



Fouling resistant nanocomposite cation exchange membrane with enhanced power generation for reverse electro dialysis

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ABSTRACT

Renewable energy can be generated from the mixing of seawater with river water by reverse electro dialysis (RED). As part of the RED system, ion exchange membranes (IEMs) are key factors to the success of future RED energy generation. This research presents the synthesis and characterization of a new kind of nanocomposite cation exchange membrane (CEM) by using oxidized multi-walled carbon nanotubes (O-MWCNTs) blended with sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (SPPO). The nanocomposite CEM showed simultaneous improvement of membrane anti-fouling performance and energy generation performance in RED systems. The physicochemical and electrochemical properties of nanocomposite CEMs were enhanced compared to pristine SPPO CEMs. The results indicated that the optimal inorganic loadings were 0.3–0.5 wt%, which showed the best anti-fouling performance and highest power density in RED. The results show that O-MWCNTs are promising materials to improve properties of IEMs, and nanocomposite IEMs are competitive candidates for application in electrochemical systems like RED.

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1. Introduction

Salinity gradient power, the energy harvested from the mixing of two aqueous solutions with different salt concentrations, is thought to be a clean energy source that can fulfill the current global electricity demand [1–4]. The free energy that comes from mixing river water with seawater equals what could be released from a 280-m waterfall [1,3]. Different technologies have been developed for capturing salinity gradient energy, which includes pressure retarded osmosis (PRO) [5], reverse electro dialysis (RED) [6,7], electrochemical capacitive method [8] and a few less developed technologies [9–11]. Among those technologies, RED is dedicated to harvesting energy from the mixing of seawater and river water [7,12], and it has seen tremendous development in recent years. In the RED system, concentrated and diluted water flows are separated by ion exchange membranes (IEMs). Positively and negatively charged ion species transport from concentrated water to diluted water through cation exchange membranes (CEMs) and anion exchange membranes (AEMs), respectively. Using alternating series of CEMs and AEMs separated by spacers, continuous ion flux can be maintained inside the RED stack. The ion flux is then converted to electric current on the surface of electrodes via redox reactions; therefore, a closed circuit could be

formed and power generated.

Low energy efficiency, low power density, and membrane fouling problems are major issues that prevent the commercialization of RED. IEM has an important role to play regarding those issues. As key components, IEMs are required to have low ionic resistance and high permselectivity in RED systems [6,13]. Ionic resistance and permselectivity of IEMs characterize the tendency to resist ion flux transport, and the ability to transport counterions and exclude co-ions, respectively [13]. Despite the importance of IEMs, most previous studies on RED have focused on stack design and system optimization [14–18]. The lack of cost-effective IEMs with low ionic resistance and high permselectivity for high energy generation has become a major challenge towards implementation of the technology [14,19]. Also, IEM fouling has also prevented RED from large-scale applications [20,21]. It has been reported that without specific anti-fouling strategies, power density could decrease by as much as 60% in the first four hours of operation [22]. In a RED system, AEMs are more prone to organic fouling, whereas CEMs are significantly affected by inorganic fouling and scaling [20]. Fouling-resistant AEMs has been synthesized for different applications, mostly by increasing the hydrophilicity and/or negatively charge density of their membrane surface [23–25]. However, work that attempts to synthesize inorganic fouling-resistant CEMs is extremely scarce, which might be due to the lack of clear, easy, and effective anti-fouling strategies for CEMs. Research focusing on electro dialysis (ED) showed that scaling can become a severe problem especially in the

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presence of calcium and carbonate species [26,27]. Although some efforts have been made to develop RED-specific IEMs on a lab scale, for enhancing power generation and/or diminishing the influence of fouling [20,28–33], much more work needs to be done in order to lower the cost as well as further enhance the properties of IEMs.

Recently, many studies on membrane technology have focused on inorganic and organic nanocomposites [28,34–37]. Nanocomposite materials have become increasingly important due to their extraordinary properties, which arise from the synergism between the properties of both inorganic and organic components [36–38]. Carbon nanotubes (CNTs) are one type of inorganic nanomaterial that have gained a lot of attention due to their high flexibility, low mass density, large aspect ratio, excellent mechanical property, and good electronic conductivity [39–41]. In order for CNT properties to transfer to CNT-based composites, CNTs should be homogeneously dispersed in the composites [40]. Aggregation of CNTs has become a major obstacle in their application. Research has been conducted to achieve homogeneous dispersion of CNT nanocomposites, which is primarily accomplished through the functionalization of CNTs [39–42]. The functionalization of CNTs via covalent or noncovalent attachment of functional groups onto the surface of CNTs [42] can enhance the dispersion property and improve chemical affinity within the polymer matrices [39]. Covalent functionalization of CNTs can be accomplished by attaching carboxyl groups or hydroxyl groups onto the CNTs surface via oxidation reactions, which is commonly referred to as the oxidation of CNTs [41]. The presence of oxygen-containing groups (–COOH and/or –OH) has been reported to increase the solubility and dispersion property of CNTs in organic solvent [40,43] as well as increase the possibility for further functionalization depending on specific application [40]. For the use of CNTs as inorganic fillers in nanocomposite polymers, the incorporation of oxygen-containing functional groups is crucial for the enhancement of interfacial adhesion, by which the unique properties of CNTs can be transferred to the composites [40]. As one-dimensional nanomaterials, CNTs have a great advantage over the application of nanocomposite IEMs, compared to zero-dimensional nanomaterials (titanium oxide, iron oxide, silica oxide nanoparticles, etc.). It has been reported that ion pathways exist at the interface of nanomaterials and polymer; hence, long-distance ionic pathways could be formed when elongated nanomaterials (nanotubes or nanofibers) are used [44]. Long-distance ionic pathways largely improve membrane inner structure and facilitate ion transport. In addition, oxidized multi-walled CNTs (O-MWCNTs) were found to effectively improve the anti-fouling properties of pressure-driven membranes due to their ability to change membrane surface morphology, surface charge density and hydrophilicity [45,46].

In the present work, a new type of nanocomposite CEM for RED applications was prepared via a blending method, in which O-MWCNTs were dispersed in sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (SPPO) to form polymer nanocomposites. PPO is an attractive and proven candidate with good chemical and thermal stability as well as mechanical properties [28,47–49]. SPPO, which is produced by introducing sulfonic acid groups into the PPO polymer chains through sulfonation reactions, has been extensively used for synthesizing CEMs [28,48,50,51]. O-MWCNTs were chosen due to their enhanced dispersion property and better chemical compatibility with polymers compared to pristine CNTs. O-MWCNTs were also chosen for their potential to improve membrane ion transport property and anti-fouling performance. The authors initiated the first use of CNTs to make nanocomposite CEMs for simultaneously improving the anti-fouling performance and enhancing the power generation in RED system. The physicochemical and electrochemical properties of all the

nanocomposite CEMs with different O-MWCNT loadings were extensively characterized. The anti-fouling properties of CEMs were also investigated by using an original custom-designed testing process. The effect of O-MWCNT loadings was investigated in order to optimize the integrated membrane power generation performance in the RED system.

2. Materials and methods

2.1. Materials

PPO (Aldrich, analytical standard) was used as received for preparing SPPO. Chloroform (Aldrich, anhydrous, 99%) was used as solvent, and chlorosulfonic acid (Aldrich, 99%) was used as sulfonation agent. Dimethyl sulfoxide (DMSO) (VWR, ACS grade, 99.9%) was used as received. O-MWCNTs (purity > 95 wt%) with an outer diameter of 1020 nm, a length of 10–30 μm , and a carboxyl group content of 2.00 wt% were purchased from Cheap Tubes, and had been oxidized by the manufacturer. The O-MWCNTs were also used as received.

2.2. Preparation of cation exchange membranes

2.2.1. Sulfonation of PPO

The PPO was sulfonated by following the process described in a previous work [28]. 6 wt% of PPO was dissolved in chloroform while stirring vigorously for 30 min at room temperature. Chlorosulfonic acid solution was used as the sulfonation agent. 8 wt% of chlorosulfonic acid solution in chloroform was slowly added into PPO-chloroform solution. Then the precipitated SPPO was filtered and washed with DI water several times until the pH became approximately neutral. The SPPO obtained from the previous step was dissolved into methanol and stirred for one hour to form a homogeneous solution. The polymer solution was then poured into a Pyrex glass plate to form a thin layer with a thickness of no more than 2 mm. The thin layer was allowed to air-dry in a fume hood at room temperature for 48 h. The dried SPPO was then cut into small pieces and stored for future use.

2.2.2. Synthesis of CEMs

The CEMs were prepared by a blending method. Known amounts of O-MWCNTs (0–1.5 wt%, according to different loadings) were dispersed into 24 g of DMSO. The mixture was sonicated for 1 h in order to get a well-dispersed suspension. Six grams of SPPO were dissolved in the suspension and stirred for 48 h to obtain homogeneous blending. The membranes marked as 0.1 wt% O-MWCNT (or SPPO-0.1 O-MWCNT) indicate that the membranes were prepared by blending with an O-MWCNT content of 0.1 wt% with respect to SPPO. The resulting mixture was sonicated for 30 min in order to remove bubbles and then cast onto glass plates by using a doctor blade with desired thickness. In order to remove any residual solvent, membranes were dried in a vacuum oven at 60 °C for 36 h. The resulting membranes were peeled off the plates by soaking in warm water at 30 °C and then conditioned in 1 M of HCl solution for 24 h. Finally the membranes were rinsed with DI water and equilibrated in 0.5 M of NaCl solution for future characterization.

2.3. Membrane characterizations

2.3.1. FTIR, SEM, AFM, contact angle and surface charge density

A Fourier transform infrared (FTIR) spectrometer (Digilab FTS7000) was used to obtain the FTIR spectra of membrane materials. A resolution of 4 cm^{-1} and a spectra range of 4000–650 cm^{-1} was applied.

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