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Development of heterogeneous cation exchange membranes using functional polymer powders for desalination applications

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ABSTRACT

Heterogeneous cation exchange membranes for potential electrodialysis (ED) seawater desalination were fabricated using poly (vinyl chloride) (PVC) as binder and functional polymer powders (sPSt-co-DVB) as polyelectrolyte by a cost effective hot-press process. Physical and electrochemical properties of the prepared membranes were investigated to evaluate the suitability of this method for membrane formation in ED desalination applications. The results revealed that the concentration of resin particles in the membrane matrix affects the ion exchange capacity (IEC), water uptake and fixed ion concentration of the composite membrane, which in turn improves the electrochemical properties of the heterogeneous membrane. The prepared composite showed excellent performance in the desalination of NaCl solution by ED, which was remarkably better than the performance of commercial Qianqiu® heterogeneous membrane. These developed membranes by this technique can be used as decent applicants suitable for ED desalination.

1. Introduction

In addition to other water conservation and reuse strategies, desalination is a key separation strategy to supplement water supplies given the rising global demand for water. Electro-driven membrane separation techniques involving ion-exchange membranes (IEMs) are not only part of applied electrochemistry but also belong to the field of separation processes such as electrodialysis [1,2] and capacitive-deionization [3,4]. Electrodialysis (ED) has been employed to produce pure water from brackish water for over 50 years [5,6], because ED can be easily scaled-up and combined with other processes [7–9]. The advantages such as its low-operating cost (especially for small to medium size plants), high water recovery rates, mild operation (temperature not higher than 50 °C) and less membrane fouling (due to reversed process), allow ED with great application potential. Additionally, the final salinity of the dilute can be adjusted as required [10].

Ion exchange membrane (either anion exchange membrane or cation exchange membrane) is undoubtedly critical for the successful application of ED desalination [11]. From the viewpoints of structure, ion exchange membranes can be classified into two mainly kinds: homogeneous membranes and heterogeneous membrane. The main difference is that the functional groups have been chemically bonded with the membrane polymer chains in homogenous membranes but it is not in heterogeneous membrane. Though a homogenous membrane has good electro-chemical properties but in general it is poor in mechanical strengths and highly costive. For industrial ED applications, heterogeneous membranes were also widespread used because such membranes have some beneficial characteristics such as possessing good ionic conductivity, good mechanical strengths and good dimensional stability under different ionic forms and also it is less costive and easily sealed in the module. The ionic conductivity of heterogeneous membranes depends (i) on the concentration of ion-exchange particles in the membrane, (ii) on the bulk morphology of the membrane and (iii) on the surface morphology (“skin”) of the membrane [12]. The concentration of resin particles in the membrane matrix affects the ion exchange capacity (IEC), water uptake and fixed ion concentration of the composite membrane, which in turn influences the electrochemical properties of the heterogeneous membrane. Therefore, adjusting the resin concentration is an important factor for producing good membrane.

For preparing a heterogeneous membrane, the routes mainly concerns with (i) milling the ion exchange resin into fine powders, dispersing the resin powders with polymer solution and forming the membrane by evaporating the solvents; or (ii) dispersing

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Nomenclature

ED	electrodialysis
IEC	ion exchange capacity (mequiv/g)
W_R	water content
FIC	fixed ion concentration
V	applied potential (V)
PVC	poly(vinyl chloride)
St	Styrene
DVB	divinylbenzene
E_m	membrane potential
E_0	theoretical potential between two KCl solutions
W_w	mass of hydrated membrane (g)
W_d	mass of dehydrated membrane (g)
R_{sol}	electrolyte resistance ($\Omega\,cm^2$)
R_{cell}	resistance of membrane equilibrated in electrolyte solution ($\Omega\,cm^2$)
R_{mem}	membrane resistance ($\Omega\,cm^2$)
A	effective area of the membranes (cm^2)
F	Faraday constant (C/mol)
t_+	transport number of counter-ion in the membrane
t_0	transport number of counter-ion in free solution
D	diffusional coefficient
L	slope of conductivity (μs)–time (min) curves
CE	current efficiency (%)
Δn	mole difference (mole)
P	power consumption (kW/h/kg)
Z_i	valence of ith ion
I	current intensity
K	instrumental constant
D	diffusion coefficient (cm^2/s)
δ	diffusion boundary layer thickness (cm)
R_m	area resistance ($\Omega\,cm^2$)
P_s	permselectivity
DC	dilute chamber
CC	concentrate chamber

the resin powders with polymer binder and then pressing at high temperature; or (iii) dispersing the resin powders with monomer and then conducting polymerization [13–15]. In these routes, the ion exchange resin made from styrene-divinylbenzene copolymer is commonly utilized as functional materials. The first milling step is very hard because the resins have strong crosslinking structure, and also, such process often cause much dust and is harmful to workers. Thus the conventional route through incorporating resin powder will give rise to both complexity and high membrane cost in the manufacturing.

Therefore, in this study, we attempt to develop heterogeneous membrane using resin powder instead of milling ion exchange resin. Such route was exemplified with heterogeneous cation exchange membrane. A commercialized sulfonated styrene-divinylbenzene copolymer (sPSt-co-DVB) polyelectrolyte, which was obtained by suspension polymerization, was used as functional group agent and poly(vinyl chloride) (PVC), which is a polar, flexible and durable polymer with good mechanical strength and chemical resistance, was used as binder. By taking advantage of the above mentioned properties of PVC and the commercialized polyelectrolyte, a heterogeneous cation exchange membrane was prepared by blending and hot-pressing for ED water desalination. The properties of the membranes such as water content, ion exchange capacity (IEC), membrane area resistance, transport number, diffusion coefficient etc., were fully investigated and discussed with the loading of powder resin. The optimized membrane was tested in ED for desalination from water. The desalination rate, current efficiency and energy consumption were calculated and compared with commercialized heterogeneous membrane. These performances of an IEM mainly depend on the applied current density, temperature, circulating flow rate, salt concentration and operating time [16,17]. However, at a constant applied current density, temperature, flow rate and salt concentration, the performances of an IEM mainly depend on operating time.

2. Experimental

2.1. Materials

Cation exchange resin (sulfonated styrene-divinylbenzene copolymer powder (sPSt-co-DVB, H^+ form, IEC = 2.44 mmol/g) was obtained from Zhengjiang Jiulong Chemical Reagents Co., Ltd. (China). Polyvinyl chloride (PVC) was purchased from Shanghai Chlor-Alkali Chemical Co., Ltd. (China). Dioctyl phthalate (DOP) is analytical reagent and bought from Sinopharm Chemical Reagent Co., Ltd., China. Inorganic salt stabilizer is of industrial grade and kindly supplied by Anhui unilever paper-plastic packaging Co., Ltd., China. Chloroform, NaCl and Na_2SO_4 are of analytical grade and bought from domestic chemical reagents company and were used without further purification. Deionized (DI) water was used throughout the experiment. The commercial heterogeneous cation exchange membrane was kindly provided by Qianqiu Membrane Technology Development Co. Ltd. (Zhejiang, China). Its main properties are: thickness, 0.4 mm, ion exchange capacity, 2.0 meq/g, area resistance, 10.0 $\Omega\,cm^2$, water content, 50% and transport number, 0.92.

2.2. Membrane preparation

0.5 g of the binder polymer PVC, 0.25 g of plasticizer DOP and 5 mg lead salt stabilizer was dissolved in 3 ml chloroform in a glass vial equipped with a magnetic stirrer. This was followed by dispersing a specific quantity of grinded resin particle as functional group agent in polymeric solution. The mixture was then stirred for 24 h at room temperature. Then the resultant solution was cast onto a clean glass plate and dried at 60 °C for 24 h. The dry membrane was then peeled off from the glass plate and hot-pressed (2 MPa) at 160 °C for 3 min on a clean polyethylene terephthalate plate. This procedure is depicted in Fig. 1. Membranes with different IEC values were fabricated by adjusting the grinded resin particle composition of the casting solution (as listed in Table 1).

2.3. Membrane characterization

2.3.1. Ion exchange capacity (IEC), water content (W_R) and fixed ion concentration (FIC)

IEC of the prepared membranes were measured by the classical titration method. In order to measure the ion exchange capacity,

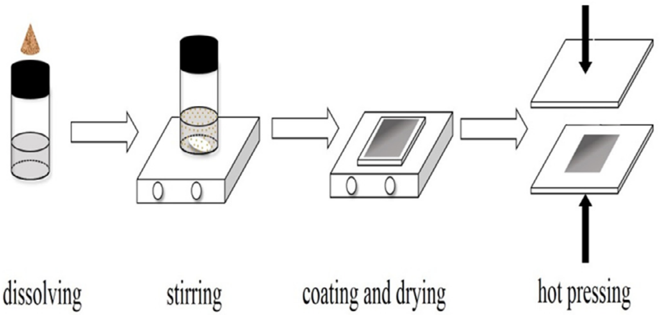

Fig. 1. Preparation process of heterogeneous membranes.

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