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# Effect of inorganic filler size on electrochemical performance of nanocomposite cation exchange membranes for salinity gradient power generation

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## ABSTRACT

Reverse electrodialysis (RED) is a technique that can capture electrical potential from mixing two water streams of different salt concentrations through permselective ion exchange membranes. Effective design of ion exchange membranes through structure optimization is critical to increase the feasibility of salinity gradient power production by RED. In this work, we present the preparation of organic–inorganic nanocomposite cation exchange membranes (CEMs) containing sulfonated polymer, poly (2,6-dimethyl-1,4-phenylene oxide), and sulfonated silica ( $\text{SiO}_2\text{-SO}_3\text{H}$ ). The effect of silica filler size at various loading concentrations on membrane structures, electrochemical properties, and the RED power performance is investigated. The membranes containing larger fillers (70 nm) at 0.5 wt%  $\text{SiO}_2\text{-SO}_3\text{H}$  exhibited a relatively favorable electrochemical characteristic for power performance: an area resistance of  $0.85 \Omega \text{ cm}^2$ , which is around 9.3% lower than the resistance of the membranes with smaller particle fillers (15 nm). The power performance of this nanocomposite CEM in a RED stack showed the highest gross power density of  $1.3 \text{ W m}^{-2}$ : 10% higher power output compared with the membranes containing small particle size and 21% higher than that of commercially available FKS membrane. The goal of the present work is to develop an effective design for tailor-made CEMs for RED applications. Thus, a further optimized combination of material properties and membrane structure appears to be a viable option for the development of nanocomposite ion exchange materials that could provide greater power production by RED.

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## 1. Introduction

Salinity gradient energy (SGE) is a membrane-based technology that has gained increasing attention as a potential renewable and nonpolluting sustainable energy source [1–4]. Salinity gradient power captures energy from mixing two water streams with different salinities (e.g., sea and river water). Thus, this energy source is available globally where river water flows into seawater (e.g., estuary). In theory, the chemical potential difference between seawater and river water is equivalent to the energy generated from 280 m high water fall when total discharge of all river water streams is considered, resulting in an estimated potential of 2.4–2.6 TW [2,3,5]. The use of salt as an energy source can also be an adequate treatment solution for excessive “left-over” salts that result from agricultural irrigation, desalination, and reverse osmosis (RO) practices [6]. One of the most promising techniques to harvest SGE is reverse electrodialysis (RED). In RED, the mixing of

two aqueous solutions with different salinities leads to a change in Gibbs free energy that can be liberated as electrical energy through ion transport in selective membranes [7].

A detailed principle of RED is well illustrated in many reported studies [7–12]. RED utilizes the transport of cations and anions in the water through ion selective membranes to produce electricity. In a RED stack, cation exchange membranes (CEMs) and anion exchange membranes (AEMs) are placed alternately in between electrodes (Fig. 1). The concentrated salt water and diluted fresh water are fed through narrow compartments, which are formed by spacers in between each membrane. Ionic diffusion in water allows the migration of ions that are selectively determined by corresponding ion exchange membranes (IEMs): the passage of cations through CEMs and anions through AEMs. This ion discrimination by IEMs results in an electrochemical potential difference and further drives cations toward the cathode and anions in the other direction toward the anode. At the electrodes, these ionic motion convert to electron current via redox reactions. Electrons travel from anode to cathode through an external electrical circuit and generate electrical current [13,14].

The role of IEMs is of considerable importance in maximizing the RED power performance. The performance of IEMs in

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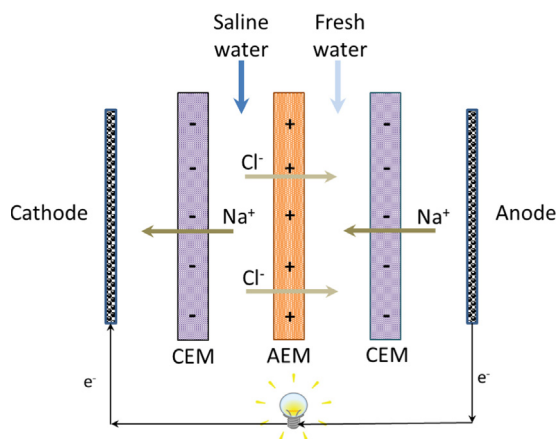


Fig. 1. Simplified schematic of a RED stack.

electrochemical processes is often determined by physicochemical (e.g., swelling degree (SD) and thickness) and electrochemical (e.g., ion exchange capacity (IEC), permselectivity, charge density (CD), and membrane area resistance) characteristics of the membrane. For RED, ideal IEMs should carry high permselectivity and low area resistance. However, the counteracting effects of such properties are often observed on their performance characteristics [15–18]. For example, the effort of increasing the functional groups within the polymer backbone by chemical modification to obtain a high degree of ion exchangeable capacity with low area resistance often results in a low mechanical stability, permselectivity, and highly swollen membrane structure [16,19,20]. On the other hand, permselectivity and mechanical stability may improve through cross-linking reactions, but these have the side effect of having high area resistance, which is not desirable in RED [17,21–23]. The concept of combining organic polymer and inorganic nanoparticles to form composite membranes have gained much interest in the development of IEMs owing to the ability to retain those desired properties from both components. The aim of incorporating inorganic filler materials in polymer-based materials is often to enhance mechanical, chemical, and thermal stabilities of polymer matrix. However, their synergy can also provide extra ion exchange functional groups to the membrane, which helps more ion migration, and thus allows improved conductivity as a single molecular composite [24,25]. Although formation of nanocomposites has been well studied, particularly for fuel cell and water purification applications [19,24,26,27], only a few studies have been reported in salinity gradient energy application, such as RED [25].

In fact, the structural properties of the membrane often influence its ionic mobility and electrochemical performance [28]. Organic–inorganic composite IEMs with controlled porosity exhibited significant improvement in IEC, water uptake, conductivity, and permselectivity, while maintaining adequate thermal and mechanical properties of the polymer matrix [29]. The presence of inorganic particle fillers increase the porosity and the pore size of the membrane [20,30], because a higher particle loading results in apparent particle agglomeration, creating larger pores and voids. Such pore formation in the membrane, with the help of additional functional groups (i.e., functionalized nanoparticles) and phase inversion provides more space with shorter ion channel, which will facilitate enhanced ion migration. Although large pores may weaken the selectivity of the membrane as they can disrupt the functional groups of the polymer matrix, the area resistance of the membrane can be decreased, which is often considered as more critically important in RED [16,30]. Considering the role of inorganic nanoparticles in forming such free pores when combined with a polymer matrix [31], it is crucial to

understand the effect of particle filler size on the membrane structure and performance in RED applications. The size of inorganic fillers may alter the condition of the membrane structure and pore formation, especially at the polymer–particle interfacial zone [32]. In our previous work, we have developed a series of new nanocomposite IEMs based on sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [25]. PPO carries high film-forming properties, good mechanical, thermal, and chemical stabilities, and low-moisture uptake [29,33–35]. For ion exchangeable inorganic materials, silica ( $\text{SiO}_2$ ) has been widely used for the synthesis of composite membranes, mostly for fuel cell and desalination applications [20,36,37]. Through suitable surface modification, such inorganic filler material also plays a role as a charge carrier in the composite membrane. The surface of  $\text{SiO}_2$  nanoparticle can be modified with  $-\text{SO}_3\text{H}$  group via a sulfonation reaction, which makes the material more hydrophilic and more functional in transporting ionic charges. The studies reported that its versatility due to wide porosities and functionalities allows improved conductivity, water uptake, and mechanical stability of the membranes [24,26]. In this study, we investigate the effect of inorganic particle filler size on the structure and electrochemical performance of silica nanocomposite CEMs for RED power generation. Structural properties of the membranes were tailored by varying nanoparticle loadings and inorganic particle size. The effect of such transformation of interfacial properties in the nanocomposites on physical and electrochemical properties was evaluated and further tested in a RED stack for power production.

## 2. Experimental

### 2.1. Materials

Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) (Aldrich, analytical standard), was used for the polymer membrane. The solvent for PPO was chloroform (Aldrich, anhydrous, 99%). Chlorosulfonic acid (Aldrich, 99%) and sulfuric acid (Aldrich, 98%) were used in sulfonation of the polymer material and the inorganic particle fillers, respectively. Dimethylsulfoxide (DMSO) (ACS grade, 99.9%) was obtained from VWR. Silicon dioxide ( $\text{SiO}_2$ , silica) nanopowder in two different sizes was used as the inorganic particle fillers: 15 nm  $\text{SiO}_2$  (US Research Nanomaterials, 99.5%) and 70 nm (US Research Nanomaterials, 98%). All materials were used as received.

### 2.2. Material preparation

First, the appropriate amount of PPO was added to the chloroform solvent and stirred vigorously to yield a 6 wt% solution at room temperature. Once dissolved, the PPO was sulfonated with an 8 wt% chlorosulfonic acid and chloroform solution. The chlorosulfonic acid–chloroform solution was added dropwise to the PPO–chloroform solution over a time period of 30 min with vigorous stirring. During this time, the sulfonated PPO (sPPO) was kept at room temperature as it started to precipitate out of solution. After the sPPO was fully precipitated, it was washed with deionized (DI) water numerous times until the pH was between 5 and 6. The sPPO was then dissolved in methanol over light heating (50 °C) for about an hour. The milky solution was poured into a Pyrex glass tray to form a thin film of about 1 mm thickness. This thin film was allowed to air-dry overnight at room temperature. After 24 h, the dry sPPO was washed with DI water, left to dry overnight, and then cut into small pieces.

The silica nanopowder was sulfonated with concentrated sulfuric acid (98%). The appropriate amount of  $\text{SiO}_2$  was dissolved in 0.25 M  $\text{H}_2\text{SO}_4$  solution and left soaking for 24 h. The sulfonated

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