



The permselectivity and water transference number of ion exchange membranes in reverse electrodialysis



A. Zlotorowicz^a, R.V. Strand^a, O.S. Burheim^b, Ø. Wilhelmsen^{b,c}, S. Kjelstrup^{a,*}

^a Department of Chemistry, Norwegian University of Science and Technology (NTNU), Trondheim, Norway

^b Department of Electrical Engineering and Renewable Energy, Norwegian University of Science and Technology (NTNU), Trondheim, Norway

^c SINTEF Energy Research, Trondheim, Norway

ARTICLE INFO

Keywords:

Thermodynamics
Membrane
Transport
Permselectivity
Water
RED
Salt
Ion selective

ABSTRACT

Reverse electrodialysis of saline solutions (RED) is a renewable energy technology with large potential. Key components in the system are the ion exchange membranes. This work evaluates the efficiency of commercially available anion and cation selective membranes for RED. Their efficiency is often described with the apparent transport number for the ion in question, and this number depends on the salt concentration. It is known since long that the water transference coefficient contributes to the apparent transport number, but much of the recent literature on RED takes the permselectivity as defined by the apparent transport number as a direct measure of the membrane selectivity. The purpose of this paper is to clarify that situation with new data on Fumasep membranes. Concentration cell potentials were measured for anion- and cation exchange membranes from Fumasep (FAD and FKS, respectively, Fumatech, Germany) in the temperature range 12 – 45°C in salt solutions relevant for reverse electrodialysis. The results show that the anion exchange membrane is a perfectly selective ion exchange membrane, and has a water transference coefficient of -6 ± 1 . The cation selective membrane has a cation transport number of 0.93 and a water transference coefficient of 8 ± 7 . We suggest that the developers of membranes should pay more attention to the water transference coefficient. To enhance the performance of ion selective membranes and RED, it is beneficial to have water transference coefficients as close to zero as possible.

1. Introduction

The Gibbs energy of mixing of seawater and freshwater can be converted into electrical energy in several ways [1–3], including in reverse electrodialysis (RED) [4–6]. This promising renewable energy technology is at focus here. The key components in the RED system are the ion exchange membranes (IEMs). IEMs are also widely used for separation purposes, including microfiltration [7,8], nanofiltration [9], reverse osmosis [8], evaporation [10] and separation from gas or liquid-phases [11,12]. Ion exchange membranes are also applied to waste water treatment in electrodialysis cells. Electrodialysis is a practical and most important technology for the treatment of unusable water; it is in general used for demineralization of solutions in a wide variety of industrial fluids encountered in the food industry [13–15], and in pharmaceutical industries [16]. It is therefore important for several reasons to have a precise understanding of the coupled transport processes that take place in the IEMs, in particular of how the ion and water transports interact. This work evaluates interaction in commercially available anion- and cation exchange membranes, for

application in reverse electrodialysis. In this context, their permselectivity is described with the apparent transport number, defined as the ratio between the measurable electromotive force (Emf) over the membrane and the ideal electric potential, which is the maximum achievable value [17]. When the apparent transport number is unity, the membrane has been said to be perfectly permselective. Alternatively, when the apparent transport number is below unity, it has been understood that the IEM is not perfectly selective to one ion, but allows more ions to pass.

It is well established experimentally that the water transference coefficient of a membrane decreases with increasing salt content in the solution [18–24], and that water transfer constitutes a major part of electroosmosis [24–27]. According to the literature [28], there is also a small temperature variation in these numbers. Values for the cation transport number in a cation exchange membrane, t_{Na^+} , is close to unity; 0.95 (Nafion 120) [29], 0.97–0.99 (MF-4SK) [30], 0.89 (FKD-Fumasep), 0.99 (CMX-Neosepta) [31,32], where the transport number in an anion exchange membrane is close to zero; 0.140 (FAD-Fumasep), 0.09 (AMX-Neosepta) [31,32]. The water transference

* Corresponding author.

E-mail address: signe.kjelstrup@ntnu.no (S. Kjelstrup).

coefficient, t_{w} , has a different sign in cation- and anion exchange membranes. For cation exchange membranes, reported values of t_{w} vary from 6.9 to 9.6 for Na^+ salt solutions [26,33]. The membrane in the H-form (the fuel cell membrane) has an exceptionally high water content, but a low water transference coefficient ($t_{w}=2.6$) [34–36]. The sign variation can be explained by a water transport which follows the main conducting ion. Protons are unable to carry much water along. The ion transport promotes simultaneous water transport in two ways. In the first place, there is an electrostatic drag on the water dipoles by the ion, which increases with increasing field strength. This effect is therefore larger for cations than for anions. The second effect is more of a bulk effect; clusters of water can be “pushed” along the membrane channel, forced by the ion transport [37]. Also this effect is larger for smaller ions. The transference coefficient is therefore not the same as the waters of hydration around the ion. Anion exchange membranes have accordingly relatively smaller values of t_{w} .

Direct measurement of the water transference coefficient is difficult, and is probably most accurately performed by using the streaming potential technique [38]. Few experimental values for t_{w} have been reported for anion exchange membranes. These observations are extended experimentally in this work. Emf measurements are done in the temperature range 12 – 45°C with Fumasep anion- and cation exchange membranes and electrolyte solutions varying in concentration between 2 and 30 g dm⁻³ NaCl (similar to fresh- and seawater). Fumasep membranes have good electrochemical properties in terms of low membrane resistance and high selectivity [39], so they are good candidates for RED. It is perceived that imperfect membranes, having an apparent transport number different from unity, allows to some small degree a transport of the counter-ion. We shall see that this may not be the case.

Using a simple assumption about the concentration dependence of the various contributions to the apparent transport number, we shall see that it is possible to decompose the data to obtain information about the water transport, in addition to the ion transport. The theory of non-equilibrium thermodynamics is essential in this respect. Using this, we find that a membrane may appear not to have a supreme selectivity, while the deviation from an ideal selective membrane is caused by the transfer of water and not of any counter-ion. This leads us to suggest that membrane manufacturers and users should pay more attention to water transference coefficients. In the future, the performance of ion selective membranes can be enhanced by developing membranes that have water transference coefficients as close to zero as possible.

2. Theory

The electrochemical cell we consider in this work is, with standard notation:



Here, MEM is a cation or anion exchange membrane. The purpose is now to find a more explicit expression for the permselectivity α of the membranes as a function of the salt molality, m_s , where the permselectivity, α , is defined as the ratio of the electrical potential difference E at open circuit conditions (the *Emf*), to the ideal potential difference, E_{ideal} :

$$\alpha = \frac{E}{E_{ideal}} \quad (1)$$

The ideal potential difference is taken as the maximum value obtainable from the difference in the chemical potential of the salt across the membrane, $\Delta\mu_s$:

$$E_{ideal} = -\frac{\Delta\mu_s}{F} \quad (2)$$

Here, F is Faraday's constant. An expression for E can be found from

the force-flux equations defined in irreversible thermodynamics [40,41]:

$$J_s = -L_{ss} \frac{\partial\mu_s}{\partial x} - L_{sw} \frac{\partial\mu_w}{\partial x} - L_{s\phi} \frac{\partial\phi}{\partial x} \quad (3)$$

$$J_w = -L_{ws} \frac{\partial\mu_s}{\partial x} - L_{ww} \frac{\partial\mu_w}{\partial x} - L_{w\phi} \frac{\partial\phi}{\partial x} \quad (4)$$

$$j = -L_{\phi s} \frac{\partial\mu_s}{\partial x} - L_{\phi w} \frac{\partial\mu_w}{\partial x} - L_{\phi\phi} \frac{\partial\phi}{\partial x} \quad (5)$$

Here, L_{ij} are Onsager coefficients, μ_s is the chemical potential of the salt, μ_w is the chemical potential of water, ϕ is the electric potential, and j is the electric current density. The subscripts s , w and ϕ refer to salt, water and current respectively. We have considered transport in the x -direction only, i.e. the direction perpendicular to the membrane surface. In order to find the apparent transport number, t' , we solve the last equation for the gradient in electric potential with the condition, $j \approx 0$:

$$\left(\frac{d\phi}{dx}\right)_{j=0} = -\frac{L_{\phi s}}{L_{\phi\phi}} \frac{d\mu_s}{dx} - \frac{L_{\phi w}}{L_{\phi\phi}} \frac{d\mu_w}{dx} \quad (6)$$

The transport number for the salt is defined as:

$$t_s \equiv F \frac{L_{\phi s}}{L_{\phi\phi}} \quad (7)$$

In the present cell with Ag|AgCl-electrodes, t_s is equal to the transport number of Na^+ or one minus the transport number of Cl^- :

$$t_s = t_{\text{Na}^+} = 1 - t_{\text{Cl}^-} \quad (8)$$

This identification depends on the electrodes and applies to cation as well as anion exchange membranes. A perfect cation exchange membrane has $t_s=1$, while a perfect anion exchange membrane has $t_s=0$. Similarly, the transference coefficient of water is defined as:

$$t_w \equiv F \frac{L_{\phi w}}{L_{\phi\phi}} \quad (9)$$

The transference coefficient measures how many moles of a component that is transported through the membrane from left to right per mole of electrons that are transferred between the electrodes in the external circuit. We introduce the definitions of the transference coefficients into Eq. (6):

$$\frac{d\phi}{dx} = -\frac{t_s}{F} \frac{d\mu_s}{dx} - \frac{t_w}{F} \frac{d\mu_w}{dx} \quad (10)$$

where the chemical potential μ_s of an electrolyte (NaCl) in a solution is:

$$\mu_s = \mu_s^0 + 2RT \ln \left(\frac{m_s \gamma_s}{m^0} \right) \quad (11)$$

Here, μ_s^0 is the standard chemical potential for salt (a solution of 1 molal), $R=8.314 \text{ J}/(\text{mol K})$ is the universal gas constant, m_s is the concentration of NaCl in mol/kg water and γ_s is the dimensionless activity coefficient of the salt. Eq. (11) gives that:

$$d\mu_s = 2RT \left(\frac{1}{m_s} + \frac{1}{\gamma_s} \left(\frac{\partial\gamma_s}{\partial m_s} \right) \right) dm_s \quad (12)$$

In the following, we omit the last term on the right hand side of Eq. (12) since we find numerically that $m_s^{-1} \gg \gamma_s^{-1} (\partial\gamma/\partial m_s)$ in the range considered. Moreover, the Gibbs-Duhem equation relates the chemical potential of water to the chemical potential of the salt:

$$d\mu_w = -\frac{m_s}{m_w} d\mu_s \quad (13)$$

where m_w is the molality of water, which is the mole number of water in 1 kg, equal to $1/M_w$, where M_w is the molar mass, $M_w = 18.015 \times 10^{-3} \text{ kg/mol}$. The molality of water is expressed by

n_s/b_w , where n_s is the mole number and b_w is the weight of water. We introduce these expressions into Eq. (10) and obtain:

$$\frac{d\varphi}{dx} = -\frac{2RT}{F}(t_s - t_w M_w m_s) \frac{d \ln m_s}{dx} \quad (14)$$

where the following quantity has, in the literature, been referred to as the apparent transport number:

$$t' = t_s - t_w M_w m_s \quad (15)$$

We do not know these properties as functions of the membrane composition. But rather than integrating across the membrane, we can integrate over salt solutions that are at local equilibrium in the membrane at any position, x . This is a valid assumption, first proposed by Scatchard and tested by others [23,42,43], which allows us to use Gibbs-Duhem's equation. The electrodes on the two sides are the same ($\text{Ag}(s)|\text{AgCl}(s)$), and do not have any net contribution to the cell potential at isothermal, isobaric conditions. The only contribution comes therefore from the membrane itself.

The measurable electrical potential across the membrane is found by integrating Eq. (10) from one side of the membrane to the other, where the salt molalities at each side are denoted m_1 and m_2 respectively.

$$E = \int_1^2 \left(\frac{d\varphi}{dx} \right)_{j=0} dx \quad (16)$$

$$\approx -\frac{2RT}{F} \int_{m_1}^{m_2} \left(\frac{t_s}{m_s} - t_w M_w \right) dm_s \quad (17)$$

$$= -\frac{2RT}{F} \left(t_s \ln \frac{m_2}{m_1} - t_w M_w (m_2 - m_1) \right) \quad (18)$$

We next consider a case where $\Delta m = m_2 - m_1$ is so small that $\ln(m_2/m_1) \approx \Delta m/m_1$. We then obtain:

$$E = \frac{2RT}{F} \left(M_w t_w \Delta m - t_s \frac{\Delta m}{m_1} \right) \quad (19)$$

Eq. (19) states that for experiments with a small difference in molality between the two sides of the membrane, the quantity $\frac{EF}{2RT\Delta m}$ should be linear in $1/m_s$, $m_2 > m_1$, where the extrapolation to $m_1 = 0$ gives $M_w t_w$ and the slope gives $-t_s$. We shall use Eq. (19) to analyze the measured values of E . The expression for the ideal potential difference is:

$$E_{ideal} = -\frac{\mu_s(m_2) - \mu_s(m_1)}{F} = -\frac{2RT}{F} \ln \frac{m_2}{m_1} \quad (20)$$

Using Eqs. (18) and (20), we can define the permselectivity of the membrane as a function of salt molality:

$$\alpha = \frac{E}{E_{ideal}} = t_s - t_w M_w \frac{m_2 - m_1}{\ln(m_2/m_1)} \quad (21)$$

The permselectivity, α is a function of the salt molality at the two sides of the membrane as well as t_s and t_w . In the case of a small difference in salt molality across the membrane, we obtain:

$$\Rightarrow \alpha(m_s) = t_s - M_w t_w m_1 \quad (22)$$

which shows that the permselectivity is equal to the apparent transport number (see Eq. (15)) when $|\Delta m|$ is small. Thus, in the remaining part of this work, we shall use the concepts of permselectivity and apparent transfer number interchangeably. The sign of t_w is positive (cation exchange membranes) or negative (anion exchange membranes), depending on the direction water is taken along with the charge carrying species.

Fig. 1 shows how α depends on m_1 and m_2 , using Eq. (21) for $m_1 \neq m_2$. The transport numbers of the sodium ion and water are set to the constant values, 1 and 10, respectively. In this perfect cation exchange membrane, the permselectivity varies from 1 to 0.92 (high Δm and m_1). This is a substantial reduction, and means that the

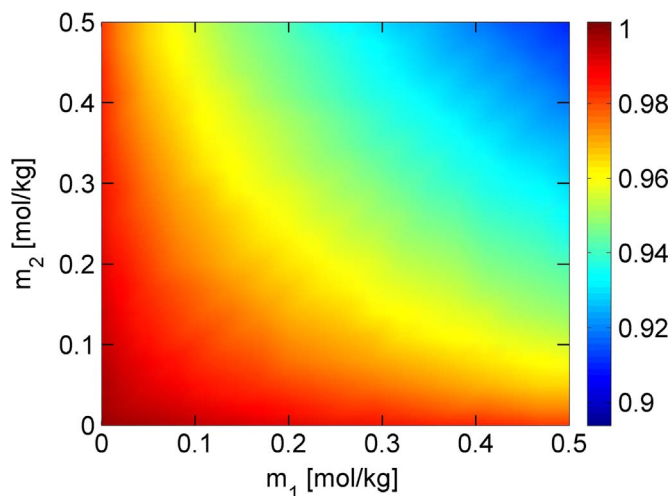


Fig. 1. The permselectivity as a function of molalities surrounding a cation exchange membrane, shown in color codes, given $t_s=1$ and $t_w=10$. The permselectivity decreases with increasing molality and increasing molality differences.

permselectivity must be understood, not only by the ion transport, but also by the water transport.

The permselectivity in Fig. 1 increases with decreasing concentration of either solution. If the highest concentration is kept constant, an increased concentration difference would give an increased permselectivity. A typical such variation for a cation exchange membrane is shown in Fig. 2.

In Fig. 2, the permselectivity is increasing in value as a function of the concentration difference used, from 0.91 with a small difference, to about 0.98–0.99 with a difference of approximately 0.5 mol/kg, even though the cation exchange membrane has been assumed to be perfectly selective. Since we have set $t_s=1$ in the calculations in Figs. 1 and 2, the reason for the discrepancy between $t' \approx \alpha$ and t_s originates from the term containing t_w .

The contribution from the water to the permselectivity has a physical explanation as follows. The controlled movement of salt down its gradient in chemical potential, creates electric energy. But this movement is accompanied by an unavoidable movement of water to a higher chemical potential for water. The last process consumes work or Gibbs energy, and reduces the net work output. The effect of the water transfer increases with increasing difference in chemical potential of

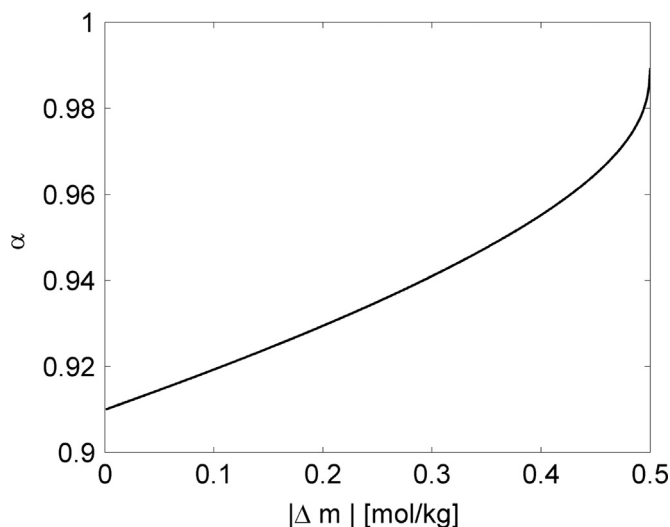


Fig. 2. The permselectivity of a cation exchange membrane as a function of concentration difference across the membrane, for $t_s=1.0$ and $t_w=10$. One of the concentrations is kept at 0.5 mol/kg.

salts or water between the two sides of the membrane, as seen in Fig. 2.

3. Experimental part

3.1. Membranes and electrodes preparation

The membranes were acquired from Fuma-Tech GmbH (Germany). The anion exchange membrane was Fumasep, FAD-PET-75 reinforced and the cation exchange membrane was Fumasep, FKD-PET-75 reinforced. The thickness of the membrane was 0.10 mm. The membrane sheet was cut into circles of 5 cm in diameter, but the effective area of the membrane under the investigation was 9.6 cm². The membranes were kept in a glass beaker of soaking solutions of NaCl (AnalR Normaput, VWR Chemicals Prolabo, Switzerland). The soaking solutions with the membranes were kept at 21 ± 0.3°C, and the solution was replaced twice during a period of 48 h to ensure that the membrane was in equilibrium with the solution. The solutions with the membranes were kept in a water bath (at 25.0 ± 0.1°C) during the experiment. Silver-silver chloride electrodes were prepared, using platinum metal wire as a basis. On the platinum metal, a layer of silver was electro-deposited and chloridized by anodizing it in a dilute solution of a chloride salt. The procedure of preparing electrodes was taken from Ives and Janz [44]. Deconex 11 Universal (Borer Chemie) was used as cleaning agent instead of chromic acid.

3.2. Experimental set-up

The experimental set-up consisted of two glass flasks separated by the membrane under the investigation (see Fig. 3). In order to avoid that diffusion alters the concentrations in the flasks, the experiment was done with stacks of membranes, following the procedure presented by Ottøy et al. [36]. Sixteen membranes were soaked in two solutions for 48 h, half of the membranes in one and the other half in the other. The membranes were taken directly from the storing solutions. Magnetic stirrers were used to avoid concentration polarization near the membranes. The experimental set-up was put in a water bath at temperature 25.0 ± 0.1°C. The concentration potential across the membrane, E , was measured with Ag(s)|AgCl(s) electrodes after 30–45 min, when steady state was reached. Before and after each experi-

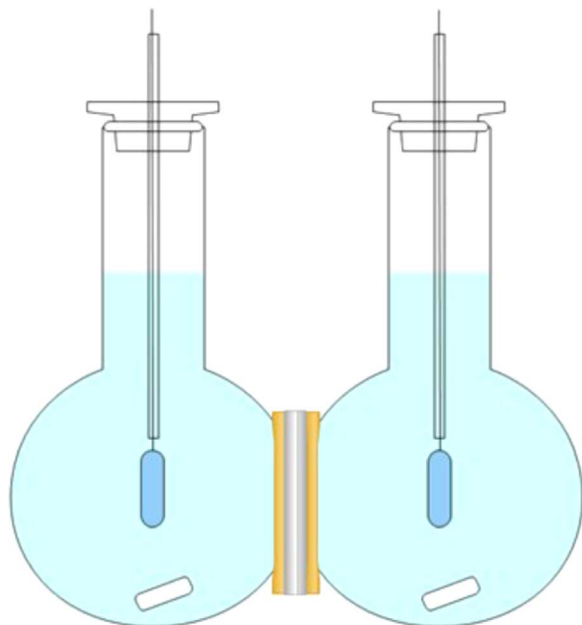


Fig. 3. Experimental set-up. The cell consists of two glass flasks connected by a membrane stack. The electrodes were Ag|AgCl electrodes. The cell was placed in a water bath.

Table 1

The measured potential E as a function of the concentrations of the sodium chloride at 25.0 ± 0.1°C for the cation exchange membrane Fumasep, FKD-PET-75 reinforced.

m_1 [mol/kg]	m_2 [mol/kg]	E_{emf} [V]
0.0999	0.1129	-0.00569
0.1001	0.0873	0.00658
0.1001	0.0873	0.00628
0.1001	0.0873	0.00631
0.1700	0.1760	-0.0014
0.1700	0.1760	-0.0014
0.1700	0.1760	-0.0014
0.1700	0.1660	0.0014
0.1700	0.1660	0.0014
0.1700	0.1660	0.0014
0.2000	0.2155	-0.00319
0.2000	0.2155	-0.00321
0.2000	0.2155	-0.00319
0.2001	0.1848	0.00365
0.2001	0.1848	0.00364
0.3000	0.2600	0.00730
0.3000	0.2600	0.00710
0.3000	0.2600	0.00740
m_1 [mol/kg]	m_2 [mol/kg]	E_{emf} [V]
0.3000	0.2859	0.00218
0.3000	0.2859	0.00224
0.3000	0.2859	0.00204
0.3000	0.2859	0.00239
0.3000	0.3166	-0.00234
0.3000	0.3166	-0.00250
0.3000	0.3600	-0.00830
0.3000	0.3600	-0.00840
0.3000	0.3600	-0.00780
0.3900	0.3800	0.00140
0.3900	0.3800	0.00150
0.3900	0.4100	-0.00130
0.3900	0.4100	-0.00140
0.4000	0.4109	-0.00124
0.4000	0.4109	-0.00120
0.4000	0.4109	-0.00121
0.4000	0.3861	0.00183
0.4000	0.3861	0.00155
0.4000	0.3850	0.00189
0.4000	0.3850	0.00173
m_1 [mol/kg]	m_2 [mol/kg]	E_{emf} [V]
0.5000	0.4500	0.00460
0.5001	0.4500	0.00150
0.5001	0.4792	0.00163
0.5001	0.4792	0.00172
0.5000	0.4797	0.00180
0.5001	0.4800	0.00180
0.5001	0.4800	0.0020
0.5001	0.5133	-0.00148
0.5001	0.5133	-0.00125
0.5000	0.5300	-0.00250
0.5000	0.5300	-0.00210
0.5000	0.5300	-0.00217
0.6001	0.5852	0.00109
0.6000	0.5852	0.00092
0.6001	0.5852	0.00124
0.6000	0.6160	-0.00127
0.6000	0.6160	-0.00120
0.6000	0.6160	-0.00134

ment, the bias potential was determined. If the bias was more than 0.025 mV, the electrodes were refreshed. The concentrations of the solutions used for anion- and cation- exchange membranes are shown in Table 1. We used eight different salt concentration combinations. Each experiment was repeated more than 3 times.

3.3. Data reduction

The permselectivity characterizes a heterogeneous system, a membrane and its two adjacent solutions. Its value is therefore a function of the two salt molalities, m_1 and m_2 . This concentration dependency was investigated by the series of Emf measurements listed in Table 1 for cation exchange membranes. The permselectivity was calculated from the parameters in Table 1, using multiple linear regression (see Section 4). From the measurements, we used Eq. (19) to analyze the results to obtain t_w and t_s , and we calculated the permselectivity from Eq. (21).

4. Results and discussion

4.1. Cation and anion exchange membranes with water transport

The most accurate measurements were performed at 25.0°C. These results, presented in Table 1, were analyzed according to the procedure described in Section 3.3. By using the theoretical foundation elaborated in Section 2, we could extract information about both the ion transport number as well as the water transference coefficient. In Fig. 4, we have plotted $\frac{E_{emf} F}{2RT \Delta m}$ as a function of $1/m_1$. Using the slope and interception with the y-axis of the linear trend presented in Fig. 4, we used Eq. (19) to obtain $t_{Na^+} = 0.93 \pm 0.03$, and $t_w = 8 \pm 7$. In comparison, the cation exchange membrane Nafion 120 has $t_s = 0.95$ [29]. All membranes of the type MF-4SK ($t_s = 0.97 - 0.99$) can be used in reverse electro dialysis [30]. The membrane CMX from Neosepta has a similar value ($t_s = 0.99$) [31,32]. The membrane type FKD Fumasep from Fumatech data on the other hand, has a significantly lower value of $t_s = 0.89$. The water transference coefficient we obtained in this work ($t_w = 8$) is within the range of the data collected by Lakshminarayanaiah and Okada ($t_w = 6.9 - 9.6$) [26,33]. Hence, the transport number for sodium and the water transference coefficient we present in this work agree well with previous results reported in the literature.

From non-equilibrium thermodynamics [45], it is known that the conductivities (L 's in Section 2) can have a significant temperature dependence. However, since the transport numbers represent a ratio of

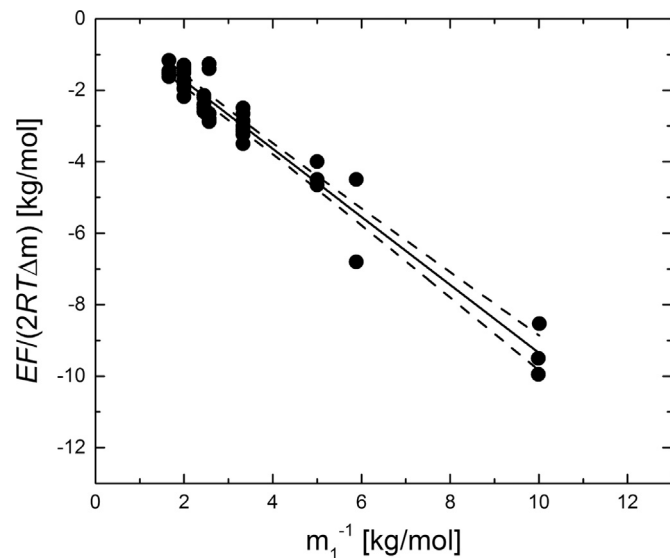


Fig. 4. The value of $EF/(2RT\Delta m)$ versus $1/m_1$ for the cation exchange membrane at $25.0 \pm 0.1^\circ\text{C}$. The solid line represents the linear fit and the dashed lines give the 95% confidence interval.

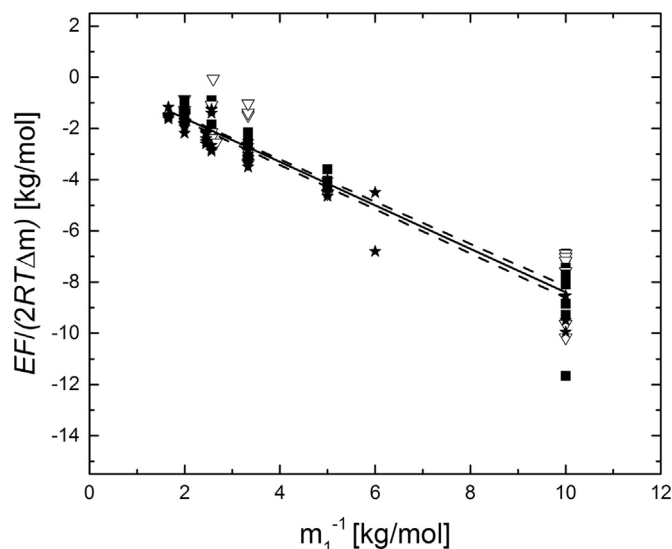


Fig. 5. The value of $EF/(2RT\Delta m)$ versus $1/m_1$ for the cation exchange membrane for the temperature range $12.0 - 45.0 \pm 0.1^\circ\text{C}$. The open triangles represent the data at $12 \pm 0.1^\circ\text{C}$, the solid stars represent the data at $25 \pm 0.1^\circ\text{C}$ and the bold squares represent the data at $45 \pm 0.1^\circ\text{C}$. The solid line represents a linear fit and the dashed lines give the 95% confidence interval.

conductivities, (see Eqs. (7) and (9)), they should not depend much on the temperature. To confirm this, we also performed experiments at 12°C and 45°C . In Fig. 5, we have plotted all results obtained within the temperature range $(12.0 - 45.0) \pm 0.1^\circ\text{C}$ in the same figure. The figure shows that no statistically significant temperature dependence of the transport numbers could be extracted from the measurements. Within the experimental accuracy, the data presented in Fig. 5 gives the same transport numbers as the data at $25 \pm 0.1^\circ\text{C}$.

This result is reasonable, and in agreement with literature data for ion exchange membranes. At the salt concentrations in question ($m \sim 0.1 - 0.6 \text{ mol/kg}$), the membrane is not perfectly selective. Water transference coefficients of around 10 are typical for monovalent ions [28,33,41]. Evidently, a small variation in the slope can alter the result for t_w much. It was therefore interesting to impose the condition $t_s = 1$ in all plots. For the cation exchange membrane, this gave $t_w \approx 30$ for all three temperatures. This number is unrealistically high, supporting the idea that the cation exchange membrane of Fumasep is neither perfectly selective, nor excluding electro-osmosis.

For the anion exchange membrane from Fumasep, the experimental data plotted in Fig. 6 gave $t_{Na^+} = 0.002 \pm 0.01$, and a negative transference coefficient for water: $t_w = -6 \pm 1$. A negative value for t_w is expected, when the charge is carried by the chloride ion. A small participation of the sodium ion in the charge transport is also likely to occur. A linear slope with a 95% confidence interval is shown in the figure. In the literature, small but positive transport numbers have been reported for anion exchange membranes; 0.140 (FAD-Fumasep), 0.09 (AMX-Neosepta) [31,32].

Much care was taken in the experimental routine to avoid concentration polarization. Solutions were stirred at constant speed. The use of a stack of membranes [36], also prevents diffusion and therefore the chemical potential in the two solutions to change over the time course of the experiment. The uncertainty in the results, in particular for the transference coefficient of water, is nevertheless significant, as it is computed from an intercept of the plot of the curve with the y-axis. Other measuring techniques to measure the transference coefficients are available and has been used. In the streaming potential method [33,38,46] one can use electrolytes with the same composition, but at different pressures. These measurements give the combination $t_s V_s + t_w V_w$, where V_i is the partial molar volume of $i = s, w$. To separate t_s from t_w in the experiment, however, is still challenging. The

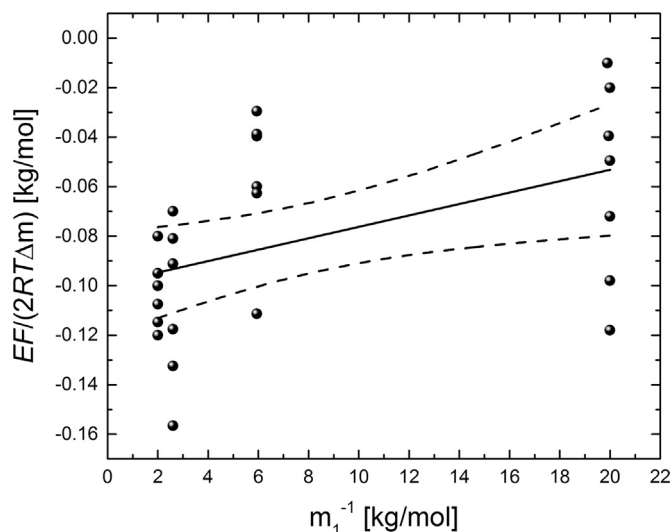


Fig. 6. The value of $EF/2RT\Delta m$ versus $1/m_1$ for the anion exchange membrane at $25.0 \pm 0.1^\circ\text{C}$. The solid line represents the linear fit, and the dashed lines give the 95 % confidence interval.

determination of t_s by the Hittorf method is also hampered by the difficulty in extrapolating to the limit of zero polarization.

4.2. The permselectivity concept in RED

We have seen above, that only the apparent transport number, t' , is directly available from the experimental results with a reasonable accuracy (a few per cent). But the concentration dependence of t' , allows us to separate between the contributions from the ions and from water. In the decomposition performed in Figs. 4–6, we assume that the transport numbers are constant, and that the concentration difference across the membrane is small. The first assumption might not be entirely true for the concentration interval investigated, and may in part account for the uncertainty in the obtained transport numbers. Most of the uncertainty derives from the regression analysis of the plots in Figs. 4–6, and the case of the anion membrane, from the small value of the measured potential.

The variation in the plots in Figs. 4–6 show, nevertheless, that the trends explained in Figs. 1 and 2 are likely for membranes relevant for RED. A value of $t_w=10$ is reasonable for many monovalent cations. A value of $\alpha \neq 1$ can thus be explained, not only by water transport, but also the concentration, at which this water transport takes place. The value of t_w can easily double for divalent cations [41], leading to an even larger deviation. Clearly, the concept of permselectivity, as it is now used in the literature about RED [6,47] needs to be further specified. We propose that the permselectivity should be replaced by the two variables t_s and t_w , which have more definite meanings, can be better related to the transport mechanism, and to membrane properties.

This could be used to resolve disputes in the literature. It has for instance been argued that the transport number of an ion (t_s) in a membrane depends on the concentration of the receiving solution only [48]. This may be true, in the situation that the receiving side decides the composition in the membrane (for thin membranes with back diffusion). In this experiment, however, it is not true, as illustrated in Figs. 1 and 2. Fig. 2 shows that not only the receiving side decides the value of the apparent transport number. It might be true under cell operating conditions [49]. A distinction between the two situations seems essential.

5. Conclusions and perspectives

The permselectivity as defined by the apparent transport number

has been used to characterize the selectivity of ion exchange membranes. We have seen in this work that the concept lacks precision and can benefit from a more explicit formulation obtained from non-equilibrium thermodynamics. The explicit formulation uses not only the ion transport number, but also the water transference coefficient. This is useful in the evaluation of membranes relevant for reverse electro dialysis, where it is important to understand the difference between ion and water transport properties.

The expression obtained from nonequilibrium thermodynamics was used to determine the salt and water transfer coefficients in Fumasep membranes. For the cation exchange membrane, the sodium transport number was 0.93, and the water transference coefficient equal to 8. For the anion exchange membrane the sodium transport number was zero within the accuracy of the experiments, while the water transference coefficient was negative. Water and salt transference coefficients contribute both to the permselectivity, and knowledge of both is required to give advice on membrane development. We propose that membrane producers should pay more attention to the water transport properties of the membrane. In the future, the performance of ion selective membranes can be enhanced by developing membranes that have small water transference coefficients. This would benefit the power production in saline power plants. The unit cell of such plants consists of a cation exchange membrane (superscript C) and an anion exchange membrane (superscript A). The membranes are bounding a common weak electrolyte solution, e, while brine is used on the two outer sides, o. The cell potential of such a unit cell, with chloride reversible electrodes, is given by the integral:

$$EF = - \int_o^e [(t_s^C - t_s^A)d\mu_s - (t_w^A - t_w^C)d\mu_w] \quad (23)$$

where the first term on the right hand side has its maximum value when $t_s^C = 1$, and $t_s^A = 0$. The last term will always reduce the cell potential, E , because water is transported against its chemical potential. The difference $t_w^A - t_w^C$ is negative, because $t_w^A < 0$ and $t_w^C > 0$. The difference is therefore small for small transference coefficients. Such values could possibly be achieved by designing membranes with a hydrophobic interior or with hydrophobic surfaces.

Acknowledgment

The Norwegian Research Council is acknowledged for financial support from the ENERGIX program, Grant Number 197598. The authors acknowledge Åshild Samseth and Knut Sverdrup Kleppetø from NTNU and Malgorzata Nowak from Wetsus, Centre of Excellence for Sustainable Water Technology, for help with experiments. ENERSENSE (Grant Number 68024013) is acknowledged for financial support.

References

- [1] M. Rahimnejad, A.A. Ghoreysbi, G. Najafpour, T. Jafary, Power generation from organic substrate in batch and continuous flow microbial fuel cell operations, *Appl. Energy* 88 (2011) 3999–4004.
- [2] A. Tardast, M. Rahimnejad, G. Najafpour, A.A. Ghoreysbi, H. Zare, Fabrication and operation of a novel membrane-less microbial fuel cell as a bioelectricity generator, *Int. J. Environ. Eng.* 3 (2012) 1–5.
- [3] H. Philamore, J. Rossiter, P. Walters, J. Winfield, I. Ieropoulos, Cast and 3D printed ion exchange membranes for monolithic microbial fuel cell fabrication, *J. Power Sources* 289 (2015) 91–99.
- [4] R.E. Pattle, Production of electric power by mixing fresh and salt water in the hydroelectric pile, *Nature* 174 (1954) 660.
- [5] J.N. Weinstein, F.B. Leitz, Electric power from differences in salinity: the dialytic battery, *Science* 191 (1976) 557–559.
- [6] R.E. Lacey, Energy by reverse electro dialysis, *Ocean Eng.* 7 (1980) 1–47.
- [7] A. Bódalo, J.L. Gómez, E. Gómez, G. León, M. Tejera, Sulfonated polyethersulfone membranes in the desalination of aqueous solutions, *Desalination* 168 (2004) 277–282.
- [8] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, *Science* 333 (2011) 712–717.
- [9] D. Brogioli, Extracting renewable energy from a salinity difference using a capacitor, *Phys. Rev. Lett.* 103 (2009) 058501.

- [10] R. Simons, J. Zuccon, M.R. Dickson, M. Shaw, Pervaporation and evaporation characteristics of a new type of ion exchange membrane, *J. Membr. Sci.* 78 (1993) 63–67.
- [11] M. Hong, S. Li, H.F. Funke, J.L. Falconer, R.D. Noble, Ion-exchanged sapo-34 membranes for light gas separations, *Microporous Mesoporous Mater.* 106 (2007) 140–146.
- [12] T.C. Browen, R.D. Noble, J.L. Falconer, Fundamentals and applications of pervaporation through zeolite membranes, *J. Membr. Sci.* 245 (2004) 1–33.
- [13] G. Daufin, J.P. Escudier, H. Carrère, S. Bérot, L. Filaudeau, M. Decloux, Recent emerging applications of membrane processes in the food and dairy industry, *Food Bioprod. Process* 79 (2001) 89–102.
- [14] L. Bazinet, F. Lamarche, D. Ippersiel, Bipolar membrane electrodialysis: applications of electrodialysis in the food industry, *Trans. Food Sci. Technol.* 9 (1998) 107–113.
- [15] H.K. Bishop, J.A. Bittels, G.A. Guter, Investigation of inorganic ion exchange membranes for electrodialysis, *Desalination* 6 (1969) 369–380.
- [16] T. Tarvainen, B. Svarfvar, S. Åkerman, J. Savolainen, M. Karhu, P. Paronen, K. Järvinen, Drug release from a porous ion exchange membrane in vitro, *Biomaterials* 20 (1999) 2177–2183.
- [17] H. Strathmann, *Introduction to Membrane Science and Technology*, 58th edition, Wiley-VCH, Weinheim, 2013.
- [18] F.A. Siddiqi, S. Pratap, Studies of membrane phenomena: II. determination of membrane potentials and evaluation of the membrane fixed charge density and permselectivity of parchment-supported silver iodide membrane, *J. Electroanal. Chem. Interfacial Electrochem.* 23 (1969) 147–156.
- [19] J. Ceynowa, Hydrogen-ion transport numbers in cation exchange membrane determined by emf method, *Polymer* 23 (1982) 203–206.
- [20] M. Leveque, J.F.L. Nest, A. Gandini, H. Cheradame, Ionic transport numbers in polyether networks containing different metal salts: theory and measurements by anovel technique to determine the ion transport numbers in active layers of nanofiltration membranes, *Die Makromol. Chem. Rapid Commun.* 4 (1983) 497–502.
- [21] A.E. Yaroshchuk, A.L. Makovetskiy, Y.P. Boiko, E.W. Galinker, Non-steady-state membrane potential: theory and measurements by anovel technique to determine the ion transport numbers in active layers of nanofiltration membranes, *J. Membr. Sci.* 172 (2000) 203–221.
- [22] H.L. Yeager, B. O'dell, Z. Twardowski, Transport properties of nafion membranes in concentrated solution environments, *J. Electrochem. Soc.* 129 (1982) 85–89.
- [23] C. Larchet, B. Auclair, V. Nikonenko, Approximate evaluation of water transport number in ion-exchange membranes, *Electrochim. Acta* 49 (2004) 1711–1717.
- [24] N.D. Pis'menskaya, V. Nikonenko, N.A. Mel'nik, G. Pourcelli, G. Larchet, Effect of the ion-exchange-membrane/solution interfacial characteristics on the mass transfer at severe current regimes, *Russ. J. Electrochem.* 48 (2012) 610–628.
- [25] R.C. Coulter, R. Boehlert, Legislative history: saline water conversion act. United States. Office of Saline Water, in: *Proceedings of the 39th Congress, Parts 1–2*, 6, pp. 186–188.
- [26] N. Lakshminarayanaiah, V. Subrahmanyam, Current dependence of water transport in cation-exchange membranes, *J. Phys. Chem.* 72 (1968) 1253–1258.
- [27] N. Lakshminarayanaiah, Transport phenomena in artificial membranes, *Chem. Rev.* 65 (1965) 491–565.
- [28] P. Trivijitkasem, T. Østvald, Water transport in ion exchange membranes, *Electrochim. Acta* 25 (1980) 171–178.
- [29] E.H. Cwirko, R.G. Carbonell, Ionic equilibria in ion-exchange membranes - a comparison of pore model predictions with experimental results, *J. Membr. Sci.* 67 (1992) 211–226.
- [30] L.G. Wu, C.L. Zhu, M. Liu, Study of a new pervaporation membrane: Part 2. Performance test and analysis of the new membrane, *J. Membr. Sci.* 90 (1994) 207–212.
- [31] P. Dlugolecki, B. Anet, S.J. Metz, K. Nijmeijer, M. Wessling, Transport limitations in ion exchange membranes at low salt concentrations, *J. Membr. Sci.* 346 (2010) 163–171.
- [32] P. Dlugolecki, K. Nijmeijer, S. Metz, M. Wessling, Current status of ion exchange membranes for power generation from salinity gradients, *J. Membr. Sci.* 319 (2008) 214–222.
- [33] T. Okada, G. Xie, O. Gorseth, S. Kjelstrup, N. Nakamura, T. Arimura, Ion and water transport characteristics of nafion membranes as electrolytes, *Electrochim. Acta* 43 (1998) 3741–3747.
- [34] G. Xie, T. Okada, Water transport behavior in nafion 117 membranes, *J. Electrochem. Soc.* 142 (1995) 3057–3062.
- [35] T.A. Zawodzinski, J. Davey, J. Valerio, S. Gottesfeld, The water content dependence of electro-osmotic drag in proton-conducting polymer electrolytes, *Electrochim. Acta* 40 (1995) 297–302.
- [36] M. Ottøy, T. Førland, S. Kjelstrup Ratkje, S. Møller-Holst, Membrane transference numbers from a new emf method, *J. Membr. Sci.* 74 (1992) 1–8.
- [37] B.R. Breslau, I.F. Miller, A hydrodynamic model for electroosmosis, *Ind. Eng. Chem. Fundam.* 10 (1971) 554–565.
- [38] T.S. Brun, D. Vaula, Correlation of measurements of electroosmosis and streaming potentials in ion exchanger membranes, *Ber. Bunsenges. Phys. Chem.* 71 (1967) 824–829.
- [39] S. Srinivasan, D.J. Manko, H. Koch, M.A. Enayetullah, A.J. Appleby, Recent advances in solid polymer electrolyte fuel cell technology with low platinum loading electrodes, *J. Power Sources* 29 (1990) 367–387.
- [40] T. Førland, S. Kjelstrup Ratkje, *Transport Process in Electrolytes and Membranes* 6, Taylor and Francis, New York, NY, 1992.
- [41] T. Førland, S. Kjelstrup Ratkje, *Irreversible thermodynamics theory and applications*, 1988.
- [42] B. Auclair, V. Nikonenko, C. Larchet, M. Metayer, L. Dammak, Correlation between transport parameters of ion-exchange membranes, *J. Membr. Sci.* 195 (2002) 89–102.
- [43] J. Benavente, C. Fernandez-Pineda, Electrokinetic phenomena in porous membranes: determination of phenomenological coefficients and transport numbers, *J. Membr. Sci.* 23 (1985) 121–136.
- [44] D.J.G. Ives, G.J. Janz, *Reference Electrodes: Theory and Practice*, Academic Press Inc, New York, NY, 1961.
- [45] K.S. Førland, S. Førland, T. Kjelstrup, *Irreversible Thermodynamics* Reprint from Jon Wiley and Sons, 3rd edition, Tapir Academic Press, Trondheim, 2001.
- [46] T. Okada, S. Kjelstrup Ratkje, H. Hanche-Olsen, Water transport in cation exchange membranes, *J. Membr. Sci.* 66 (1992) 179–192.
- [47] O. Schaetzle, C.J.N. Buisman, Salinity gradient energy: current state and new trends, *Engineering* 1 (2015) 164–166.
- [48] J. Veerman, M. Saakes, S.J. Metz, G.J. Harmsen, Reverse electrodialysis: evaluation of suitable electrode systems, *J. Appl. Electrochem.* 40 (2010) 1461–1474.
- [49] T.R.E. Kressman, F.L. Tye, The effect of concentration on the transport of ions through ion-selective membranes, *J. Chem. Soc. Faraday Trans.* 55 (1959) 1441–1450.