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Early detection of preferential channeling in reverse electrodialysis

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ABSTRACT

Membrane applications often experience fouling, which prevent uniform flow distribution through the feed water compartments, i.e. preferential channeling may occur. This research shows the effect of preferential channeling on energy generation from mixing salt water and fresh water using reverse electrodialysis (RED). The experimentally obtained power density, electrical resistance and pressure drop are evaluated for artificially controlled preferential channeling. The obtained power density decreases significantly when part of the feed water compartment is inaccessible for flow; a blockage of only 10% of the feed water compartments decreases the net power density by approximately 20%. When 80% of the feed water channels is inaccessible, the net power densities are only marginally positive. This decrease in power density is due to an increase in non-ohmic resistance, which is related to the concentration changes in the feed water compartments when ions are transported from the seawater to the river water side. Chronopotentiometric measurements show that the typical response time to establish a non-ohmic overpotential is an even more sensitive and easily scalable parameter to detect preferential channeling (and the presence of possible fouling) in an early stage. In practical applications, this response time can thus be used as an indicator for preferential channeling and serve to decide on and selectively apply cleaning in RED and other applications.

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1. Introduction

Renewable energy can be generated when waters with different salinity (e.g. river and seawater) mix. The theoretical potential of such a process is huge; considering the mixing of the global river discharge into the sea generates a decrease in Gibbs free energy in the order of 2 TW [1,2]. The theoretical potential of this renewable energy source is comparable to the current global electricity consumption [3].

Reverse electrodialysis (RED) is one of the technologies that can capture the available energy when waters with different salinity mix. See Fig. 1 for an illustration of the principle of RED. A RED module comprises ion exchange membranes selective for either cations (cation exchange membrane, CEM) or anions (anion exchange membrane, AEM). When waters with different salinity are supplied at either side of an ion exchange membrane, an electrical potential difference over the membrane (the Donnan potential) exists. When multiple cation and anion exchange membranes are stacked alternately, with fresh and salt water flowing in between, the voltage over these membranes accumulates.

Electrodes and a reversible redox reaction [4,5] or capacitive electrodes [6] can be used to transfer the ionic current into an electrical current.

The obtained power per installed membrane area, i.e. the gross power density, was recently increased to more than 2 W/m² [7]. Improvements in power density have been obtained by reducing the intermembrane distance (i.e. thin feed water compartments) and by removing the non-conductive spacers that serve to keep the membranes separated and provide a channel for the feed water flow [8]. The use of profiled membranes, with ion conductive ridges on their surface, integrating the membrane and spacer functionality, makes the use of (non-conductive) spacers obsolete. A stack with such profiled membranes has a reduced ohmic resistance compared to a stack with non-conductive spacers. Additionally, it has a lower power consumption to pump the feed waters, overall resulting in a higher net power density [9].

These improvements significantly increased the obtained net power density for a RED module at laboratory conditions. However, in practical cases when natural feed waters are used, fouling occurs [10]. In that case, membrane stacks are subject to a non-uniform flow due to colloidal, chemical (i.e. scaling) or biological fouling [11]. Although stacks with profiled membranes are less sensitive to fouling compared to stacks with spacers, fouling was also observed in stacks with profiled membranes [10]. Fouling accumulates at positions with a locally lower velocity (such as spacer

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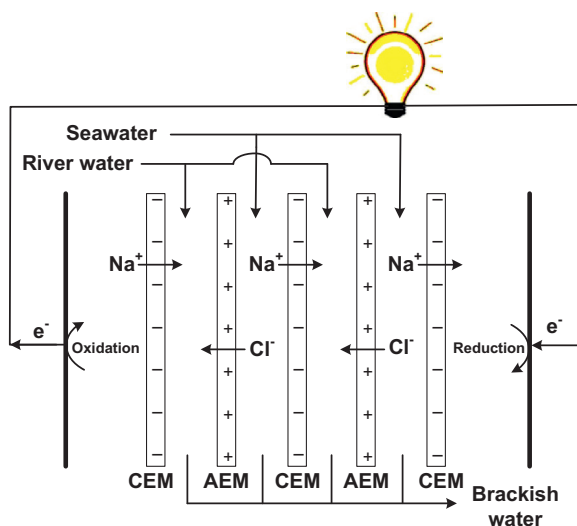E-mail address: d.c.nijmeijer@utwente.nl (K. Nijmeijer).

Fig. 1. Principle of reverse electrodialysis (RED), in this case with 2 cells, each comprised of an anion exchange membrane (AEM), a cation exchange membrane (CEM), seawater and river water. In this case, a (reversible) redox reaction is used to transfer the ionic current into an electrical current.

knits [10,12–15] or irregularities of the membrane surface) thereby locally blocking the flow and further decreasing the local velocity in these regions. Hence, the non-uniformity of the feed water distribution intensifies, such that in the end all feed water flows over a very limited membrane area only, which limits the membrane area that is available for ion transport. In other applications, this is known as preferential channeling [12,13].

As preferential channeling reduces the effective membrane area, the performance of the stack decreases (e.g. lower power density or higher pressure drop). Even at laboratory conditions without fouling, the uniformity of feed water flow has a significant effect on the obtained power density in RED [9,16]. Previous research showed that a uniform distribution of the feed water in a RED stack due to improved inflows for the feed waters increased the net power density by more than 50% compared to a system with less uniform feed water inflow [9,16]. The non-ohmic resistance, due to the diffusive boundary layer near the membrane surface (also referred to as concentration polarization [17]) is only significant for a non-uniform distribution of the feed water [16], as the diffusive boundary layers grow especially at zones with low velocity or even no flow (i.e. dead zones) [18]. The observed decrease in power density can thus indicate the occurrence of preferential channeling. However, the power density is influenced by many other fluctuating factors as well, such as the feed water salinities [19,20], concentrations of multivalent ions [21] and possibly organic foulants [10], which camouflages the effects of preferential channeling at an early stage. Nevertheless, it is desired to detect preferential channeling at an early stage and distinguish this phenomenon from other factors. In that way, effective cleaning can be scheduled and performed before the performance is significantly reduced.

We present a method for early detection of preferential channeling in reverse electrodialysis, justified by laboratory experiments. First, a theoretical framework is given to describe the non-ohmic resistance. Then, chronopotentiometric experiments on RED stacks with artificially induced preferential channeling are presented, indicating the effects of preferential channeling. This research reveals what is the most sensitive and scale-independent method for an early detection of preferential channeling. This approach can be used to prevent preferential channeling in practical applications.

2. Theory

2.1. Generated voltage

At open circuit, the voltage over a RED stack is given by the Nernst equation, adapted for the number of membranes and corrected for the apparent permselectivity of the membranes, α (-):

$$E_{OCV} = N_m \cdot \alpha \frac{R \cdot T}{z \cdot F} \ln \left(\frac{\gamma_s \cdot c_s}{\gamma_r \cdot c_r} \right) \tag{1}$$

In which E_{OCV} is the open circuit voltage (V), N_m is the number of membranes (-), R is the universal gas constant (8.314 J/(mol · K)), z is the valence of the ions (-), F is the Faraday constant (96485 C/mol), γ is the molar activity coefficient (-) and c is the salt concentration (M). The subscripts s and r indicate seawater and river water, respectively.

2.2. Resistance

When the electrical circuit is closed and the RED system can supply an electrical current, the voltage over the stack will decrease, caused by the electrical resistance of the stack. This stack resistance is composed of an ohmic resistance, due to the membrane resistance and the limited conductivity of the feed waters, and a non-ohmic resistance, which is due to the change in concentrations when an electrical current is produced. The electrical current implies ion transport from the seawater side to the river water side. This ion transport results in a decrease in salinity difference over the membrane and as such the generated voltage decreases, as can be deduced from eq. 1. The corresponding decrease in electromotive force is defined as $\eta_{non-ohmic}$ (in V), similar to a concentration overpotential in other applications [4,22]. The voltage over the stack, U (in V), can be described as:

$$U = E_{OCV} - \eta_{non-ohmic} - R_{ohmic} \cdot j \tag{2}$$

Or, when $\eta_{non-ohmic}$ is normalized with respect to j:

$$U = E_{OCV} - (R_{ohmic} + R_{non-ohmic}) \cdot j \tag{3}$$

In which R_{ohmic} is the ohmic area resistance and $R_{non-ohmic}$ is the non-ohmic area resistance (both in $\Omega \cdot m^2$) and j is the current density (A/m²).

The ohmic and non-ohmic resistances can be distinguished in several ways, e.g. using impedance spectroscopy [23,24], comparing AC- and DC-resistances [25] or using chronopotentiometry [1,7,9], which is used in the present research. The ohmic and non-ohmic resistances can be identified separately when a sudden change in electrical current is induced; the ohmic resistance causes a prompt change in stack voltage, while the response of the non-ohmic resistance is much slower and induces a gradual, time-dependent, change in stack voltage. A typical chronopotentiometric series for the electrode voltage (in time) is given in Fig. 2, indicating the E_{OCV}, $\eta_{non-ohmic}$, R_{ohmic} and the typical time scale for establishing a steady voltage, τ (in s).

In theory, the ohmic and non-ohmic resistances can be measured at the sudden start or at the sudden stop of each electrical current. However, the resistances are slightly dependent on the current density itself [9], due to the change in feed water concentrations (and the corresponding conductivity) as induced by the ion transport. Therefore, the resistances are most representative for the obtained power density when measured after a stage with electrical current i.e. at the sudden stop of the electrical current j, as indicated in Fig. 2.