



Impact of cation-exchange membrane scaling nature on the electrochemical characteristics of membrane system

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ABSTRACT

The membrane fouling formation during electro dialysis of complex solutions is one of the main issues affecting the process performance and costs. This work was focused on the investigation of electrochemical behavior of membrane systems containing a cation-exchange membrane whose surface was affected by mineral fouling of different composition. Together with the scaled membranes, the pristine membrane was studied for comparison.

For membrane without scaling on its surface, it was found that the limiting current value exceeded the one theoretically calculated by the convection-diffusion model. It is most likely related to equilibrium electroconvection developed at the membrane surface. The presence of magnesium and calcium hydroxides on the membrane surface leads to an intensification of water splitting at the depleted membrane surface, resulting in suppression of electroconvection and reduction of the overlimiting current. The presence of calcium carbonate on top of magnesium and calcium hydroxides prevents their contact with water molecules. The current-voltage characteristic of such membrane system was almost identical to the characteristics of the membrane system containing the pristine membrane. To our knowledge, it was the first time that the impact of scaling nature on the electrochemical behavior of membrane system was revealed and the relative mechanisms identified and explained.

1. Introduction

Electromembrane methods for separation and purification are increasingly used in industries (e.g. medicine, agriculture and food) dealing with solutions containing large amounts of dissolved components [1–3]. Thus, separation by electro dialysis (ED) in conjunction with other membrane methods is used for the treatment of sea water [4], industrial brackish water [5], fruit juice [6], wine [7], milk and whey [8], purification and separation of proteins [8], etc.

However, the large number of ionic and molecular components present in the treated solutions, including calcium or magnesium ions and particles entering the protolytic reactions (e.g., carbonate, phosphate ions) entails the formation of a fouling on ion-exchange membranes (IEMs). Previous researches on ED separation of model salt solutions close to the milk mineral content [9] and milk [10] have shown that scaling formation on the surface of the cation-exchange membrane (CEM) is a major concern of electromembrane separation. The formation of scaling leads to an increase in membrane resistance, resulting in

an energy consumption increase, to a reduction of mass transfer, thereby decreasing the process efficiency. Moreover, scaling impacts severely the life duration of the membrane and consequently the cost of the process [11–13]. During ED separation of solutions with high Ca^{2+} and Mg^{2+} content, the scaling on CEM surface is formed largely on the concentrate side [9] due to the high pH value favorable for the mineral precipitation. However, scaling can appear on the diluate side of CEM but in substantially lower quantities [9], but its influence on the electrochemical behavior of the membrane system can be significant. The scaling formation on the diluate side of the IEM reduces the membrane working area and leads to an increase in the local current density of the conductive region. This in turn can reduce the limiting current value [14] at which the concentration of counter-ions at the membrane solution interface from the side of desalting channel becomes close to zero. In addition, the formation of metal hydroxides on the membrane surface can also affect the mass transfer mechanism at overlimiting currents due to their participation in the catalytic reaction of water dissociation [15].

Abbreviations: CEM, cation-exchange membrane; CVC, current-voltage characteristic; ED, electro dialysis; EDL, electric double layer; EDS, energy dispersive X-ray spectroscopy; IEM, ion-exchange membrane; SEM, scanning electron microscopy; XRD, X-ray diffraction analysis

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Furthermore, the scaling formation on the concentrate side of the membrane becomes significant in the EDR system, when the concentration channel becomes a desalination channel after the polarity reversal. The scale formed on the surface of the membrane facing the concentrating channel on the first cycle will affect the electrochemical behavior of the membrane system in the second cycle, when this scale appears from the desalination channel side. In this case, the quantity and composition of the scale on the membrane side facing the concentration channel can play an essential role in the functioning of the membrane system. All these aspects should be considered when selecting the current regime and the composition of treated solution.

Previous works involving model salt solutions [9] and skim milk [10], investigated the nature of membrane scaling and its impact on global ED performance, such as current efficiency, system resistance, etc.. The effect of physico-chemical properties of cation-exchange membranes on the quantity and composition of precipitate on their surface was studied in [16]. However, the detailed comparative study of electrochemical characteristics of a pristine membrane and the membrane with a scale on its surface was not undertaken. The aim of this work is to find out how the occurrence of a scale on the membrane surface affects its current-voltage characteristic and the current-induced pH variation of the depleted solution at the membrane surface. A special importance is given to the dependence of these characteristics on the nature of scaling agents such as compounds of Ca^{2+} and Mg^{2+} ions.

2. Experimental part

The study is conducted in three stages. The first stage aims the formation of scaling of different compositions on the CEM surface by treating model salts solutions by ED: in the first case, a scaling contains a mixture of magnesium hydroxide and calcium carbonate and in the second case, a scaling mainly composes of magnesium hydroxide with traces of calcium hydroxide. In the second stage, the surfaces of original and fouled CEMs are analyzed using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). Finally, in a third stage, the electrochemical behaviors of the membrane systems, containing control and fouled membranes, are studied by voltammetry techniques. Additionally, the pH of the solution near the CEM surface in the desalting channel is measured. The scale formed on CEM surface is unstable: during the electrochemical measurements when the membrane is bathed in a solution, the amount of the scale crystals decreases with time. The period of time where the scale quantity and, consequently, the membrane properties does not change significantly is about 8 hours. The latter has determined the duration of experimental investigation of a scaled membrane sample in conditions of bathing solution.

2.1. Formation of a scaling on the membrane surface

Scaling formation at the surface of the cation-exchange membrane Neosepta CMX-SB (Astom, Tokyo, Japan) is conducted in a laboratory Microflow-type cell (Electro-Cell AB, Täby, Sweden) under the conditions described in [17]. In particular, ED is carried out at an over-limiting current density (40 mA/cm^2) in batch mode. This current density is chosen in order to promote scaling generation when water splitting and current-induced convection occurred. The ED treatments are conducted until the maximum voltage capacity of the power supply (62.5 V) is reached [18].

The experiments are carried out, in triplicate, for both solution compositions in the desalting channel. For a scaling composed of a mixture of calcium carbonate and magnesium hydroxide, the solution circulating in the desalting channel is composed of Na_2CO_3 (1000 mg/L), KCl (800 mg/L), CaCl_2 (800 mg/L) and MgCl_2 (452 mg/L). The diluate model salt solution (330 ml) circulates at a flow rate of 600 mL/min (Fig. 1). The concentrate solution contains a 2 g/L KCl (330 mL, 600 mL/min), the pH is maintained constant (pH = 12) during the

whole ED process by manual additions of NaOH (1 M) to ensure the continuous precipitation of minerals [9,19]. It should be noted that in real operating system, the pH is maintained at lower values to prevent scaling. In this work, conditions were specially created for accelerating the formation of scale on the membrane surface: the pH in the concentration channel was kept high enough to produce a precipitation of minerals in large amounts over a short period.

A 20 g/L NaCl (500 mL, 900 mL/min) solution circulates in the channels adjacent to the electrodes. The solutions are prepared just before the beginning of ED treatment. The initial pH of the model salt solution is fixed at 6.5 by manual addition of HCl (1 M).

The CMX-SB membrane containing on its surface the scale formed under the conditions described above is named as CMX-SB-S1. In the second case, the diluate solution composition is the same, but without Na_2CO_3 , to exclude the formation of carbonate salts. In this case, the membrane/scale system is designated as CMX-SB-S2.

As a result of ED treatments, both CMX-SB-S1 and CMX-SB-S2 membrane/scale “sandwiches” contains a scale deposit on both sides. Thereafter, the analysis of only the scale on the concentrate membrane side is conducted, since the deposit amount on this side significantly exceeds that on the diluate side, as previously was observed in similar conditions [9,17,18].

2.2. Membranes analyses

2.2.1. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)

Images of membrane concentrate side are taken with a scanning electron microscope JEOL (Japan Electro Optic Laboratory, model JSM840A, Peabody, Massachusetts, USA) equipped with an energy dispersive spectrometer (Princeton Gamma Tech., Princeton, New Jersey, USA). The EDS conditions are 15 kV accelerating voltage with a 13-mm working distance. The dried samples of initial and fouled membranes are coated with a thin layer of gold/palladium in order to make them electrically conductive and to improve the quality of the microscopy photographs [18]. For EDS X-ray analysis, membrane sample preparation is the same like for SEM.

2.2.2. X-ray diffraction

The analyses of the dry CEMs (drying procedure like for SEM) are performed by X-ray powder diffraction using a D5000 Siemens diffractometer (Montreal, QC, Canada) equipped with a curved graphite crystal monochromator and a goniometer theta-theta (in reflection) with a rotating sample holder. The radiation source (Cu K_α) is a copper lamp with a wavelength of $\lambda = 1.5406 \text{ \AA}$. The K_α radiation of copper is generated at 30 mA and 40 kV. The scan rate of $0.02^\circ (2\theta)$ is applied to record patterns for 2θ ranging between 20° and 70° , with a counting time of 1.2 s per step.

2.2.3. Voltammetry and pH measurement

The fouled membranes are tested in a 0.02 M NaCl solution using a laboratory cell previously described in [20]. The cell is equipped with special input and output solution devices allowing the formation of a laminar flow regime in each channel. Thereby, the theoretical value of the limiting current is calculated by the L ev eque equation [21]

$$i_{\text{lim}}^{\text{theor}} = 1.47 \frac{FDC}{h(T_1 - t_1)} \left(\frac{h^2 V}{LD} \right)^{1/3}, \quad (1)$$

where F is the Faraday number; D is the electrolyte diffusion coefficient; C is the input concentration of electrolyte; L is the desalting channel length; h is the intermembrane distance; V is the linear flow velocity of the model solution; T_1 and t_1 are the effective transport number of counter-ions in the membrane and their transport number in a solution, respectively.

The fouled CMX-SB-S1 and CMX-SB-S2 membranes are placed in the

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