Evaluation of electrochemical properties and reverse electrodialysis performance for porous cation exchange membranes with sulfate-functionalized iron oxide

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ABSTRACT

Reverse electrodialysis (RED) is a process that can capture electrical energy from salinity gradients between seawater and river water through permselective ion exchange membranes. As ion exchange membranes are a key element in a RED system, enhancing their electrochemical characteristics is critical to maximizing system power performance. This study presents the preparation of porous nanocomposite cation exchange membranes via a two-step phase inversion technique. The phase inversion process controlled the structural variation (porosity) of the polymeric membranes in the presence of functionalized iron (III) oxide (Fe_2O_3–SO_4^{2-}), which subsequently led to significantly improved electrochemical performance. A porous nanocomposite membrane containing an optimal amount of Fe_2O_3–SO_4^{2-} (0.7 wt%) at a thickness of 30 μm performed best, as it had an area resistance of 0.82 Ω cm^2 and a permselectivity of 85.6%. Application of this membrane in a RED system achieved gross power density of up to 1.4 W m^{-2}, which exceeds the power density obtained with the commercially available CSO (Selemion^{TM}, Japan) membranes. Thus, effective design of ion exchange membranes through structure optimization increases the feasibility of salinity gradient power generation by RED.

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1. Introduction

The oceans are a largely untapped renewable energy resource that could provide clean and sustainable energy. Ocean energy technologies have boundless potential for harnessing waves, tides, and thermal and salinity gradients. In particular, salinity gradient energy (SGE) is a membrane-based technology that has gained increasing attention as a nonpolluting and sustainable energy source [1–4]. Mixing two water streams with different salt concentrations (e.g., sea and river water) generates SGE. According to published studies, the worldwide availability of SGE makes it the second largest marine-based energy source, with an estimated global power production potential of 2.4–2.6 TW [3,5,6]; this would cover 80% of the current global electricity demand [7].

There are two main techniques for extracting energy from a salinity gradient: pressure-retarded osmosis (PRO) and reverse electrodialysis (RED) [3,8]. PRO allows only water to diffuse through semipermeable membranes, which creates a pressurized stream that passes through a hydroelectric turbine to extract the electrical energy [9]. In contrast, RED is an electrochemical process that utilizes the ionic flux through selective ion exchange

membranes (IEMs) to produce electrical power. Post et al. showed that these two methods are suitable for different applications [9–12]; for higher power density and energy recovery, RED may be more applicable with the mixing of seawater and river water, whereas PRO can be preferable with more concentrated brines.

A typical RED stack consists of an alternating pattern of anion exchange membranes (AEMs) and cation exchange membranes (CEMs). In RED, a relatively concentrated salt solution and a dilute solution are fed to corresponding compartments and make contact with the AEM/CEM stack, which produces an electrochemical potential gradient. Such a chemical potential gradient between each water compartment (i.e., concentrated and dilute compartments) drives cations in the direction of a cathode and anions toward an anode. The electrodes convert the ionic species into an electric current via oxidation–reduction reactions (Fig. 1). The IEM is a major component in a RED system, and its importance is even more critical for a full-scale RED system with multiple membrane cell pairs. The large-scale energy conversion may become feasible only with the development of IEMs specifically tailored to RED.

Despite the important role of membranes in a RED system, research has focused primarily on the stack [11,13], solution compositions [14–16], and operating conditions [13,17,18] to maximize the power density and efficiency. Until now, investigations of RED stack performance mostly used electrodialysis (ED) membranes; however, different applications normally require specific

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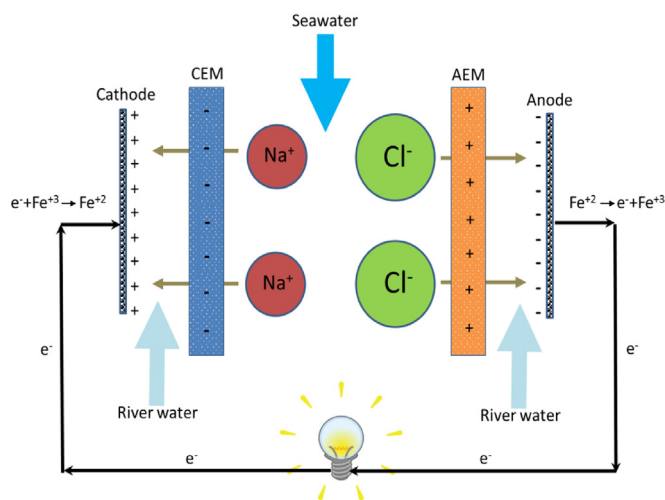E-mail address: yongsheng.chen@ce.gatech.edu (Y. Chen).

Fig. 1. Simplified schematic representation of a RED stack.

physical and electrochemical properties of the membranes. For the RED process, the key properties are ion exchange capacity (IEC), swelling degree (SD), fixed charge density (CD), membrane area resistance, and permselectivity. It is often challenging to optimize such properties because of their counteracting effects on performance characteristics [19]. Thus, it is worthwhile to study the membrane properties important for RED if overall performance optimization is the goal. Some effort has been made to investigate the applicability of various commercially available [20,21] and tailor-made membranes [22–24], but better optimized RED membranes are still greatly needed.

Ideal IEMs for optimum RED performance would have high fixed CD, high ion permselectivity, and low electrical resistance. The fixed CD is the amount of ion exchange functional groups attached to the membrane per volume of water, and it affects the transport of counter ions through the membranes. The ability to discriminate between ions of opposite charges is required to create chemical potentials and is closely related to the performance of IEMs. Organic–inorganic composite IEMs can adequately provide such properties for RED [25]. However, nanocomposite membranes have gained increasing attention for their remarkable synergized properties as they are expected to have enhanced IEC, conductivity, and permselectivity owing to their homogeneity up to certain level of filler loadings [26]. Although formation of nanocomposites has been well studied, they have not been applied to RED energy generation.

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a viable candidate for IEMs because it possesses excellent membrane-forming properties, good mechanical and chemical properties, high thermal stability, and low moisture uptake at low cost [27–30]. To enhance the hydrophilicity and IEC of the PPO, a sulfonation reaction was carried out that functionalized the aromatic rings of the polymer chains with charged groups, typically from sulfonic acid. Mixing Nafion® with a variety of inorganic fillers, such as silica, titanium, zirconium phosphates, and ceria, has been widely used for creation of composite membranes, mostly for fuel cell applications [31–33]. Recently, sulfonated iron (III) oxides (designated as Fe_2O_3–SO_4^{2-} in the following and is not implying 1:1 M ratio of Fe_2O_3 to SO_4^{2-}) have received increasing attention as inorganic filler materials owing to their versatile characteristics. Sulfonated Fe_2O_3 is strongly hydrophilic and has large specific surface area owing to the SO_4^{2-} group on the Fe_2O_3 surface, which makes it easier to incorporate the compound into the polymer membrane matrix [34]. In our previous work, we used the solvent evaporation technique to prepare a series of new organic–inorganic composite IEMs using Fe_2O_3–SO_4^{2-} nanoparticles in the sPPO polymer matrix.

The resulting highly dense structured membranes had fine electrochemical characteristics [25]. Structural modification of a membrane often influences its ionic transport capability and electrochemical performance [35]. In this paper, we present pore-induced nanocomposite membranes using sulfonated PPO and iron oxide via two-step phase inversion. Highly viscous polymer solutions were used to tailor porous membrane structures of various thicknesses, inorganic nanoparticle loadings, and aging (evaporation) time. We focus on the range of inorganic nanoparticle loadings at 0–0.7 wt% based on the results of our previous work. The membranes containing 0.7 wt% Fe_2O_3–SO_4^{2-} was best performed in RED stack with enhanced electrochemical properties, but the membrane performance did not continue to improve as more filler loading was incorporated. This phenomenon was found to be the effect of particle aggregation, which disrupted the functional group of the polymer matrix. In addition, two evaporation times were selected to tailor the porosity, expectedly to observe the differences in the degree of pore formation at two distinct aging times, thus better comparison of different pore structures should be expected. The effect of such structural modifications of the nanocomposite membranes on ionic transport characteristics and electrochemical properties was investigated and its impact on RED power generation tested.

2. Experimental

2.1. Preparation of the material

PPO sulfonation was carried out, based on the procedure described elsewhere [25,36], in a chloroform solvent using chlorosulfonic acid as the sulfonating agent (Fig. 2). The fine Fe_2O_3 nanoparticle powder (Aldrich, < 50 nm) was sulfonated by concentrated sulfuric acid (98%). The required amount of Fe_2O_3 was placed in 0.25 M concentrated H_2SO_4 (98%) at room temperature for 24 h. The sulfonated Fe_2O_3 was then filtered at bottle-top filter unit using a diaphragm pump (2032, Welch) and dried at 80 °C in a vacuum oven for 1 h. The dried product was then calcined at 500 °C for 3 h and ground in an agate mortar to obtain a fine red powder.

2.2. Preparation of Fe_2O_3–SO_4^{2-}/sPPO nanocomposite membranes

Fe_2O_3–SO_4^{2-}/sPPO nanocomposite membranes were prepared using a two-step phase inversion method. First, 25 wt% sPPO polymer solutions were prepared using dimethylsulfoxide (DMSO) as the solvent. The sPPO polymer solution was then mixed with various amounts of Fe_2O_3–SO_4^{2-} (0–0.7 wt%) at 40 °C for 24 h. The solution was sonicated for 10 min to obtain an optimal dispersion of the particles before it was cast on glass substrates. The doctor blade method was used to obtain the desired thickness of the membrane (30–150 μm). The cast film was then dried in a vacuum oven at 80 °C with an aging time of either 10 or 40 min before precipitation in a 60–70 °C deionized (DI) water bath. After a few minutes, the film was peeled off the glass substrate. The obtained composite membrane was treated in warm water for 2 h to remove residual solvents and then immersed in 1 M HCl for 24 h. Finally, the membranes were rinsed with DI water and stored in 0.5 M NaCl solution. CEMs with different weight ratios of
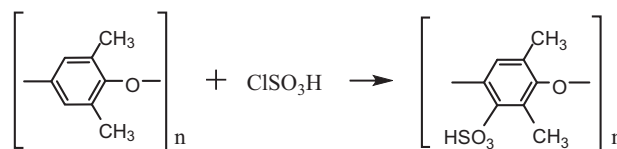

Fig. 2. Sulfonation of poly(2,6-dimethyl-1,4-phenylene oxide).