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Multi-physical modelling of reverse electrodialysis

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G R A P H I C A L A B S T R A C T



ARTICLE INFO

Keywords: Reverse electrodialysis Multi-physical model Finite element method Power density Profiled membranes

ABSTRACT

Reverse electrodialysis (RED) is an electrochemical membrane process that directly converts the energy associated with the concentration difference between two salt solutions into electrical energy by means of a selective controlled mixing. The physics of RED involves the interaction of several phenomena of different nature and space-time scales. Therefore, mathematical modelling and numerical simulation tools are crucial for performance prediction. In this work, a multi-physical modelling approach for the simulation of RED units was developed. A periodic portion of a single cell pair was simulated in two dimensions. Fluid dynamics was simulated by the Navier-Stokes and continuity equations, and ion transfer by the Nernst–Planck approach along with the local electroneutrality condition. The Donnan exclusion theory was implemented in order to simulate interfacial phenomena. A sensitivity analysis of the process performance was carried out. Different membrane/channel geometrical configurations were investigated, including flat membranes, either with or without non-conductive spacers, and profiled membranes. The influence of feeds concentration/velocity was also evaluated. Results confirmed that, with respect to the ideal case of plane (empty) channels and planar membranes, non-conductive spacers always reduce the power produced, while profiled membranes may or may not perform better, depending on stack features and operating conditions.

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http://dx.doi.org/10.1016/j.desal.2017.09.006

Received 19 May 2017; Received in revised form 6 August 2017; Accepted 8 September 2017 0011-9164/ @ 2017 Elsevier B.V. All rights reserved.



1. Introduction

1.1. Principle of RED

Different technologies have been proposed in order to exploit the energy of salinity gradients [1–4]. Reverse electrodialysis (RED) was the first concept proposed [5] and appears to be the most promising, as it exhibits the highest power density [6] and can become competitive with the other renewable energy processes thanks to process optimization [7] and membrane cost abatement.

The basic repetitive unit of a RED stack (Fig. 1) comprises an anion exchange membrane (AEM), a concentrate compartment (CONC), a cation exchange membrane (CEM), and a dilute compartment (DIL). This repetitive unit is usually denoted as a *cell pair*, although some may prefer the term *cell*. Throughout this paper, the notation "cell pair" will be adopted.

Flat AEMs and CEMs are usually separated by net spacers, but the process performance may be enhanced by the use of self-supporting profiled membranes [8].

Due to the electrochemical equilibrium, an ion exchange membrane (IEM) immersed between two solutions at different concentrations is subject to a voltage difference (Donnan exclusion) [9], and the sum of all the membrane potentials of a stack is the open circuit voltage (OCV). Under closed circuit conditions, redox reactions arise due to the voltage difference at the electrodes, thus providing an electrical current to the load. At the same time, a selective ionic transport takes place within the stack from each concentrated channel to the adjacent dilute channels.

1.2. Critical aspects

The theoretical (maximum) electromotive force, or OCV, is proportional to the logarithm of the ratio between the ion activities in the two solutions. However, the use of highly concentrated solutions may imply a significant reduction of the IEMs ability to allow the passage of a single ionic species (permselectivity) [10,11]. The voltage over the external load can be expressed as OCV less the voltage loss due to the internal resistance of the stack, which takes into account different phenomena.

Ohmic losses (η_{Ω}) are mainly due to the resistance of the dilute

channel when low concentration solutions, e.g. river water, are used [12–14]. Stacks with net spacers made by non-conductive material may cause an increase of η_{Ω} by > 50% [10,12–15], while stacks with profiled membranes perform better [8,16]. Very recently, stacks equipped with chevron profiled membranes exhibited higher net power density values with respect to other stacks with net spacers or pillar profiled membranes [17].

The ion transport across IEMs causes a streamwise concentration variation in the bulk of the solution and a concentration variation perpendicular to the membranes within the diffusion boundary layers. These concentration non-uniformities give rise to further voltage drops, referred to as non-Ohmic losses ($\eta_{\Delta c}$ and η_{BL}) [18]. $\eta_{\Delta c}$ is determined by the ion mass balance within the channels. In stacks fed by river water - seawater solutions, under conditions of maximum net power density, $\eta_{\Delta c}$ is a relevant contribution to the total voltage loss [10,14,16].

Concentration polarization phenomena cause a change of the Donnan potential with consequent reduction of the actual voltage over the membrane [19]. With the standard river water – seawater solutions η_{BL} may be significant [13,14,16,20]; however, at the flow rates allowing the maximum net power density it is usually lower than the other contributions to the overall voltage drop when using spacers [10,14,16], although Vermaas et al. [16] found it to be larger than $\eta_{\Delta c}$ and only slightly lower than η_{Ω} when using profiled membranes (mixing not favoured). As the feeds concentrations increase, concentration variations are relatively lower and thus non-Ohmic effects decrease [10,21].

The pumping power consumption may considerably reduce the actual power. Net spacers may increase by several times hydraulic friction in the channel with respect to the ideal case of a spacer-less channel [8,21,22], while simple profiled membranes may be preferable [8,16,23]. Several experimental data showed pressure drop within the manifolds comparable or higher than those distributed in the channels [8,16,24–26]. However, pressure drop within the manifolds can be significantly reduced by adopting a suitable geometry [8,27].

1.3. State of the art of the small scale simulation

In several studies, e.g. Veerman et al. 2011 [28], RED stacks have been simulated taking no account of concentration polarization effects,

Fig. 1. Sketch of a reverse electrodialysis stack.



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