



Electrochemical characterizations and reverse electrodialysis performance of hybrid anion exchange membranes for salinity gradient energy

Jin Gi Hong^{a,*}, Tae-Won Park^b

^a Department of Civil Engineering and Construction Engineering Management, California State University, Long Beach, CA 90840, United States

^b Department of Earth Science Education, Chonnam National University, Gwangju, South Korea



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ABSTRACT

Reverse electrodialysis (RED) is a technique that utilizes the salinity gradient through ion exchange membranes to generate electrical power. In order to make this technology feasible, innovation is required to improve a critical subcomponent, the ion exchange membrane, especially in the selection of appropriate membrane materials and the design of proper RED membranes. This study presents a novel and cost-competitive method for the design of anion exchange membranes (AEMs) by organic-organic hybridization. The low-cost and charge-possessing polymer, poly (diallyldimethylammonium chloride) and poly (vinyl alcohol) (abbreviated as PDDA and PVA, respectively) are blended in different mass ratios to form an AEM. The effect of various PDDA loadings on the electrochemical characterizations of the membranes was investigated. The key properties such as electrical resistance, permselectivity and ion exchange capacity were found to be improved with increasing the mass blend ratio of PDPA. Specifically, the increase of PDPA mass ratio significantly decreased the level of membrane resistance, which majorly contributed to the performance of RED power generation: reached the maximum power density of 0.58 W/m². Such fabrication method of AEMs may provide the feasible design strategy of potential ion exchange membranes for a viable RED energy conversion.

1. Introduction

Salinity gradient energy (SGE) or blue energy has gained considerable amount of attention as a zero emitting and nonpolluting energy technology. In theory, the worldwide availability of SGE estimates global power production of 2.4–2.6 TW if all river mouths are considered. The maximum energy that is theoretically extractable from the mixing of river water with seawater is about 0.75 kWh/m³ [1–5]. Today, two main membrane-based technologies stand out for SGE: pressure-retarded osmosis (PRO) and reverse electrodialysis (RED) [6,7]. Both techniques utilize two water streams of different salinity as their energy source to extract electricity. Each technique has its favorable salinity condition: PRO suits more for the mixing concentrated brines with diluted solutions and RED may be more applicable with the mixing of seawater and river water [3,8]. PRO is especially more competent at harvesting energy from larger salinity differences. Thus, many recent studies of PRO have focused on examining the performance using concentrated anthropogenic and engineered hypersaline solutions. In contrast, RED is not often adaptive to achieve appreciable power output from large concentration differences due to limited selectivity of current membranes used in RED. So, the recent efforts have

leaned toward more on membrane development to overcome such constraints [9]. The membranes used in PRO and RED are in different stages of development. Compared to current availability of reverse osmosis (RO) membranes used in PRO, the access to RED ion exchange membranes (IEM) is relatively limited due to the high cost of membranes. Currently, the costs of commercially available IEMs are ranging between \$100 and 200/m², which is 2–3 times higher than RO membranes used in PRO. Increasing accessibility and availability of IEMs at reduced costs are challenging but could become more feasible as global demand grows and simpler fabrication methods develop with cost-competitive materials [10,11].

In RED, a concentrated salt solution and dilute solution are continuously fed to the RED stack where the streams are separated by alternately installed cation- (CEM) and anion-exchange membranes (AEM) (Fig. 1). Ionic migration through corresponding IEMs results in a chemical potential difference and drives cations toward the cathode and anions in the other direction toward the anode. At the electrodes, these ionic species convert to electron current via oxidation-reduction reactions facilitated by the electrode rinse used in the system.

The successful application of RED in SGE technology mainly depends on membrane performance like many other membrane-based

* Corresponding author.

E-mail address: JinGi.Hong@csulb.edu (J.G. Hong).

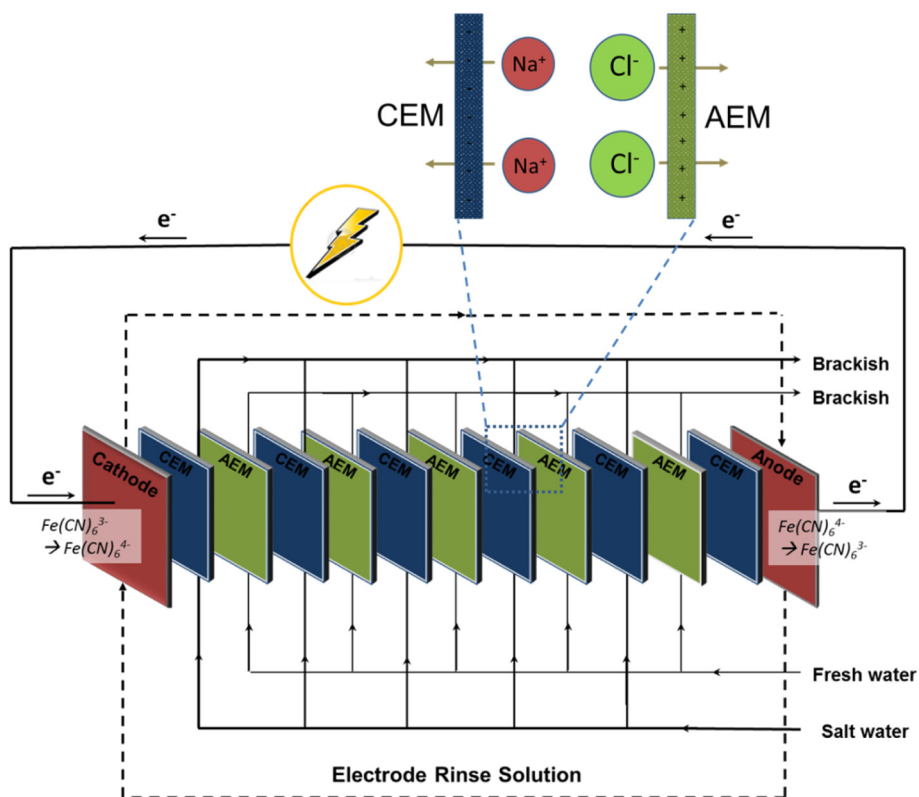


Fig. 1. A schematic view of an RED stack representing the fluid transport through the ion exchange membranes; CEM: cation exchange membrane, AEM: anion exchange membrane.

processes. However, currently available commercial IEMs are primarily designed for electrodialysis (ED) and fuel-cell applications. The performance of IEMs in electrochemical processes is often characterized by physico- and electrochemical properties of the membrane such as ion exchange capacity (IEC), permselectivity, fixed charge density, resistance, swelling degree, and thickness. Often, the relationship between these properties is complicated because of the interactive effects that each property can influence on its performance. Nonetheless, the main goal of RED is to produce electricity and thus the improvement in membrane conductivity (low resistance) is of critical importance, whereas in ED and fuel cell, the effective ion selection and high mechanical strength are also desired for their applications [12].

There have been some studies of CEM synthesis reported in recent years [13–15], but fewer studies have been reported for the design and preparation of AEMs for application in RED [16]. The conventional method of synthesizing AEMs is rather complicated compared to the preparation of CEMs since it normally requires more steps including chloromethylation and amination. Also, AEMs are often more susceptible to have higher swelling than that of CEMs, which weakens the ability to discriminate ions (i.e., lowering the permselectivity) and reduces the effective charge density in AEMs. Generally, chloromethyl methyl ether and bis-chloromethyl, known as carcinogens, are used as AEM precursors [17]. In recent years, several groups have proposed alternative AEM synthesis routes to avoid the use of such chloromethylating agents for applications in fuel cell [18–21]. Vinodh et al. used para-formaldehyde and concentrated hydrochloric acid to replace chloromethyl methyl ether [18]. Lin et al. synthesized AEMs using a solvent-free method which employed in-situ bulk polymerization. In this process, cardo polyetherketone (PEK-C) was dissolved by vinylbenzyl chloride (VBC) and divinylbenzene (DVB) monomers to form a uniform solution [20]. Maurya et al. also proposed a simple method of preparing AEM for flow battery application, which eliminated the step of potential chloromethylation by using polyvinyl chloride (PVC) and

4-vinylpyridine [21]. For applications in RED, Guler et al. has reported several studies on AEM synthesis [16,22,23]. In these studies, the structure of AEM is mainly comprised of polyepichlorohydrin (PECH) and polyacrylonitrile and functionalized by a tertiary diamine (1,4-diazabicyclo[2.2.2]octane). These PECH-based AEMs were further modified and improved the electrochemical performance by controlling the amount of diamine ratio and structural figures.

In this study, a new type of AEMs based on poly (diallyldimethylammonium chloride) (PDDA) and poly(vinyl alcohol) (PVA) is prepared and tested for the application in RED power generation. PDDA is a water soluble copolymer and possesses charged quaternary ammonium group in its cyclic structure (Fig. 2(a)). Thus, it is often used in biological, pharmaceutical related industries, as well as in waste water treatment process as a primary organic coagulant to destabilize negatively charged colloidal [24]. PVA, a polyhydroxy polymer, is commonly used in IEM applications because of its good membrane forming ability, high hydrophilic properties, good chemical resistance, and low cost [25–28] (Fig. 2(b)). Until now, many researches of PVA based membranes were the fabrication of CEMs and mostly applied in fuel cell operations [29,30]. The fabrication of PDDA/PVA based AEMs via simple blending technique provides cost-effective, safe and easy preparation route with attractive features that requires for the performance of RED. The aim of the present study is to investigate the effect of PDDA

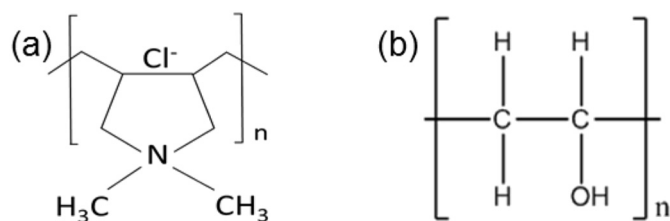


Fig. 2. Basic chemical structures of (a) PDPA and (b) PVA.

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