



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Probing membrane and interface properties in concentrated electrolyte solutions

Enrica Fontananova^{a,*}, Wenjuan Zhang^a, Isabella Nicotera^b, Cataldo Simari^b,
Willem van Baak^c, Gianluca Di Profio^a, Efrem Curcio^d, Enrico Drioli^{a,d}

^a Institute on Membrane Technology of the National Research Council (ITM-CNR), c/o University of Calabria Via P. Bucci, cubo 17/C, 87036 Rende (CS), Italy

^b Department of Chemistry and Chemical Technologies, Via P. Bucci, University of Calabria, 87036 Rende (CS), Italy

^c Fujifilm Manufacturing Europe BV, Tilburg, The Netherlands

^d Department of Environmental Engineering and Land and Chemical Engineering, University of Calabria Via P. Bucci, cubo 44A, 87036 Rende (CS), Italy

ARTICLE INFO

Article history:

Received 23 August 2013

Received in revised form

24 January 2014

Accepted 25 January 2014

Available online 17 February 2014

Keywords:

Concentrated electrolyte solution

Impedance

Interface

Ion exchange membrane

PGSE-NMR

ABSTRACT

This study deals with the membrane and interface electrical properties investigation by electrochemical impedance spectroscopy (EIS). The EIS is a powerful technique for characterizing electrical behavior of systems in which coupled electrical processes occur at different rates. A systematic study on the effect of solution concentration, temperature and velocity, on the electrical resistance of anion- and cation-exchange membranes (AEMs and CEMs) and their interfaces (electrical double layer and diffusion boundary layer), was carried out. At the best of our knowledge, for the first time electrolyte concentrations up to 4 M were used for the study of membranes and interface by EIS.

Moreover, Pulsed Gradient Spin Echo Nuclear Magnetic Resonance (PGSE-NMR) technique was used to measure the water self-diffusion coefficients in swelled membrane as a function of the solution concentration and temperature. These measurements gave additional important insights about the effect of the electrolyte solution and fixed charges concentration in membrane, on membrane microstructure and its transport and electrical properties.

© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

1. Introduction

One of the major concerns of membranologists operating in the field of electro-membranes processes, is the depth knowledge of the membrane electrical and mass-transport properties. It is known that at the interface between a solid ionic conductor and a liquid electrolyte, physical and electrical properties change suddenly because of an heterogeneous charges distribution (polarization) which reduce the overall electrical conductivity of the system [1–3].

The membrane electrical resistance is usually measured by direct current (DC) method. In DC measurements the membrane is installed in a cell which consists of two chambers containing the testing solutions separated by the membrane. A DC signal is applied and the voltage drop across the membrane is measured. The electrical resistance is given by the slope of the current vs. the voltage drop curve, in agreement with Ohm's law [4]:

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

where R [Ω] is the resistance, U [V] is the voltage drop measured between the two sides of the membrane; I [A] is the current.

To obtain the membrane resistance, the resistance of the cell filled with the solution, but without the membrane, is subtracted from the resistance of the cell containing both, the solution and the membrane. The method is simple, but it is not able to distinguish the membrane from the interface resistance. On the contrary of the measurement in direct current, using an alternate current (AC) over a frequency range, it is possible to distinguish phenomena proceeding at different rates. Electrochemical Impedance Spectroscopy (EIS) is a powerful technique in which an AC is used to measure quantitatively the resistance to the charge transport in the bulk and interfacial regions of solid and liquid electrolyte materials [1,5–7].

In EIS experiments a sinusoidal electrical stimulus (voltage or current) is applied over a frequency range to a pair of electrodes and the response of the system under investigation is observed (current or voltage) by the same, or different electrodes. In the first case the configuration is indicated as two probes (or two electrodes) configuration; when two additional electrodes are used to collect the response of the system, the configuration is indicated as a four probes [1]. In membrane characterization field, the two probe configuration is usually applied when the membrane is pressed

* Corresponding author. Tel.: +39 098 449 2010; fax: +39 098 440 2103.

E-mail addresses: e.fontananova@itm.cnr.it,
enrica.fontananova@cnr.it (E. Fontananova).

between two solid conductive electrodes, like in the case of the membrane electrode assembly (MEA) for fuel cells [8–11].

Despite some examples of the use of the two probes configuration can be found in literature for the study of the ion transport through a membrane separating two liquid electrolyte solutions [12–14], the four probe configuration is the most convenient and commonly used. The four probes, with respect to the two probes configuration, has the advantage to eliminate from the impedance spectra the contribution of the electrode injecting stimulus/electrolyte charge transfer resistance, focusing the probing on the membrane and its interface [15–21]. Impedance spectroscopy was also used for the in-situ non-destructive structural characterization of membranes and fouling phenomena [17,22–24].

Another possible configuration in EIS experiments consist in the use of three electrodes, but it is usually employed to characterize only one half of an electrolytic/electrochemical cell, or phenomena occurring on an electrode [25], but not to investigate membrane properties.

This study deals with the membranes and interface electrical properties investigation by EIS. A systematic analyses on the effect of solution concentration, temperature and velocity on the electrical resistance of anion and cation exchange membranes (CEMs and AEMs) and their interfaces, was carried out. At the best of our knowledge, for the first time electrolyte concentrations up to 4 M were used for the study of membranes and interface properties by EIS. Moreover, Pulsed Gradient Spin Echo Nuclear Magnetic Resonance (PGSE-NMR) technique was used to characterize AEMs and CEMs swelled in concentrated electrolyte solutions. NMR spectroscopy provides information on the microscopic, as well as, macroscopic nuclear environments by determination of parameters such as relaxation times, self-diffusion coefficients, and structural information.

The interest towards concentrated solutions lies in the high salinity-gradient power (SGP) that can be extracted by membrane-based energy conversion processes, like pressure-retarded osmosis (PRO) and reverse electrodialysis (RE). The maximum theoretical obtainable energy during the reversible mixed of a diluted stream with a saline concentrated solution, ranges from 0.75 kW-h/m³ to 14.1 kW-h/m³ of diluted solution, going from seawater (osmotic pressure 2.7 MPa) to Dead Sea water (osmotic pressure 50.7 MPa) as saline solution [26]. Concentrated solutions are produced in numerous industrial activities such as saltworks and salt mines. Membrane-based integrated systems open interesting perspectives for sustainable and efficient energy conversion using natural and abundant water resources. Brine solutions can be produced by reverse osmosis and/or membrane distillation of seawater [27–30], and they can be used as concentrated stream in SGP-RE stack employing as diluted stream sea or brackish water. This idea is at the basis of the European FP7 Project Reapower (www.reapower.eu), and it can offer a huge potential for the improvement of the electrical performance of SGP-RE system, which usually focus on the combination of fresh water, as the diluted solution, and

seawater, as the concentrated solution. The use of concentrated solution allows to reduce the electrical resistance within the low concentration compartment of the SGP-RE stack, boosting the power that can be extracted from the SGP [26,31,32].

2. Materials and methods

2.1. Membranes samples

Three homogeneous reinforced cation exchange membranes (CEMs) and three homogenous reinforced anion exchange membranes (AEMs) produced by Fuji, were investigated (Table 1). Before the use the membranes were washed with a 0.5 M NaCl solution for 24 h changing the solution 4 times to remove residual traces of solvents and/or chemical agents. After this procedure the samples were indicated as “activated”.

2.2. Electrochemical impedance spectroscopy (EIS) experiments

In EIS experiments the response of a system to a sinewave voltage or current excitation is investigated in the frequency domain. Voltage ($U_{(\omega)}$ [V]) and current ($I_{(\omega)}$ [A]) depend from the circular velocity or circular frequency ω [s⁻¹] as follow:

$$U_{(\omega)} = U_o \sin \omega t \quad (2)$$

$$I_{(\omega)} = I_o \sin(\omega t + \varphi) \quad (3)$$

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

where t [s] is the time, φ [°] is the phase shift between voltage and current, and the subscript o refers to the amplitude of voltage and current in phase, ν [s⁻¹] is the frequency.

By using the Euler form:

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

where j is the imaginary number ($j = \sqrt{-1}$)

The impedance $Z_{(\omega)}$ [Ω] can be expressed in a form similar to Ohm's law:

$$Z_{(\omega)} = \frac{U_o e^{j\omega t}}{I_o e^{j(\omega t + \varphi)}} = \frac{U_o}{I_o} e^{j\varphi} = |Z| \cos \varphi + j|Z| \sin \varphi \quad (6)$$

where $|Z|$ is the impedance modulus.

The Eq. (6) indicates that the impedance is composed of two parts, i.e. the real part:

$$Z' = |Z| \cos \varphi \quad (7)$$

and the imaginary part:

$$Z'' = |Z| \sin \varphi \quad (8)$$

The real part of the impedance is the resistance, the imaginary part is called reactance [1,4].

Table 1

List and some experimentally determined properties of the membranes.

Membrane	Thickness (μm)*	Ion exchange capacity (mmol/g membrane)	Density of fixed charges (mol/L)*	Membrane areal resistance ($\Omega \text{ cm}^2$)**
Fuji-AEM-0150	166 ± 1	1.1 ± 0.1	2.2 ± 0.3	1.631 ± 0.001
Fuji-AEM-80045	129 ± 2	1.4 ± 0.1	3.8 ± 0.2	1.551 ± 0.001
Fuji-AEM-90025	109 ± 2	1.6 ± 0.3	2.9 ± 0.6	1.102 ± 0.001
Fuji-CEM-0150	170 ± 1	1.6 ± 0.1	3.4 ± 0.2	2.647 ± 0.001
Fuji-CEM-80050	114 ± 2	1.1 ± 0.1	2.4 ± 0.2	2.974 ± 0.001
Fuji-CEM-90026	113 ± 2	1.0 ± 0.3	1.8 ± 0.5	1.642 ± 0.001

* Conditions: NaCl 0.5 M, 20 °C.

** Conditions: NaCl 0.5 M, 20 °C, 2.8 cm s⁻¹.

Download English Version:

<https://daneshyari.com/en/article/7022215>

Download Persian Version:

<https://daneshyari.com/article/7022215>

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