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Micro-structured membranes for electricity generation by reverse electrodialysis

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ABSTRACT

Reverse electrodialysis (RED) is a technology for extracting salinity gradient power by contacting waters with different salinity, i.e. seawater and river water, through ion exchange membranes. Conventionally, non-conductive spacers are used to separate these ion exchange membranes from each other in RED. The power output is hampered by these non-conductive elements which increase electrical resistance in the RED stack. To eliminate the use of these spacers, structured anion exchange membranes with a structure height of 100 μm were prepared by casting a polymer solution on stainless steel molds followed by solvent evaporation. These self-standing membranes with straight-ridge, wave and pillar structures as well as similarly prepared flat membranes were installed on the river water side in a RED stack (where electrical resistance is the highest). 38% higher gross power density and 20% higher net power density were achieved with the pillar-structured membranes when compared to that of flat membranes with spacers. Further optimization of the structure geometry in combination with the possibility to cast membranes of different chemistries offer a huge potential for further development of homogeneous membranes with the desired electrochemical and physical properties, which could provide high power densities in RED.

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1. Introduction

As the amount of fossil fuels is limited and their use has environmental consequences, the development of clean and sustainable forms of energy receives much attention. One of these promising new energy sources is salinity gradient power, which can be harvested from the mixing of two water streams with different salt concentrations (e.g. seawater and river water). The driving force for mixing is the change in the Gibbs free energy that can be converted into electricity via direct ion transport through ion-selective membranes [1]. When all river water streams are considered that discharge into the sea, the global potential of salinity gradient power is huge with an estimated potential power of 2.4–2.6 TW [2,3]. Therefore, the importance of technologies that can efficiently harvest salinity gradient energy is growing rapidly.

Several ways of generating energy from salinity gradients have been previously proposed, such as pressure-retarded osmosis (PRO) and reverse electrodialysis (RED) [4,5]. PRO uses an induced fluid flow that occurs when two solutions of different concentrations are placed in contact through a barrier (i.e. membrane) that is permeable to water only, but impermeable to ions [6]. On the other hand, RED uses an ion flow that is induced when seawater and fresh water are brought in contact through ion-selective membranes [6]. Recent studies have concluded that RED is more appropriate for use with seawater and river water, whereas PRO is more favorable for power generation from brines [4].

The principle of RED is well described in the literature [1,7–9]. A typical RED stack consists of a series of alternating anion exchange membranes and cation exchange membranes (Fig. 1). Spacers between the membranes separate the membranes, forming narrow compartments for water to flow through. Ions are then transported from the concentrated side (e.g. seawater) to the diluted side (e.g. fresh water), promoted by the salinity gradient. Since the membranes are selective for only specific types of ions (i.e. cation exchange membranes allow the passage of cations, and anion exchange membranes allow the passage of anions), cations migrate to one side and anions migrate to the other side, resulting in a potential difference. Electro-neutrality of the solutions in electrode compartments is maintained through redox reactions at the electrodes. Electrons are transferred from anode to cathode via an external electrical circuit, and this current can be used to power an external energy consumer.

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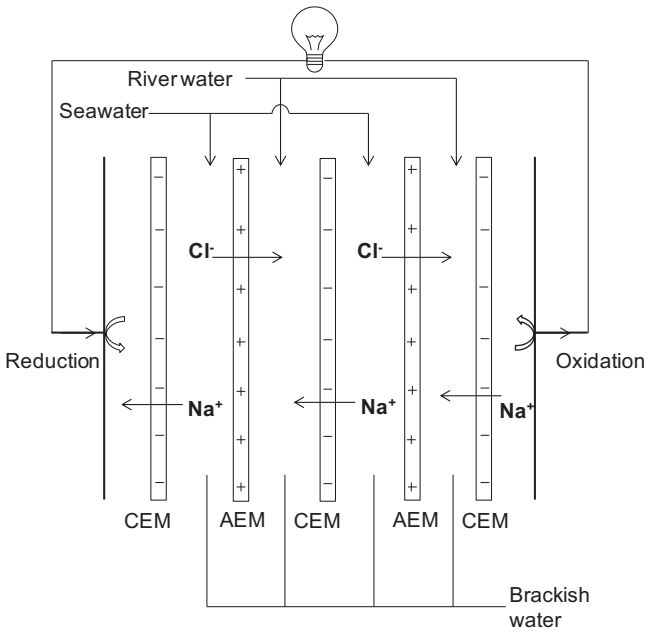

Fig. 1. Principle of reverse electrodialysis (RED).

It is vital to achieve a high net power density (i.e. gross power density minus required pumping power). To achieve such a high power density, the internal electrical resistance of the stack and the hydraulic friction losses inside the stack should be low. A low electrical resistance of the stack enables the desired ion transfer as it makes the stack more conductive, and low hydraulic friction minimizes the power consumed in pumping the feed waters through the stack [10]. In conventional RED and ED, non-conductive spacers are used to separate the membranes from each other to allow water flow between them. These spacers cover part of the conductive membrane area, resulting in a smaller membrane area available for ion transport and an increased electrical resistance, the so-called spacer shadow effect [11]. Moreover, spacers usually have woven or non-woven structures which are formed by knits (where the spacer filaments meet), causing tortuous flow resulting in additional hydraulic friction. In addition, this undesired flow enables fouling in the spacers, which is the most common problem in many membrane processes [12,13].

One possible remedy to reduce the stack resistance in RED is to use ion-conductive spacers instead of the conventional inert spacers. Długołecki et al. cut Neosepta CMX and Neosepta AMX membranes into spacer-shaped pieces, and used them as spacers, resulting in a power density increase by a factor of 3 relative to when using conventional non-conductive spacers [11]. However, hydraulic friction was not reduced as the spacer design of these hand-made spacers used was far from optimal. Another remedy is to use micro-structured membranes (also called profiled or corrugated membranes), which integrate the membrane and spacer functionality. Such membranes provide channels for feed water to flow through and at the same time keep the membranes apart in the stack. Because of their fully conductive character, electrical resistance in the stack is significantly reduced and the hydraulic friction remains low because of the open-channel geometry [10].

Although profiled membranes have been used in electrodialysis (ED) in several previous studies [14–16], the first successful application of such membranes in RED was achieved by Vermaas et al., who investigated heterogeneous membranes with straight ridges [10]. A high net power density, 10% higher than with conventional flat membranes, was obtained; a hot-pressing technique was used to prepare these profiled membranes [10]. Profiled membranes also significantly reduce hydraulic friction, not only in RED [10] but also in ED [15]. Thus, the use of such membranes has become a prerequisite for obtaining high performance in RED.

Micro-structured membranes can be produced by different techniques, such as calendering (roll-pressing) of a thermoplastic ion-exchange film between corrugated rollers at elevated temperature [17], hot pressing of a thermoplastic polymer containing suitable functional groups [10,17], and casting a solution of an ion-exchange polymer into a mold followed by evaporation of the solvent [18,19]. Hot pressing and calendering are usually advantageous for making membranes that are structured on both sides, but are only applicable for thermoplastics. Most problems in hot pressing (sometimes referred to as hot embossing) occur during the release of the membrane film from the mold, generally related to rupture or deformation of the microstructures [20,21]. Release problems can be reduced when the mold has slightly inclined sidewalls, or when anti-adhesive coatings are used that ease the release of the film from the mold. The dimensions of the mold play a role as well. Moreover, electrochemical properties usually are not always preserved during hot pressing; previous studies showed that electrical resistance increases and permselectivity may decrease when heterogeneous membranes are hot-pressed [10,22].

To overcome these drawbacks, we propose the use of membrane casting to prepare micro-structured homogeneous anion exchange membranes. This method provides more freedom for preparing a variety of homogeneously dense polymeric membranes with various structures. Casting of structured membranes can be performed using several techniques. One of these methods is “capillary force induced surface structuring” in which two layers of the membrane are created in contact with each other [19]. After casting and drying of the first layer, a second layer is cast on top of the first and a commercial spacer with the desired structures is placed on top of the second layer. After solvent evaporation and immersion in a water bath, the spacer is removed and a replica of the shape of the spacer has formed on the membrane. Another technique to cast structured membranes involves the use of molds with the desired structures and casting the polymer solution into the mold [23,24]. The phase separation of the solvent/polymer mixture can be performed either with liquid-induced phase separation (i.e. immersing the polymer solution in a nonsolvent bath and removing the solid membrane) or by simply evaporating the solvent followed by rinsing the solid polymer film [17,20]. In general, liquid-induced phase separation results in membranes with a certain porosity [24]. With solvent evaporation, dense membranes are created, as required in RED applications [25,26]. Since casting requires no force to form the microstructures, rupturing and deformation of these structures are less likely to happen. In addition, electrochemical and mechanical properties of the membranes can be tailored and preserved depending on the characteristics of the casting solution and reaction conditions. However, it is still a challenge to make membranes that are structured on both sides. The molds contacting both sides of the membranes make it difficult to evaporate the solvent.

A variety of geometrical structures can be created in this way as was shown previously for mostly non-ion exchange materials and other applications (e.g. ultrafiltration, gas separation and electrodialysis). Structures involving continuous ridges, e.g. straight lines or wave-shaped, allow water flow in channel-type ducts [15,17,24]. On the other hand, non-continuous structures can be created as pillar shapes with different geometries, such as circular, tear drop, kite (diamond) or star structures [23]. Depending on the number of structures per unit surface area and the dimensions of the structures on the membrane surface, pillar structures generally

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