Effect of homogenization and hydrophobization of a cation-exchange membrane surface on its scaling in the presence of calcium and magnesium chlorides during electrodialysis

M.A. Andreeva[a,b], V.V. Gil[b], N.D. Pismenskaya[b], V.V. Nikonenko[b,*], L. Dammak[a], C. Larchet[a], D. Grande[a], N.A. Kononenko[b]

[a] Institut de Chimie et des Matériaux Paris-Est (ICMPE) UMR 7182 CNRS – Université Paris-Est, 2 Rue Henri Dunant, 94320 Thiais, France
[b] Kuban State University, 149 Stavropolskaya st., 350040 Krasnodar, Russia

A B S T R A C T

In this paper, two cation-exchange membranes, i.e. MK-40 and MK-40$_{MOD}$, were studied by chronopotentiometry and voltammetry, MK-40$_{MOD}$ being obtained by covering the heterogeneous surface of a commercial MK-40 membrane with a homogeneous 20 μm thick Nafion® film. Electrodialysis process was realized in an electro-dialysis flow-through laboratory cell, in which the cation-exchange membrane under study formed a desalina-tion chamber with an auxiliary anion-exchange (Neosepta AMX-SB) membrane. 0.02 M and 0.04 M solutions of CaCl$_2$, MgCl$_2$ and NaCl were used. The current densities were changed in the range from 0.25 i_{lim}^{th} to 2.5 i_{lim}^{th}, where the theoretical limiting current density, i_{lim}^{th}, was calculated using the Leveque equation. The potential drop over the modified MK-40$_{MOD}$ membrane and the water splitting at this membrane turned out to be lower in all studied cases. Formation of scaling was observed only in the case of the MK-40/0.04 M MgCl$_2$ system at current densities in the range from 1.1 i_{lim}^{th} to 1.4 i_{lim}^{th}. For these current densities, the (quasi)steady state value of potential drop slowly increased with time and the crystals of Mg(OH)$_2$ were found on the ion-exchange particles embedded onto the MK-40 membrane surface facing the desalination chamber. At higher currents, stronger electroconvection at this membrane and higher water splitting at the AMX-SB membrane (the latter providing lower pH in the desalination chamber) prevented scaling. No scaling was found on the modified membrane at any current. It is due to the Nafion® film, which is relatively more hydrophobic than pristine MK-40 and which provides a "better" distribution of current lines near the surface, thus enhancing electroconvection and de-creasing water splitting.

1. Introduction

Electrodialysis (ED) with ion-exchange membranes (IEMs) is one of the efficient methods for water desalination and solution concentration [1,2]. It is reasonable to use this method in combination with reverse osmosis (RO) in brackish water desalination [3,4]. Ultrapure water and ultra-concentrated electrolyte solutions can be obtained by means of this hybrid process. Conventional ED can also be coupled with bipolar membrane ED to generate bases and acids from salts [5], or even pro-tein recovery from the tofu whey [6]. Two other important ED appli-cations are developed: casein production in milk industry [7,8] and tartaric stabilization of wines [9].

In ED, due to different ion transport numbers in the membrane and solution, concentration polarization (CP) occurs [10]. This phenom-enon can result in salt precipitation on the membrane surface facing the concentration and/or desalination chambers [7,10,11]. The scaling layer reduces the effective surface area of the membrane, which causes additional resistance to the flow and mass transfer. The scaling phe-nomenon can be aggravated by membrane fouling in presence of or-ganic matters (proteins, sugars, polyphenols, tannins…) [12,13].

CaCO$_3$ and CaSO$_4$ are generally the main salts, which form a pre-cipitate on the membrane surfaces during ED of seawater, [14]. The fouling layer consisting of CaCO$_3$, Mg(OH)$_2$, and Ca(OH)$_2$ forms on cation-exchange membrane (CEM) interfaces during electromembrane

processes used in dairy industry [15]. In the 1950's, Ionics started experiments with systems which showed a radical improvement in scaling control [16]. They proposed to use ED reversal process (EDR), which results in the prevention of calcium carbonate and calcium sulfate scale formation. It was found that EDR may be successfully applied to the production of sodium chloride from the seawater [10,17]. The key moment in the EDR is the changing of the electrode polarity and the flow direction at the same time [1,10,16]. The desalination chambers become concentration chambers, and vice versa. The disadvantage of this method is the loss in the current efficiency, capacity and in the final product during the operation of electrode polarity changing.

Pulsed electric field (PEF) modes are proposed as another effective way for combating the consequences of CP, such as the scaling formation at IEM interfaces [18,19]. In this regime the pulses of current or voltage alternate with pauses. Karlin et al. [20], Sistat et al. [21], Mikhaylin et al. [7] showed that the duration of pulse and pause lapses affects essentially the amount and the composition of the salt deposits. During pause lapses, the concentration depolarization occurs. As a result, the electric resistance of depleted solution reduces [22] and the salt deposits dissolve, at least partially. Electroconvection (EC) plays an important role in this process. EC appears as a result of the action of electric field on the space electric charge at the membrane surface. The transfer of solution by EC intensifies the exchange between the near-surface solution layer and the bulk solution [23–26] and contributes to reducing scaling [27].

A modification of a membrane surface by a layer selective to the transfer of singly charged ions is another option, which can be used for mitigation of the scaling and fouling. It is known that the deposition of organic substances on the membrane surface can be reduced when the membrane is covered with a thin ion-conductive layer bearing a fixed charge opposite to the charge of the supporting membrane matrix [28]. As a result, the resistance of the composite membrane is increasing towards multiply charged counter-ions, which causes scaling. A similar effect is obtained by modification of the membrane surface with high-molecular surface active substances [29].

Asraf-Snir et al. [30,31] investigated the effect of IEM surface structure on gypsum scale formation. They found that in the case of heterogeneous anion-exchange MA-40 membrane, the scale formation occurs mainly on the surface of conductive areas, which are ion-exchange resin beads incorporated in the polyethylene supporting matrix. The amount of deposit is essentially lower on the surface of a homogeneous anion-exchange AMV membrane [30,31]. Moreover, the scale forms not only on the heterogeneous membrane surface, but within its macropores also. Based on the latter results [30,31], it can be expected that coating a homogeneous conductive film on a heterogeneous membrane surface could improve its resistance towards fouling.

In practice, the casting of conductive perfluorinated resin solution of Nafion® or its Russian analogue MF-4SK on the surface of a cation-exchange membrane leads to the growth of limiting current density by 1.5 times in comparison with unmodified membrane [32–34]. This effect is explained by a better distribution of the current lines after the surface modification. Besides, the membrane surface becomes relatively more hydrophobic that is beneficial for EC [34,35].

The positive effect of application a homogeneous film to the membrane surface is supported by theoretical studies of Rubinstein et al. [36]. The current lines are distorted in solution near an electrically heterogeneous surface: they are accumulated at the conductive areas causing higher CP [36], which should lead to increasing scale formation. It is shown [36] that application of a homogeneous conductive layer on heterogeneous surface diminishes the effect of formation of funnel-shaped distribution of current lines in the solution near the membrane surface. Even a very thin and weakly charged conductive layer results in homogenization of current lines distribution over the membrane surface and in the near-surface solution. As a consequence, the CP at the membrane surface decreases and the limiting current density increases [36].

In the present paper, we study the effect of surface modification of a heterogeneous cation-exchange MK-40 membrane with a thin film of Nafion® on the scale formation. From the literature reviewed above, it can be expected that the application of a thin homogeneous and relatively hydrophobic layer on the surface of a heterogeneous membrane would produce a double effect: it will reduce CP due to homogenization of the current density distribution over the membrane surface, and will stimulate EC. As a consequence, the rate of salt precipitation should be lower than that at the pristine heterogeneous membrane.

Despite the extensive literature in this field, the effect of modification of heterogeneous membranes by a thin conductive homogeneous layer on scaling process has not been studied yet. We will explore this effect in calcium and magnesium chloride solutions of different concentrations.

2. Experimental

Two cation-exchange membranes were used in this study. The MK-40 membrane (Shchekinoazot, Russia) is a heterogeneous membrane containing sulfonic acid fixed groups. It is produced by hot pressing from the mixture of dispersed cation-exchange resin KU-2 and polyethylene as a binder filler. About 80% of the MK-40 surface is covered by polyethylene [37] (Fig. 1a). The size of ion-exchange KU-2 resin particles is 10–50 µm. These particles form "hills" of 5–6 µm height on the membrane surface mainly covered by polyethylene. The height of hills was determined by focusing the optical microscope consecutively on the tops and bottoms of the membrane surface relief (Fig. 1b). The MK-40$_{MOD}$ membrane (Fig. 1c) is obtained by coating the MK-40 membrane surface with a homogeneous film obtained from a Nafion® perfluorinated resin solution after evaporation of the solvent in an oven at 80 °C [33]. The film thickness in the dry state is 12–15 µm (Fig. 1d). The copolymer film covering the surface of the MK-40$_{MOD}$ membrane does not include non-conductive macroscopic regions, but it is not perfectly smooth. The difference in height between peaks and valleys for this membrane is about 2 µm.

The bulk and surface properties of the MK-40 and the MK-40$_{MOD}$ membranes were previously described elsewhere [33]. After modification, the ion-exchange capacity, electrical conductivity and diffusion permeability vary only slightly, within the margin of experimental error. In contrast, the conductive surface fraction of MK-40$_{MOD}$ becomes 100% instead of 20% for the pristine membrane, and the contact angle increases from 55° to 64° (± 3°) [33,34]. The contact angle characterizes hydrophobic/hydrophilic balance of an ion-exchange membrane surface. It depends on the fixed ions, which attract water molecules, and on the matrix polymer material not containing fixed charged groups. Generally, the morphology of ion-exchange membranes (or the resins constituting the main part of them) may be presented as a system of hydrophilic conducting channels confined within a hydrophobic polymer phase [38]. When comparing the surface of Nafion and MK-40, one can distinguish there hydrophobic and hydrophilic areas. The perfluorinated matrix of Nafion is rather hydrophobic. The contact angle of Teflon having the same chemical structure as the Nafion matrix is 115°. The surface fraction of pore mouths forming hydrophilic areas of the surface can be evaluated as about 20% (equal to the water content in the membrane). Two main components of MK-40 membrane are polystyrene (making the matrix in KU-2 cation-exchange resin) and polyethylene. Polyethylene covers about 80% of the MK-40, however, its contact angle (about 92°) is essentially lower than that of Teflon. The contact angle of polystyrene is 86°, however, the exchange capacity (5.0 meq/g dry) and water content (43–53%) of KU-2 [39] are much higher than respective parameters of Nafion (0.83 meq g^{-1} dry and 22% [40]). Thus, the surface areas occupied by the particles of KU-2 on the MK-40 are quite hydrophilic. As a result, the surface of MK-40 is more hydrophilic than that of Nafion.

A flow-through four-chamber ED cell shown in Fig. 2 was used in the study. The central desalination chamber (3) was formed by an