and 1 mol/L NaOH solutions alternately. The membranes were stored in deionized water before use.

Anion-exchange membranes with different weight ratio of SiO2 were prepared in this work. The PVDF content was kept at 14 wt% of the membrane-forming materials. The SiO2 contents were 0, 0.5, 1.0, 1.5 and 2.0% of PVDF in weight, and the corresponding PVDF–SiO2 membranes are designated as PVDF-0, PVDF-1, PVDF-2, PVDF-3 and PVDF-4, respectively.

**Characterization of membrane**

**Thermogravimetric analysis (TGA)**

The degradation process and the thermal stability of the membranes were investigated using thermogravimetric analysis (TGA) (NETZSCHSTA 449C, Germany) under a nitrogen atmosphere using a heating rate of 10 °C/min from 50 to 800 °C.

**Tensile properties**

The tensile properties were measured using an electronic strength measurement at 25 °C and a strain rate of 2 mm/min was employed (Mirmohseni & Wallace 2003). Tensile strength (TS) and elongation at break (Ebb) were recorded.

**Contact angle and water content**

Contact angle between water and the membrane surface was measured in a contact angle measurement (DSA10, American): a water droplet was placed onto a flat membrane surface and the contact angle of the droplet with the surface was measured. The value was observed until there was no change in contact angle.

Water uptake was measured as follows: the dried membranes were weighed and immersed in distilled water at 25 °C for 48 hours. Surfaces of the wet membranes were then carefully dried and the membranes weighed. Water uptake was measured as follows: the dried membranes were weighed and immersed in distilled water at 25 °C for 48 hours. Surfaces of the wet membranes were then carefully dried and the membranes weighed.

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uptake was calculated as the relative weight gain per gram of the dry membrane sample.

**Ion-exchange capacity (IEC)**

IEC measurements were carried out as described in the literature (Li et al. 2006). Accurately weighed dry membranes were converted to \( \text{Cl}^-/\text{C}_0 \), and then immersed in 200 mL \( \text{Na}_2\text{SO}_4 \) at a concentration of 0.5 mol/L. Anion exchange values of the membranes were obtained by determining the amount of the generated \( \text{Cl}^- \) through titration with \( \text{AgNO}_3 \).

**Membrane conductivity**

Membrane conductance measurements for all the prepared membranes were carried out in \( \text{NaCl} \) solution using a clip cell as reported earlier (Ohya et al. 1995). This cell was composed of two black graphite electrodes fixed on Plexiglas plates. The membrane conductance was measured with the help of a digital conductivity meter (Century, model CC601). The process was repeated till reproducible values within ±0.01 mS were obtained. Specific conductivity of the membrane was estimated by:

\[
\kappa = \frac{\Delta x}{AR}
\]

where \( \Delta x \) is the thickness of the wet membrane, \( A \) is its area and \( 1/R \) is its electrical conductivity.

**RESULTS AND DISCUSSION**

**Ion-exchange capacity (IEC) studies**

Table 1 illustrates the IEC of the prepared membrane. It can be seen that the measured IECs of the hybrid membranes were in the range of 0.79–1.23 mmol/g. IEC values of hybrid membranes increased with increasing silica content in the membrane-forming materials, as could be seen in the gradually higher IECs from membranes PVDF-0 to PVDF-4. This can be ascribed to an increase in the concentration of functional groups in the membrane phase, and then the ion exchange possibilities increased (Khodabakhshi et al. 2012).

**Contact angle and water uptake studies**

The contact angle is an important parameter in the measurement of the surface hydrophilicity (Palacio et al. 1999). In general, membrane surface hydrophilicity is higher while its contact angle is smaller. Contact angle and water uptake of these membranes are presented in Figure 1. As can be seen, an increase of SiO\(_2\) particles content led to a decrease in the contact angle, revealing that incorporation of inorganic silica particles into PVDF can improve its hydrophilicity. This was due to the high hydrophilicity of the SiO\(_2\) nanoparticles and the ion-exchange groups (quaternary ammonium) in the PVDF-SiO\(_2\) anion-exchange membranes.

It is clearly observed that the water uptake values of membranes PVDF-0, PVDF-2 and PVDF-4 were 9.5, 13.5 and 21.2%, respectively, which showed that water content of the membranes increased with the increase of silica content. In addition, the water content of all the prepared membranes were lower (<25%). It was inferred that the polycondensation processes should be completed when nano-sized particles were added, resulting in a high degree of crosslinkage of the inorganic silica network in the hybrid membranes. The PVDF–SiO\(_2\) membranes with such a network structure contained relatively fewer Si-OH groups and would present lower water uptake (Wu et al. 2008). The increasing tendency of water uptake was mainly attributed to the increased IEC of the hybrid membranes, as has been discussed above, and the high hydrophilicity of the SiO\(_2\) component.

![Figure 1](https://iwaponline.com/wst/article-pdf/66/11/2343/441004/2343.pdf)
Thermal stability (TGA analysis) studies

Thermal stability of membrane material is essential for their better application in water treatment and biotechnology. The short-term thermal stability of the prepared membranes was investigated by means of TGA and the diagrams obtained for PVDF-0, PVDF-2 and PVDF-4 are plotted in Figure 2. Thermal stability parameters, including initial decomposition temperature (IDT) and thermal degradation temperature at 5% weight loss (Td), as determined from TGA thermograms, are summarized in Table 2.

The IDT values of all the prepared PVDF–SiO2 membranes were higher than 180 °C and their Td values were in the range of 220–250 °C, which suggested that these membranes can endure relatively high temperature. Furthermore, an increase of SiO2 content in the membrane phase resulted in increased IDT and Td values correspondingly, as shown in Figure 2. It is evident that the IDT value of membrane PVDF-4 was higher than that of membrane PVDF-2, and the IDT of membrane PVDF-2 was higher than that of membrane PVDF-0. This result confirmed the fact that the thermal stability of the hybrid material increases with the inorganic silica content (Han et al. 2010; Tripathi & Shahi 2011). In addition, as discussed above, the presence of SiO2 in the membrane matrix would strengthen the inorganic silica network of the hybrid membranes and thus allowed a corresponding enhancement in their thermal stability.

Tensile properties studies

The specific values for all the prepared membranes are presented in Figure 3, including TS and Eb.

Both of the values, especially TS, were improved. TS values increased as the silica weight ratio in the membrane-forming materials increased. It should be noted that the value of membrane PVDF-4 (27.95N) was little higher than that of membrane PVDF-3 (27.63N) as shown in Figure 3, which suggested that the TS values increased slowly when the silica content was beyond 1.5%. Also, it can be seen that the Eb values increased with increasing SiO2 nanoparticles content when silica concentration in the membrane-forming materials was lower than 1.5%. For example, the values of membrane PVDF-3 were higher than those of membrane PVDF-2. And the values of membrane PVDF-4 were lower than those of membrane PVDF-3. It can be concluded that the TS and Eb values were decreased when the content of silica was beyond 1.5%. These results indicated that the presence of SiO2 in the membrane matrix strengthens the inorganic silica network of the membranes, thereby leading to a corresponding enhancement in their mechanical properties. However, at high loadings the poor dispersion of SiO2 resulting in formation of aggregates may be responsible for the decrement in mechanical properties (Li et al. 2009; Yu et al. 2009).

Incorporation of an appropriate amount of SiO2 nanoparticles into membrane-forming materials can improve the membrane tensile properties, but excessive amounts of inorganic particles added would cause the membrane elasticity to decline, and thus lead to a decreased membrane break.
elongation ratio (Shi et al. 2012). Additionally, the study of TGA and tensile properties revealed that the hybrid membranes with high mechanical strength and flexibility can be obtained if experimental conditions are carefully controlled.

**Membrane conductivity studies**

Conductivity is the key property of ion-exchange membrane performance used for electrodialysis. It is well reported in the literature that the effect factors on the conductivity may be types of ion-exchange group and their concentrations, types of counter ions and the concentration of the solution (Gnusin et al. 2004; Nagarale et al. 2004).

Conductivity of the PVDF–SiO₂ anion-exchange membrane in our present work was investigated and the specific membrane conductivity is shown in Figure 4. As can be seen from Figure 4, variation of values for these membranes indicated that the membrane conductivity increased with an increase in silica content, for example, the PVDF membrane with silica added was higher in conductivity than the membrane PVDF-0, and this behavior corresponded to an increase in the concentration of quaternary ammonium groups. It was inferred from these results that: (i) the strength of the static electric interaction between the anion and the positively charged fixed groups was increased with increasing silica content, resulting in increased membrane conductivity; and (ii) after the addition of silica and heat treatment, the membrane possessed favorable water uptake and membrane structure and thus increased the conductivity.

In addition, it is clear that the specific conductivity of these membranes increased with increasing NaCl concentration. This is attributed to the increased concentration, which led to increased Donna adsorption salt concentration and decreased the interaction between fixed ions and counterions.

**CONCLUSION**

Anion-exchange PVDF–SiO₂ hybrid membranes were prepared. The characterizations showed that the PVDF–SiO₂ anion-exchange membranes presented relatively high thermal stability. Appropriate addition of SiO₂ nanoparticles into membrane-forming materials can improve the PVDF-based membrane mechanical properties. Membrane transport properties such as IEC, water uptake and conductivity increased with the increasing inorganic content. The hydrophilic polymer/inorganic PVDF–SiO₂ anion-exchange membranes can be potentially used for alkaline membrane fuel cells and ion-exchange membranes for electrodialysis.

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Properties of anion-exchange PVDF–SiO2 membranes

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