Journal of Membrane Science 477 (2015) 172–182

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Characterization of the isolated active layer of a NF membrane by electrochemical impedance spectroscopy

Anthony Efligenir [a], Patrick Fievet [a,*], Sébastien Déon [a], Roland Salut [b]

[a] Institut UTINAM, UMR CNRS 6213, Université de Franche-Comté, 16 route de Gray, Besançon Cedex 25030, France
[b] Institut FEMTO-ST (UMR CNRS 6174), Centrale de Technologie MIMENTO, Université de Franche-Comté, 18 rue Alain Savary, 25000 Besançon, France

ARTICLE INFO

Article history:
Received 3 October 2014
Received in revised form
22 December 2014
Accepted 28 December 2014
Available online 5 January 2015

Keywords:
Dielectric constant
Electrochemical impedance spectroscopy
Nanofiltration membranes
Polyamide
Conductivity

ABSTRACT

The dielectric and electric properties of the isolated active layer of an NF membrane were determined by electrochemical impedance spectroscopy (EIS). To our knowledge, this was the first attempt aimed at assessing the above properties from measurements performed directly on the active layer alone. Experiments were conducted with Desal DK membrane and various electrolyte solutions (KCl, KI, LiCl, NH_4Cl, $CaCl_2$ and $BaCl_2$) at 10^{-2} mol m^{-3}. The comparison of impedance spectra obtained for the whole membrane and active layer alone revealed very low contribution of the active layer to the overall membrane impedance. The dielectric constant (ε_p) and conductivity (κ_{ca}) inside the pores of the active layer were evaluated from capacity and resistance measurements. The dielectric constant inside the pores was found to be smaller than its bulk value, irrespective of the electrolyte used. The reduction in ε_p was attributed only to confinement effect. It was also shown that pore conductivity exceeded the bulk conductivity. This increased conduction inside the pores could have been due to the excess of counter-ions inside the pores resulting from fixed charges on the pore walls. The present study shows that the dielectric constant inside the pores of the active layer of NF membranes can be determined independently from nano-filtration measurements and without any ambiguity, provided that EIS measurements are performed directly on the isolated active layer.

1. Introduction

Over the past decades, nanofiltration (NF) technology has found a growing number of applications in many areas [1–4], thereby showing its full potential for the separation of small molecules ($< \sim 1000$ Da) and ions. At the same time, intensive research has been conducted on the study of mass transport in NF [5–11] with the aim of identifying the mechanisms involved in solute separation and the development of predictive models. In the first homogeneous transport models, which are based on the extended Nernst–Planck equation to describe the mass transport inside pores and an equilibrium partitioning relation to describe the distribution of species at the entrance and exit of the pores, the Donnan equilibrium was the only electrostatic phenomenon considered in the ion partitioning at the interfaces. Since this mechanism was unable to describe the high rejection rates observed with some NF membranes in the case of ionic solutions containing divalent counterions [10,12,13], non-Donnan mechanisms, namely, the so-called Born effect [14] and dielectric exclusion [15] were, then, included in partitioning equations at membrane/solution interfaces. These improved transport models were found to be able to describe rejection performances of many membranes vis-à-vis single salt solutions and electrolyte mixtures [10,16–19]. However, it should be stressed that the dielectric constant of the solution inside pores was used as a fitting parameter. Although the observed decrease in the dielectric constant inside the pores (with respect to its bulk value) is in qualitative agreement with molecular dynamics simulations showing the effect of confinement on the decrease of this magnitude [20], this parameter has rarely been estimated independently from NF measurements. Yet, such an independent measurement is crucial in definitively validating the lowering of the dielectric constant of a solution inside nanodimensional pores and in reducing the number of fitting parameters for a better evaluation of transport models. The measurement of the dielectric constant of the solution inside the active-layer pores is particularly made difficult by the presence of one or several supporting-layers (which reinforce the membrane mechanically) much thicker than the active layer, which rules the membrane selectivity.

Electrochemical impedance spectroscopy (EIS) (or dielectric spectroscopy) is probably the most powerful non-steady-state method for studying complex heterogeneous systems. It is based on the electrochemical relaxations related to the intrinsic properties of the studied systems. Thanks to strict theoretical analyses, it

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* Corresponding author. Tel.: +33 81 66 20 32.
E-mail address: patrick.fievet@univ-fcomte.fr (P. Fievet).

http://dx.doi.org/10.1016/j.memsci.2014.12.044
0376-7388/

provides permittivity and conductivity of membrane–solution systems, and has been used to investigate the electric and structure properties of synthetic [21–29] and biologic [30,31] membranes. However, very few studies report its use for characterization of NF membranes. Zhao et al. performed dielectric measurements on the NTR7450 NF membrane immersed in different electrolyte solutions at various concentrations [25]. On the basis of characteristics of the dielectric spectra and the Maxwell–Wagner interfacial polarization theory, two relaxations were detected; one was attributed to the interfacial polarization between the membrane and the external solution, whereas the other one to the inhomogeneity of the membrane structure itself. A multiphase dielectric model was used to determine the electric parameters of the two membrane layers. It was found that the capacitance and conductance of the two layers varied with external electrolyte concentration and species in a different manner. The two layers revealed a similar thickness (close to 60 μm) but different looseness (or water content). The double-layer structure of the membrane, consisting of a supporting fabric and an "effective" layer, was thus put in evidence. However, it is not likely that this "effective" layer is the membrane's active layer (i.e., the layer that controls selectivity) due to its too large thickness. Recently, Montalvillo et al. investigated the electric properties of Desal HL NF membrane in a wide range of KCl concentrations [29]. The results presented in Nyquist's complex impedance diagram showed three semi-circles for the membrane–solution system, which were attributed to the solution outside and inside the membrane support (high-frequency semi-circle), the membrane active layer (middle-frequency semi-circle) and the polarization layer in contact with the electrodes (low-frequency semi-circle), whereas the response of the system without the membrane was composed of only two semi-circles. The first semi-circle became larger when the membrane was in place. The increase in its size was then attributed to the membrane support. However, the increase could have also been due to thicker free solution layer, since the contribution of free solution to the impedance was poorly controllable. In order to eliminate the contribution of membrane support, Freger et al. removed it by dissolution and EIS measurements were performed directly with the free active layer placed on a solid electrode surface for characterization [26,27]. This approach was employed by the authors for investigating ion transport in polyamide selective layer of composite reverse osmosis membranes. They found that the capacitance did not vary linearly with the polyamide film resistance, apparently resulting from the non-uniform structure of the films and more complex polarization mechanisms, which precluded the use of the model of ideal dielectric capacitor.

In this paper, we used a similar approach to that of Freger et al., i.e. the membrane support was also removed by dissolution, whereas the free active layer was placed between two columns of liquid mercury for EIS measurements. The aim of the present work was to show the possibility of determining the dielectric constant of a solution confined inside nanodimensional pores from EIS measurements. To this end, experiments were conducted with the free active layer of a commercial NF membrane soaked with various salt solutions. The mean pore size and thickness-to-porosity ratio of the active layer were first determined from neutral solute rejection and water permeability measurements, respectively. The active layer porosity was, then, deduced from its thickness and thickness-to-porosity ratio. Establishing these parameters made it possible for the dielectric constant and conductivity inside nanopores to be determined. To our knowledge, this is the first attempt at determining these parameters from EIS measurements performed on the active layer alone.

It should be noted that the theoretical aspects of application of EIS to synthetic membranes have been widely developed in the literature (for example, such information can be found in [26]). That is why no theoretical section was included in the present paper.

2. Experimental section

2.1. Membranes and solutions

EIS measurements were performed with a commercially available membrane, labelled Desal DK (GE Osmonics). This membrane is a flat thin-film composite membrane with a polyamide top layer (active layer) supported on a polysulfone intermediate layer (this intermediate layer will be referenced as "the support layer") and a non-woven fabric.

For rejection experiments, a glucose solution at 10 mol m^{-3} was filtrated through the membrane. The solution was prepared from milli-Q quality water (conductivity less than 1 μS cm^{-1}). The pH of solutions was 5.9 ± 0.2 without any adjustment.

For EIS measurements, 10^{-2} mol m^{-3} electrolyte solutions were prepared from milli-Q quality water. The salts used were KCl, KI, LiCl, NH_4Cl, $CaCl_2$, $BaCl_2$ of pure analytical grade (Fisher Scientific). The pH of solutions was 5.9 ± 0.2 without any adjustment and their conductivity was in the range 1.9–3.3 μS cm^{-1}.

2.2. Filtration experiments and chemical analyses

Filtration experiments were conducted with a semi-industrial pilot plant equipped with the Osmonics Sepa CF II cell, which uses flat sheet membranes of 140 cm^2. This set-up was detailed in a previous paper [32]. Experiments were performed at transmembrane pressures ranging from 3 to 17 bars and at cross-flow velocities ranging from of 0.97 to 1.96 m s^{-1}. The temperature of the feed solution was maintained constant at 25 ± 1 °C by a heat exchanger. Retentate and permeate streams were recycled in the feed tank in order to work with a constant feed concentration. Permeate samples were weighted and analyzed for each transmembrane pressure to determine the volume flux and its composition. Samples were taken after a time sufficient to reach steady-state conditions (from 15 to 90 min depending on the applied pressure).

A correct determination of the membrane pore radius requires the knowledge of the intrinsic rejection rate. Therefore, the intrinsic rejection curves were calculated from the observed rejection data, which were measured experimentally in the presence of concentration polarization phenomenon, by the so-called velocity variation method (VVM) [33]. Rejection experiments were performed at four cross-flow velocities (0.972, 1.325, 1.688 and 1.963 m/s) and the observed rejection rates were extrapolated at infinite cross-flow velocity (see Fig. S1 in Supplementary information) by means of the film model [34], which relates the observed rejection rate to the intrinsic one. In this work, the Schock–Miquel correlation was used because of its large range of validity [35].

Before performing water permeability and rejection rate measurements, the membrane was washed (in order to release the excess of chemicals attached at the membrane sheet) and conditioned (in order to get an equal reference state) at 25 °C with a cross-flow velocity of 1.96 m s^{-1} according to the following protocol: (1) washing with HCl solution (pH=3.0) for 30 min at 20 bars; (2) demineralized water (milli-Q quality water) rinse; (3) washing with demineralized water for 30 min at 20 bars; (4) washing with NaOH solution (pH=9.0) for 30 min at 20 bars; (5) demineralized water rinse; (6) washing with demineralized water for 30 min at 20 bars.