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Journal of Membrane Science 307 (2008) 28–36

journal of
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# Free-standing anion-exchange PEO–$SiO_2$ hybrid membranes

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Received 4 May 2007; received in revised form 24 July 2007; accepted 29 July 2007
Available online 3 August 2007

## Abstract

Free-standing anion-exchange polyethylene oxide (PEO)–$SiO_2$ hybrid membranes with higher flexibility and good mechanical strength (tensile strength (TS) as high as 20.55 MPa) as well as high temperature tolerance (thermal degradation temperature in air, $T_d$, in the range of 220–240 °C) were prepared through sol–gel reaction of different precursors: charged alkoxysilane-functionalized PEO-1000 (PEO-$[Si(OCH_3)_3]_2(+)$), *N*-triethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium iodine (A-1100(+)), monophenyltriethoxysilane (EPh) and in some cases also tetraethoxysilane (TEOS). Properties of the hybrid membranes, such as the thermal stability, tensile properties, hydrophilicity, and electrical performances, can be controlled by changing the feed ratio of the different sol–gel precursors. The results showed that some of the membranes have relatively good conductivity (~0.003 S/cm) and so may find potential applications in alkaline membrane fuel cells.
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*Keywords:* Organic–inorganic hybrid membranes; Anion-exchange membranes; Sol–gel; Polyethylene oxide (PEO); Alkaline membrane fuel cell

## 1. Introduction

Ion-exchange membranes are now widely used for membrane electrolysis, solid polymer electrolytes, and fuel cell storage batteries as well as electrochemical separation, which include diffusion dialysis, electrodialysis, electro-deionization, etc. [1–4]. For these processes, it is vital to develop suitable ion-exchange materials. At present, commercial ion-exchange membranes are mostly organic ones due to the high diversification of organic polymer materials. One of the main drawbacks of organic polymeric ion-exchangers is their inherent limitation as in mechanical and thermal stability. So improvement and modification of the commercial ion-exchangers has been continuously a hot topic [5]. The study of hybrid organic–inorganic materials, as a recent but very fruitful and prolific enterprise, may provide a new and promising ideology for such improvement. Developed since 1980s, the hybrid materials have attracted much attention because of their great potential in combining the best properties of both organic and inorganic materials [6–8]. Up to now, the cation-exchange organic–inorganic hybrid materials have been frequently reported, in the hope of replacing the expensive perfluorocarbon cation-exchange materials such as Nafion [9–13]. For example, the polyethylene oxide (PEO)–$SiO_2$ composites, which had good flexibility and relatively high thermal stability, were developed as proton-conducting membranes after integrated with acidic moieties [13–16]. As for the anion-exchange hybrid materials, much less work has been conducted [4]. Besides, most of the anion-exchange hybrid materials reported to be successfully prepared, were rigid and brittle. Accordingly, when they were used for membrane applications, inorganic supports or substrates, were often used [17–19].

In our laboratory, supported anion-exchange hybrid membranes were also prepared [20–22]. For example, in our previous work [21], alkoxysillyl functionalized polyethylene oxide (PEO)-400 was prepared and subsequently conducted the sol–gel process. Since flexible PEO was utilized as the starting organic component, the flexibility of the hybrids was improved. However, the strength was limited and so inorganic support also had to be used. The supported anion-exchange hybrid membranes developed in our laboratory are mainly used for pressure-driven separation processes such as microfiltration, ultrafiltration and nanofiltration. In other fields, such as

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doi:10.1016/j.memsci.2007.07.043

membrane electrolysis, solid polymer electrolytes, and electrochemical separation, it is more suitable to prepare free-standing membranes with higher flexibility and mechanical strength as well as high temperature tolerance [1,5]. For instance, the possibility of the alkaline anion-exchange membrane fuel cell has been hotly discussed recently [3,23–25]. Merits of such fuel cell compared with proton exchange membrane fuel cell (PEMFC) include the restraint of methanol crossover, the enhancement of catalyst efficiency, the expanding of catalyst categories, easiness of water management, etc. [3]. For the development of such fuel cells, a key factor is the successful synthesis of anion exchange membranes with high conductivity and stability [3,23]. Up to now, the membranes utilized for such fuel cells are almost all of organic polymeric materials. Considering the excellences of organic–inorganic hybrid materials, the development of anion-exchange hybrid membranes for fuel cell usage will be highly desirable.

The present work is one of our series of efforts in synthesis of free-standing anion-exchange hybrid membranes for potential fuel cell applications. According to our previous research, the hybrid material prepared through sol–gel reaction of alkoxysilane-functionalized PEO possessed excellent flexibility [21], and only the strength was inadequate. So, in this work, monophenyltriethoxysilane (EPh), *N*-triethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium iodine (A-1100(+)) and in some cases also tetraethoxysilane (TEOS) will be utilized to undergo the sol–gel process together with functionalized PEO. EPh or TEOS is expected to increase the strength of the hybrids, and A-1100 (+), which is of low molecular weight and positively charged, is expected to adjust both the electrical and mechanical properties of the hybrid membranes. The influences of the feed ratio of different precursors on membrane properties, such as thermal stability, strength, hydrophilicity, and electrical performances, will be fully discussed.

## 2. Experimental

### 2.1. Materials

*N*-[3-(Trimethoxysilyl) propyl] ethylene diamine (A-1120) and 2,4-diisocyanate toluene (TDI) were purchased from Shanghai Chemical Reagent Co. and purified by distillation before use. Polyethylene oxide (PEO)-1000 and dimethyl formamide (DMF) were of analytical grade and fully dried before use (PEO, 100 °C at $2.666448 \times 10^2$ Pa (2 mmHg); DMF, dried with molecular sieve). Other reagents were of analytical grade and used as received. Deionized water was used.

### 2.2. Synthesis of charged alkoxysilane-functionalized PEO-1000 (PEO-[Si(OCH$_3$)$_3$]$_2$ (+))

PEO-[Si(OCH$_3$)$_3$]$_2$ (+) was prepared through quaternary amination of alkoxysilane-functionalized PEO-1000 with methyl iodide ($CH_3I$). Alkoxysilane-functionalized PEO-1000 was prepared through the reaction of PEO-1000 with TDI and A-1120 in sequence, as described similarly in our previous work [21]: in a $N_2$ atmosphere, a DMF solution of PEO-1000 was added dropwise into a DMF solution of TDI, and the mixture was stirred for additional 20 h at 30 °C. The resultant product was then extracted and put into the mixture of DMF and A-1120 within 12 h, stirred at 30 °C for additional 2 days. For the quaternary amination reaction, $CH_3I$ was slowly added and the mixture was stirred at 50 °C for 1 day. The excessive methyl iodide was recovered by distillation. During the above reactions, the molar ratio of PEO-1000:TDI:A-1120:$CH_3I$ was set to be 1:2:2:10 and the concentration of resultant PEO-[Si(OCH$_3$)$_3$]$_2$ (+) was 13.8 g/mL. The reaction flow chart is shown in Scheme 1.

### 2.3. Synthesis of A-1100(+)

Triethoxysilyl propyl amine (A-1100) was added dropwise into methyl iodide ($CH_3I$) with stirring at room temperature (A-1100:$CH_3I$ (molar ratio) = 1:6). Then the temperature was raised to 58 °C and the mixture was further stirred for 12 h. At the end of the reaction, the excessive methyl iodide was recovered by distillation.

### 2.4. Preparation of anion-exchange hybrid membranes

PEO-[Si(OCH$_3$)$_3$]$_2$(+), A-1100(+), monophenyltriethoxysilane (Ph-Si(OCH$_2$CH$_3$)$_3$, EPh) and in some cases also tetraethoxysilane (TEOS) were mixed, and then a certain amount of water ($H_2O$:Si (molar ratio) = 6:1) was added. The mixture was stirred at room temperature for 2 days and then maintained for aging for 8 h. The molar ratio of the Si in the different precursors was varied, as shown in Table 1 and thus eight sol–gel samples (A–H) were prepared. It should be noted that there exist two Si elements in one PEO-[Si(OCH$_3$)$_3$]$_2$(+) molecule, so the molarity of PEO-[Si(OCH$_3$)$_3$]$_2$(+) was only half that of Si, and for convenience, its equivalent concentration was used instead for the following discussions (Scheme 2).

Subsequently, the obtained sol–gel coating solution was cast onto Teflon plates, air-dried at room temperature for 2 days, then heated from 65 to 135 °C at the rate of 5 °C/h and kept at 135 °C for 2.5 h. The obtained membranes, signified

Table 1
Molar ratios of the different precursors for the preparation of the hybrid membranes A–H and A′–H′

| Membrane[a] | Si in PEO-[Si (OCH$_3$)$_3$]$_2$ (+) | A-1100(+) | Ph-Si(OCH$_2$ CH$_3$)$_3$ (EPh) | TEOS |
|---|---|---|---|---|
| A, A′ | 1 | 1 | 1 | 1 |
| B, B′ | 1 | 1 | 1 | – |
| C, C′ | 1 | 1 | 2 | – |
| D, D′ | 2 | 1 | 2 | – |
| E, E′ | 1 | 3 | 1 | – |
| F, F′ | 1 | 3 | 2 | – |
| G, G′ | 2 | 3 | 1 | – |
| H, H′ | 1 | 3 | 2 | 2 |

[a] The only difference between membranes A–H and membranes A′–H′ was that additional antifoaming organic silane was added for the preparation of the latter ones.

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