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Effect of solution concentration and composition on the electrochemical properties of ion exchange membranes for energy conversion

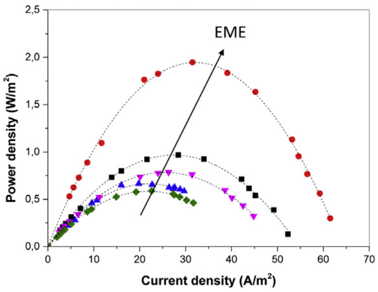
E. Fontananova [a], *, D. Messana [b], R.A. Tufa [b], I. Nicotera [c], V. Kosma [c], E. Curcio [b], W. van Baak [d], E. Drioli [a], [b], G. Di Profio [a]

[a] Institute on Membrane Technology of the National Research Council (ITM-CNR), Via P. Bucci, Cubo 17/C, 87036 Rende, CS, Italy
[b] Department of Environmental and Chemical Engineering, University of Calabria, Via P. Bucci, Cubo 44A, 87036, Rende, CS, Italy
[c] Department of Chemistry and Chemical Technologies, Via P. Bucci, University of Calabria, Cubo 14D, 87036, Rende, CS, Italy
[d] Fujifilm Manufacturing Europe BV, Oudenstaart 1, P.O. Box 90156, 5000LJ, Tilburg, The Netherlands

HIGHLIGHTS

- Solution ionic strength and composition influence the properties of IEMs.
- Increasing solution ionic strength the membrane water uptake decreases.
- Mg^{2+} has a strong negative impact on CEM resistance and permselectivity.
- A new parameter, called EME, is proposed to predict IEMs performance.

GRAPHICAL ABSTRACT



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ABSTRACT

The electrochemical properties of ion exchange membranes (IEMs) applied for salinity-gradient power (SGP) harvesting, are usually measured using diluited NaCl aqueous solutions because of the prevalence of its constituents ions in natural solutions (e.g. seawater). However, in real applications, the IEMs come in contact with other ionic species than Na^+ and Cl^- that can have a relevant effect on their properties. As a consequence, the obtained results in many cases are not really representative.

The aim of the present study was to investigate the effect of solution concentration and compositions on permselectivity, membrane and interface resistance, for both anion and cation exchange membranes (AEMs and CEMs).

Special attention was paid to the influence of the most common multivalent ions in seawater (Mg^{2+}, Ca^{2+} and SO_4^{2-}) on the electrochemical properties of the AEM and the CEM. It was possible to discriminate the impact on the AEM from that on the CEM. The results highlighted a strong negative effect of Mg^{2+} on the CEM (relevant increase of ionic resistance and permselectivity) and, at minor extent, on the AEM (moderate reduction of permselectivity).

1. Introduction

Ion exchange membranes (IEMs) have consolidated applications

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* Corresponding author.
E-mail address: e.fontananova@itm.cnr.it (E. Fontananova).

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in energy conversion and storage systems, like fuel cells and battery separators. Moreover, in the perspective to address the global need for non-carbon-based and renewable energies [1], salinity-gradient power (SGP) harvesting by reverse electrodialysis (RED), is attracting significant interest in recent years [2].

RED is an emerging IEMs-based energy conversion process able to convert the Gibbs free energy of mixing of two solutions with different salinity, in electrical energy. In a RED stack, anion and cation exchange membranes (CEMs and AEMs) are placed in alternating way to separate streams with different salinity, controlling the ion transport from the concentrated to the diluted compartments. The salinity gradient results in a potential difference over each membrane pair which induces an electrical current to flow through the external electrical load connected to the stack terminal electrodes [3].

The maximum theoretical obtainable energy during the reversible mixing of a diluted stream with a concentrated solution increases with the increasing of solutions concentrations difference. It has been calculated that it ranges from 0.75 to 14.1 kW-hours per cubic meter of diluted solution (fresh water) when shifting from seawater (osmotic pressure 27 bar) to Dead Sea water (osmotic pressure 507 bar) as concentrated solution [2]. However, the increase in global population is leading to a fresh water scarcity, and, in this perspective, the use of alternative diluted solutions than fresh water, is an important issue. A promising alternative proposed is the utilization of seawater and brine as diluted and concentrated streams, respectively [4–9]. In this way it is possible to avoid the use of fresh water, a more and more valuable mankind good. Moreover, the use of concentrated solutions allows to reduce the electrical resistance within the low concentration compartment of the RED stack, boosting the power that can be extracted from the SGP. Furthermore, this strategy could be a way to take the problems of brine disposal in desalination plant [10].

RED applications require membranes specifically designed with low ionic transport resistance and high permselectivity because of the significant role of these electrochemical properties on the RED performance [11–16]. However, these properties are not constant for a given membrane at a certain temperature, but they strongly depend on the concentration and composition of the solutions contacting it with it due to the effect on volume fraction of water and ionic concentration profile in the membrane [17–20]. Fontananova et al. [21] reported that increasing NaCl solution concentration from 0.5 to 4 M the ionic resistance of CEMs increased. This increase was ascribed to the lower ions activity in the membrane phase in comparison with the external solution, which induced the membrane shrinking (reduction of volume fraction of water) with a consequent narrowing of the hydrophilic channels pathway for the ions transport.

The electrochemical properties of the membranes, as well as their performance in RED stack, are usually tested using model solution composed by monovalent single salt solution (e.g. NaCl). However, the real composition of natural solutions, such as river water and seawater are more complex and includes mixture of several monovalent and multivalent ions, as well as, organic matter, depending on the source [22]. A drop down of RED performance is usually observed when shifting from NaCl solutions to real or multicomponent solutions. A RED demonstration plant was constructed in Marsala (Trapani, South of Italy) in a saltworks area, equipped with almost 50 m^2 of membrane and using brackish water and saturated brine from salt ponds as natural feed streams [23], obtaining power density up to 1.6 W/m^2 for cell pair. However, when the RED system was tested with artificial NaCl solutions having total salt concentration similar to the natural feed streams (i.e. 0.03 and 5 M NaCl), a higher power output was observed (up to 2.7 W/m^2 of cell pair). Such differences were attributed to the presence of various multivalent ions in the natural streams having adverse effects on RED performance in comparison with monovalent ions. Hong et al. [24,25] developed a mathematical model of RED systems to study the effect of monovalent and multivalent ions on RED power output. They observed that magnesium sulfate, sodium sulfate, and magnesium chloride in the feed solutions led to a 15–43% lower power density than operating with NaCl solutions, because of an increase of the stack resistance. Post el al [13] highlighted that the presence of Mg^{2+} and SO_4^{2-} ions decreased the open circuit voltage of a laboratory scale RED stack because of the transport of multivalent ions against the activity gradient (this phenomenon is also indicated as uphill transport). Refs. [26,27] also Vermaas et al. [28] reported a significant detrimental effect of Mg^{2+} and SO_4^{2-} ions, in particular in the diluted stream, on the obtained open circuit voltage and power densities of RED systems and they justify these results by a combination of uphill transport and permeation of co-ions through the ion exchange membranes [18].

Tufa et al. [29a] observed a drastic reduction (up to −63%) of the maximum power density when feeding a SGP-RED unit with artificial multi-ion solutions mimicking brackish water and exhaust brine (from 3.04 to 1.13 W/m^2), in comparison with experiments performed with NaCl solutions having similar total salt concentration. Using binary salts solutions it was highlighted that these effects were principally related to the presence of Mg^{2+} ions, with a minor effect of other ions like K^+, Ca^{2+} and SO_4^{2-}. The reduction in RED performance was rationalized by an increase in stack resistance (+75%).

However, to the best of our knowledge, no literature studies are available in which the effects of the multivalent ions on AEMs electrochemical properties were differentiated from those on CEMs in order to correlate different contributions with RED performance.

The present study focuses on the role of the most common multivalent ions in seawater (Mg^{2+}, Ca^{2+} and SO_4^{2-}) on the properties of AEMs and CEMs and their correlation with RED performance. With respect to previous literature works, it was possible to differentiate the impact of multivalent ions on AEMs from that on CEMs by reliable *ex-situ* measurements, less time, energy and material consumption than the direct test in a RED stack of both types of membranes.

Membrane and interface ionic resistance were measured by impedance spectroscopy varying feed ionic compositions and concentration. Moreover, membrane permselectivity was measured in order to have a deeper insight on the electrical behavior of these systems.

PGSE-NMR technique was also used to measure the water self-diffusion coefficients in swelled membrane as a function of the solution composition and temperature. These measurements gave additional important understandings about the effect of multivalent ions on the properties of each membrane type.

A good correlation between the Estimated Membrane Efficiency (EME) parameter proposed in the present work and the maximum power density measured in RED experiments, was observed.

2. Experimental part

2.1. Material

Homogeneous reinforced IEMs produced by Fujifilm Manufacturing Europe B.V were investigated: Fuji-AEM-80045 (from now AEM800) and Fuji-CEM-80050 (from now CEM800). AEM800 and CEM800 have as fixed charged groups quaternary ammonium and sulfonic groups, with ion exchange capacity (IEC) $1.4 \times 10^{-3} \pm 0.0001$ and $1.1 \times 10^{-3} \pm 0.0001$ mol per g of membrane, respectively [21].

Before the use, all the membrane samples (supplied in dry form)