



On the resistances of membrane, diffusion boundary layer and double layer in ion exchange membrane transport

Piotr Długołęcki^{a,b}, Piotr Ogonowski^b, Sybrand J. Metz^b, Michel Saakes^b, Kitty Nijmeijer^{a,*}, Matthias Wessling^a

^a Membrane Technology Group, University of Twente, Institute of Mechanics, Processes and Control Twente (IMPACT), P.O. Box 217, 7500 AE Enschede, The Netherlands

^b Wetsus, Centre of Excellence for Sustainable Water Technology, P.O. Box 1113, 8900 CC Leeuwarden, The Netherlands

ARTICLE INFO

Article history:

Received 1 April 2009

Received in revised form

22 September 2009

Accepted 30 November 2009

Available online 4 December 2009

Keywords:

Membrane resistance

Ion exchange membranes

Electrical impedance spectroscopy

Ionic charge transfer resistance

Diffusion boundary layer

Membrane characterization

Equivalent circuit model

ABSTRACT

Membrane resistances are often measured under direct current conditions using a standard 0.5 M NaCl characterization solution, although several electro-membrane processes (e.g. reverse electrodialysis, electrodialysis, fuel cells, microbial fuel cells and membrane capacitive deionization) operate in a much lower concentration range (<0.1 M NaCl). Our work reveals that at lower concentrations, the membrane resistance as measured under direct current conditions becomes strongly concentration dependent and strongly increases with decreasing concentration. The overall resistance measured under direct current conditions however, does not only include the pure membrane resistance but also takes the interfacial ionic charge transfer through the double layer and diffusion boundary layer effects into account. Because direct current methods do not allow discriminating between these individual resistances, we applied electrochemical impedance spectroscopy (EIS), which uses an alternating current, to analyze resistance phenomena in ion exchange membranes under different hydrodynamic conditions and at different temperatures.

The results clearly show that the increase in membrane resistance with decreasing concentration as measured in direct current experiments is the consequence of the strong increase in resistance of the diffusion boundary layer with decreasing concentration. This also explains the strong effect of the flow rate on the resistance. At higher concentrations, the pure membrane resistance starts to dominate the resistance as measured by direct current measurements, although also the diffusion boundary layer resistance still plays a considerable role.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Ion exchange membranes are widely used in various applications such as electrodialysis, fuel cells, diffusion dialysis, Donnan dialysis and membrane capacitive deionization. Two emerging applications for ion exchange membranes can be found in the field of sustainable energy generation and more specifically in a process called reverse electrodialysis (RED) and in microbial fuel cells [1–7]. Ion exchange membranes are membranes with fixed anionic or cationic exchange groups that are able to transport cations or anions. The specific properties of ion exchange membranes are all related to the presence of these charged groups. Membrane properties and especially membrane resistance, have a large influence on the power output obtainable in the RED and microbial fuel cells [8,9].

When a current passes through the ion exchange membrane, charge is carried through the membrane by counter ions (ions with an opposite charge relative to the fixed charge in the membrane) as a result of Donnan exclusion. In the bulk solution, current is carried by both positive and negative ions. The difference in ion transport number between the solution phase and the membrane leads to the building up of diffusion boundary layers at the membrane surface [10–14]. Also the resistance of these layers may, especially at low salt concentrations, form a significant contribution to the total system resistance thus reducing the power output obtainable.

Długołęcki et al. used a direct current method to determine the membrane resistance of ion exchange membranes as a function of the solution concentration and they observed a significant increase in membrane resistance at concentrations below 0.1 M NaCl [15]. The same was also observed in reverse electrodialysis and biological fuel cells [9,16].

In general, membrane or cell resistances are measured via the direct current method. In this case, a current is applied and the resulting potential drop over the cell is measured. Using Ohm's law, the resistance of the system (membrane + solution) and the mem-

* Corresponding author. Tel.: +31 53 489 4185; fax: +31 53 489 4611.
E-mail address: d.c.nijmeijer@utwente.nl (K. Nijmeijer).

brane, can be determined. However, direct current measurements are not able to distinguish between the individual membrane resistance and the additional resistances of the interfacial ionic charge transfer through the double layer and the diffusion boundary layer. Therefore, direct current methods not only measure the pure membrane resistance, but also include diffusion boundary layer and double layer effects. In their work, Długołęcki et al. were not able to attribute the increase in resistance to one of these effects, because they used a direct current method [15].

Electrochemical impedance spectroscopy (EIS), which in contrast to the direct current method, uses an alternating current, allows distinguishing between the individual contributions of the different phenomena occurring at the membrane surface [11,17–25]. Park et al. performed an electrochemical impedance study on an ion exchange membrane system that contained only an anion exchange membrane (Neosepta AMX) [10,11]. In this study, the authors observed that heterogeneous transport, which we believe is the transport of ionic charge from the solution phase through the double layer to the membrane matrix, strongly depends on solution mixing and that the diffusion boundary layer can be totally eliminated by solution stirring. Although we believe that the resistance of this interfacial ionic charge transfer on the membrane surface cannot be influenced by solution mixing, because ions are transferred through the double layer which thickness is in the order of a few nanometers only (the Debye length) [19,26–28] and that the resistance of the diffusion boundary layer cannot be totally eliminated, but only minimized by increased solution flow rate, because this layer is in the micrometer range, the work clearly shows the strong potential of EIS for ion exchange membrane characterization.

In this paper we use EIS to characterize four different ion exchange membranes, i.e. two anion and two cation exchange membranes. By doing so we are able to distinguish between the pure membrane resistance and the resistance of ionic transfer through the adjacent layers, i.e. the electrical double layer and the diffusion boundary layer. The effect of salt concentration, liquid flow rate and temperature is investigated.

To the best of our knowledge, there are no other scientific publications that investigate the effect of these parameters on the different resistances in a systematic way. The results of our experiments are of major importance for various electro-membrane processes, such as reverse electrodialysis, electrodialysis, fuel cells, microbial fuel cells and membrane capacitive deionization that operate at low salt concentrations and in the temperature range from 10 °C to 30 °C.

2. Theoretical background

2.1. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a powerful technique for studying electrical properties of materials and is often used to characterize a wide variety of electrochemical phenomena in porous materials, solid state, liquid electrolytes, synthetic and biological membranes [10,11,17,22,25,29]. In general, this method can be used to provide more information on the functional and structural characteristics of membrane systems [10,11,17,18,25,30]. One of the key principles of EIS is the translation of the electrochemical system under study (e.g. ion exchange membrane) to an equivalent electrical circuit consisting of e.g. capacitors and resistors.

In EIS an alternating sinusoidal current $I(t)$ or voltage (depending on the system) of a given frequency and amplitude is applied to the system and the response of the system is monitored. The resulting voltage drop over the system is measured as a function of time $U(t)$,

and the phase shift φ relative to the input signal is determined. This procedure is repeated at different frequencies, and the impedance Z can then in accordance with Ohm's law be calculated as:

$$Z = \frac{U(t)}{I(t)} \quad (1)$$

Here, $U(t)$ is the voltage as a function of time t (V) and $I(t)$ is the current as a function of time t (A).

The voltage and current vary with time and are defined as:

$$U(t) = U_0 \sin \omega t = U_0 e^{j\omega t} \quad (2)$$

and

$$I(t) = I_0 \sin(\omega t + \varphi) = I_0 e^{j(\omega t + \varphi)} \quad (3)$$

Here, $U(t)$ is the voltage at a certain time (V), U_0 is the voltage in phase (without phase shift) (V), $I(t)$ is the alternating current at a certain time t (A), I_0 is the alternating current in phase (A), φ is the phase shift (°) and j is the imaginary unity ($j = \sqrt{-1}$). The symbol ω is the circular velocity (1 rad/s) which is also referred to as circular frequency of the alternating current. It is a function of the frequency f , and is given by:

$$\omega = 2\pi f \quad (4)$$

By using Euler's formula:

$$e^{j\varphi} = \cos \varphi + j \sin \varphi \quad (5)$$

The impedance can subsequently be defined as:

$$Z(\omega) = \frac{U_0 e^{j\omega t}}{I_0 e^{j(\omega t + \varphi)}} = |Z| e^{-j\varphi} = |Z| \cos \varphi - j |Z| \sin \varphi \quad (6)$$

The impedance thus consists of a real part and an imaginary part (Eq. (6)), where the real part is:

$$\operatorname{Re}(Z) \equiv Z' = |Z| \cos \varphi \quad (7)$$

and the imaginary part is:

$$\operatorname{Im}(Z) \equiv Z'' = |Z| \sin \varphi \quad (8)$$

The impedance of an electrical resistance or a capacitance differ. When the current and the voltage are in phase, the imaginary part of the impedance is zero. The real part of this impedance is independent of frequency and in accordance with Ohm's law the impedance of an electrical resistance equals:

$$Z = \frac{U_0}{I_0} = R \quad (9)$$

A capacitor on the other hand is characterized by a phase shift with a phase angle of $\pi/2$ between current and voltage. Therefore, the impedance of a capacitance is imaginary and frequency-dependent and is given by:

$$Z = \frac{1}{j\omega C} \quad (10)$$

Here, C is the capacitance (F).

In reality, ion exchange membrane systems are not completely homogeneous and some dispersion may occur. In that case the capacitor can be represented by the constant phase element Q to obtain better data fitting [11]. The constant phase element Q is a non-intuitive circuit element that was introduced while looking at the response of real systems and it can be represented by [27,29]:

$$Z = \frac{1}{(j\omega)^n Q} \quad (11)$$

Q is the constant phase element with the units Ss^n , where S represents Siemens ($1/\Omega$) and s represent seconds. The constant phase element Q is often used to represent complex electrochemical systems to express different relaxation times, which reflect

Download English Version:

<https://daneshyari.com/en/article/636616>

Download Persian Version:

<https://daneshyari.com/article/636616>

[Daneshyari.com](https://daneshyari.com)