



ELSEVIER

Contents lists available at ScienceDirect

## Journal of Membrane Science

journal homepage: [www.elsevier.com/locate/memsci](http://www.elsevier.com/locate/memsci)

# Diffusion dialysis membranes with semi-interpenetrating network for alkali recovery

Rui Liu, Liang Wu\*, Jiefeng Pan, Chenxiao Jiang, Tongwen Xu\*

CAS Key Laboratory of Soft Matter Chemistry, Lab of Functional Membranes, School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, PR China

## ARTICLE INFO

### Article history:

Received 22 July 2013

Received in revised form

9 September 2013

Accepted 13 September 2013

Available online 27 September 2013

### Keywords:

Cation exchange membrane

Diffusion dialysis

Alkali recovery

Semi-interpenetrating network

## ABSTRACT

Cation exchange membranes based on semi-interpenetrating network (sIPN) are prepared for diffusion dialysis (DD) using poly(vinylidene difluoride) (PVDF) and sodium p-styrenesulfonate (SSS) as starting materials. Five membranes have been prepared by varying the content of PVDF and dosage of cross-linking agent. Ion exchange capacity (IEC), water uptake ( $W_R$ ), swelling resistance and mechanical property of the membranes have been measured. These membranes show excellent thermal and alkali stability due to the high-performance PVDF matrix and sIPN morphology. The membranes have been successfully applied to alkali recovery. The base dialysis coefficients ( $U_{OH}$ ) are in the range of 0.0008–0.0061 m/h and the separation factors ( $S$ ) in the range of 12.0–90.3 at 25–65 °C. Effect of PVDF content and cross-linking degree on ion permeability and selectivity has been discussed.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Alkali waste water, generated by paper, leather, printing and drying, tungsten ore smelting and man-made fiber industries [1], brings serious pollution to the environment. Direct discharge of the waste water will cause water contamination, kill animals and plants, and threaten human health [1].

To date, several methods are available to treat the alkali waste water, including neutralization with acids, concentration and burning (in paper industries) and membrane-related technology [1]. Among these methods, diffusion dialysis (DD) is the most potential one as it is low-cost and environment-friendly. DD is a spontaneous separation process based on ion diffusion from high concentration to low concentration. No additives and external driving force are needed therein. DD has been widely used in recoveries of inorganic acids including sulfuric acid ( $H_2SO_4$ ) [2], hydrochloric acid (HCl) [3] and nitric acid ( $HNO_3$ ) [4] and some organic acids [5,6], etc. However, its application in alkali recovery is far away from expectation, due to the lack of high-performance cation exchange membranes. In addition to high base permeability and selectivity, alkali resistance and thermal stability are also important properties required for membranes used in practical DD process [7]. Therefore, developing membranes with good stability and alkali resistance is the key of application of DD in alkali recovery.

One solution is to choose a material with high stability as membrane matrix. Poly(vinylidene difluoride) (PVDF) is widely used as membrane material for its excellent thermal and mechanical properties and good chemical resistance [8]. It has been used to prepare various functional membranes, such as hollow fiber membranes [9,10], ion exchange membranes [8,11] and ultrafiltration membranes [12,13]. However, hydrophobicity of PVDF membranes is a serious problem when applied to DD. For this reason, blending with hydrophilic polymers, e.g. poly(sodium p-styrenesulfonate) (PSSS), is commonly employed to improve the hydrophilicity. However, poor miscibility behavior of blending components usually results in serious loss of the hydrophilic component during DD process. Recent publications have shown that construction of semi-interpenetrating polymer network (sIPN) represents a cost-effective way to improve the compatibility between the blend polymers [14,15]. The sIPN is composed of a cross-linked polymer network and a linear polymer immobilized in the cross-linked network. Two polymer chains blended through sIPN technology show good compatibility and the blend materials usually present high mechanical property and good stability [16]. In this work, sIPN is prepared through in situ synthetic pathway. PVDF polymer chains are immobilized homogeneously in the PSSS network. The preparation procedure is illustrated in Fig. 1.

Membranes prepared this way are expected to present good performance, including (1) Excellent thermal and alkali stability benefited from PVDF matrix and sIPN morphology; (2) good hydrophilicity inherited from hydrophilic PSSS network; (3) relatively good swelling resistance at high temperature. The sIPN morphology is favorable to membrane dimensional stability [16].

\* Corresponding authors. Tel.: +86 551 360 1587; fax: +86 551 360 1592.

E-mail addresses: [liangwu8@ustc.edu.cn](mailto:liangwu8@ustc.edu.cn) (L. Wu), [twxu@ustc.edu.cn](mailto:twxu@ustc.edu.cn) (T. Xu).

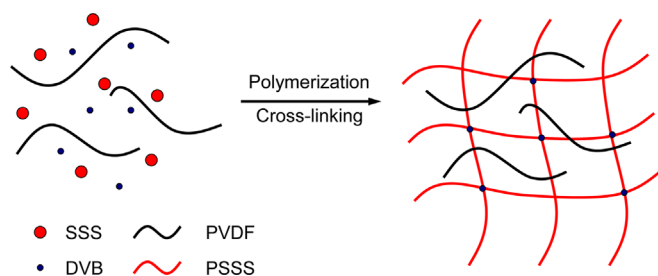


Fig. 1. Forming procedure of semi-interpenetrating network (sIPN).

Hydrophobic PVDF chains in this structure also contribute to enhancing the membrane swelling resistance at high temperature.

In this work, membranes with different component ratios and cross-linking degree have been prepared. Ion exchange capacity, water uptake, thermal stability, mechanical property and alkali stability of the membranes are characterized. Their application performance in DD process for alkali recovery is also tested. Effect of component ratio and cross-linking degree on properties and performance of membranes is discussed in detail.

## 2. Experimental

### 2.1. Materials

Poly(vinylidene difluoride) (PVDF) was purchased from Inner Mongolia 3F-Wanhao Fluorine Chemical, Co., Ltd. Divinylbenzene (DVB) was purchased from J&K Scientific Ltd. N,N-dimethylformamide (DMF) and azobisisobutyronitrile (AIBN) were supplied by Sinopharm Chemical Reagent Co., Ltd. AIBN was purified by recrystallization. Sodium p-styrenesulfonate (SSS) was purchased from XZL Bio-Technology Co., Ltd.

### 2.2. Preparation of the membranes

PVDF and SSS were dissolved in 60 mL DMF and the solution was stirred at 60 °C for 2 h to ensure the two components were completely dissolved. After that, DVB and AIBN were added into the solution. Then the solution was stirred at 80 °C for 5 h, under the protection of nitrogen.

After reaction, the solution was poured onto a glass plate and dried at 60 °C for 10 h. Then the membrane was obtained and named PxSy-z ( $x$  stands for the weight of PVDF in grams,  $y$  for the weight of SSS in grams, and  $z$  for the volume of DVB in milliliters). Five membranes have been prepared by varying the dosage of reagents and their compositions are presented in Table 1.

Our preliminary test shows that, to obtain good membrane-forming property and ion-exchange performance, dosage of PVDF is in the range of 3–5 g, when dosage of SSS is 3 g. Dosage of DVB is no more than 0.5 mL to prevent the gel formation during the cross-linking process. Besides, the second and fourth sets of experiments are designed, in which the dosage of DVB, in proportion to dosage of PVDF, is decreased compared to other three sets, to investigate the effect of cross-linking degree on membrane properties.

### 2.3. Characterization of the membranes

#### 2.3.1. Ion exchange capacity (IEC), water uptake ( $W_R$ ) and swelling resistance in 65 °C hot water

Dry membrane samples were accurately weighed and then immersed in 1 mol/L HCl for 12 h to convert to  $H^+$  form. The samples were washed by distilled water. Then the samples were immersed in 1 mol/L NaCl for 8 h. The content of HCl produced by

Table 1  
Compositions of five membrane solutions.

Membrane	PVDF (g)	SSS (g)	AIBN (g)	DVB (mL)	DMF (mL)
P5S3-0.5	5	3	0.03	0.5	60
P4S3-0.4	4	3	0.03	0.4	60
P4S3-0.5	4	3	0.03	0.5	60
P3S3-0.3	3	3	0.03	0.3	60
P3S3-0.5	3	3	0.03	0.5	60

ion exchange was determined through titration with 0.03 mol/L NaOH.

Water uptake was measured by immersing the membrane samples in distilled water for 1 day at 25 °C. All the samples were dried and weighed before the test. After immersion, surfaces of the samples were wiped and the samples were then weighed.  $W_R$  was calculated as follows:

$$W_R = \frac{W_w - W_d}{W_d} \times 100\%$$

where  $W_d$  is the dry weight of the membranes and  $W_w$  is the wet weight of the membranes after immersion in distilled water at 25 °C.

Swelling resistance was evaluated by membrane water uptake at 65 °C. Dry membranes were weighed and then immersed in 65 °C hot water. The membranes were taken out at different times and their  $W_R$  values were recorded.

#### 2.3.2. Thermal stability and mechanical property

Thermal stability of the membranes was characterized by thermogravimetric analysis (TGA) using a TG-DTA analyzer (SDT Q600) under  $N_2$  flow, with a heating rate of 10 °C/min.

Tensile strength (TS) and elongation at break ( $E_b$ ) were measured by a dynamic mechanical thermal analyzer (DMA Q800) at room temperature.

#### 2.3.3. Alkali stability

Dry membrane samples were weighed and then immersed in 65 °C NaOH (2.0 mol/L) for 60 h, then the samples were washed to be neutral and their dry weights were measured. All the membrane samples were washed by distilled water to remove unreacted SSS before test. The ratio of remaining weight and original weight was recorded. IEC and  $W_R$  at 25 °C of these treated membranes were also measured to evaluate the alkali stability.

### 2.4. Diffusion dialysis (DD)

Diffusion dialysis (DD) test was carried out using a two-compartment cell at different temperatures. The membrane was fixed between the two compartments and the effective area was about 4.5 cm<sup>2</sup>. The permeate side of the cell was filled with 100 mL mixture solution of NaOH (1.0 mol/L) and  $Na_2WO_4$  (0.1 mol/L). The diffusate side was filled with 100 mL distilled water. All the membrane samples were conditioned in the feed solution for 1 h before test.

The test was allowed for 1 h. Then the concentrations of NaOH in both sides were measured by titration with HCl, and the concentration of  $Na_2WO_4$  in diffusate side was determined by thiocyanate spectrophotometric method.

The separation factor ( $S$ ) with respect to one species over another is defined as the ratio of dialysis coefficients ( $U$ ) of the two species.  $U$  was calculated by the following formula:

$$U = \frac{M}{At\Delta C} \quad (1)$$

Download English Version:

<https://daneshyari.com/en/article/7022313>

Download Persian Version:

<https://daneshyari.com/article/7022313>

[Daneshyari.com](https://daneshyari.com)