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Ageing of ion-exchange membranes used in an electrodialysis for food industry: SEM, EDX, and limiting current investigations

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ABSTRACT

Ion-exchange membranes, used in some food industrial electrodialysis (ED) applications, were investigated by measuring their physicochemical and structural parameters, in order to evaluate their evolution during this application. Two used membranes (one cationic and one anionic) were analyzed at the end of their useful life (two years of ED operation) and compared with their respective fresh new samples to assess the evolution of their structural and physicochemical characteristics, and explore their deterioration. The limiting current density, ion-exchange capacity, water content, and contact angle values were determined for each new and used membrane. Scanning electron microscopy and energy dispersive X-ray were also performed. The used cation-exchange membranes (CEMs) suffered from significant degradation; nonetheless, it was generally more robust and resistant than the anion-exchange counterpart, which was more unstable. A significant degradation in the polymer matrix of both membrane types was found. Both used CEMs and anion-exchange membranes (AEMs) lost a part of ion-exchange sites, and the different parameters show a fouling of the AEM and a loss of functional sites of the CEM.

Keywords: Ion-exchange membrane; Ageing; Electrodialysis; Limiting current density; SEM; EDX

1. Introduction

For many years, electrodialysis (ED) has been used on a large industrial scale for water desalination, wastewater treatment [1], and has a large number of applications in biotechnology as well as in food [2] and beverage industry. In the dairy industry, ED is used for food industry using ion-exchange membranes [3]. However, very few studies have been conducted to develop reliable protocols for characterization and control of these membranes during their life cycle. Often manufacturers are resigned to watch the dropping of the membrane performance in the processes. Thus, the ageing mechanisms of materials and factors that influence their development remain unknown.

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The published information on ion-exchange membranes (IEM) ageing is scarce, and especially for the membranes used in ED for food industry applications. Some studies concerning the characterization of membranes at the end of their lifetime in ED and the effect of cleaning agents or stress conditions have been carried out [4–12]. Dammak et al. [5] have performed an artificial ageing of two membranes (a homogeneous one (MX) and a heterogeneous one (MK-40)) under oxidizing conditions, i.e. in peracetic acid, and in P3 Active Oxanias solutions, cleaning agents commonly used in industrial ED for food industry applications. It established an increase in conductivity and swelling rate, resulting from the modification of the polymer chain structure, without a significant deterioration of the functional groups, since the ion-exchange capacity remained almost constant. In another recent work, Ghalloussi et al. [6] have compared the electrolyte permeability and tensile strength of two IEM pairs. Each pair was composed of a new sample and a used one extracted from an electrodialyzer after 2 years of operation.

The authors observed a sevenfold decrease in the permeability of membranes after their use in a food industrial application, and a significant decrease in the tensile strength, which was more important for the anion-exchange membranes (AEMs) (eightfold) than for the cation-exchange membranes (CEMs) (1.5 times). They also observed inhibition and disappearance of a large part of membrane functional sites, as well as polymer degradation and fouling by organic species present in the solution.

In the present paper, two pairs of IEMs are compared, namely one pair of CEM and another of AEM. Each pair is constituted of a new sample and a sample used for 2 years in an ED process for food industry. This investigation focuses on the comparison of physicochemical and structural properties.

The limiting current density, ion-exchange capacity, water content and contact angle values were determined for each new and used membrane. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) were also performed in order to identify the main origins of the difference in the behavior of the studied membranes.

2. Methods

Two Neosepta® membranes (a CEM and an AEM) were analyzed at the end of their life cycle (after two - years of use in an ED process for food industry and named CEMU and AEMU, respectively,) and compared with the corresponding new samples (CEMN and AEMN) to understand the evolution of their physicochemical and structural parameters and to explain their ageing. The limiting current density, the exchange capacity, the water content, and the contact angle were determined for each new and used membrane. SEM and EDX were also performed.

2.1. Equilibrium an dynamic characteristics

2.1.1. Ion-exchange capacity

The ion-exchange capacity is the number of functional sites per gram of dry membrane. This parameter was determined following the NF X 45-200. The CEM samples were placed in a 1 M HCl solution. The samples were then abundantly washed with water; they were converted into the Na^+ form by soaking them in a solution obtained from mixing 230.0 mL of a 0.1 M NaCl and 20.0 mL of a 0.1 M NaOH solutions, during 2 h at 25°C. The ion-exchange capacities (E_C) were determined by titration of the remaining OH^- ions and expressed as the amount of sorbed H^+ (meq g^{-1} dry).

The AEM samples were placed in a 0.1 M HCl solution. The samples were also abundantly washed with water; they were immersed in a 1.0 M HNO_3 solution during 12 h at 25°C. The ion-exchange capacity was determined by the chloride content in the equilibrium solution.

2.1.2. Water uptake

Samples were separated from the stabilization solution, and the excess of external liquid was removed by placing them between two foils of filter paper and pressing slightly for the measurement of the wet mass W_a. And the dry mass W_b was obtained by drying the samples at 60°C for 24 h. The water uptake was then found as follows: $\% W = \frac{W_a - W_b}{W_b} \times 100$.

Before measurement, the membranes were soaked during 24 h at 25°C in an electrolyte solution (0.1 M NaCl for the CEM and 0.1 M HCl for the AEM).

2.1.3. Membrane thickness

The membrane thickness (T_m) was measured using a Käfer Thickness Dial Gauge specially devised for plastic film thickness measurements with a resolution of 1 μm. The membrane thickness value was averaged from measurements of 10 different locations on the effective surface region of the membrane.

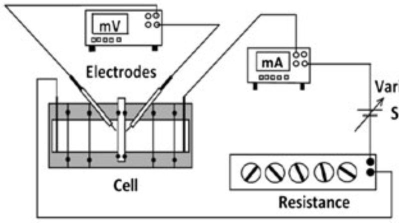

Fig. 1. Experimental setup for measuring the diffusion limitating current.

2.1.4. Contact angle

The measurements of the contact angle values were performed using a FM40 EasyDrop device from Krüss. The images of a water drop at the surface of the membrane were captured by a high resolution camera, and they were then processed by the Wingoutte software to determine the contact angle value using interpolation methods.

The measurements were repeated five times at different spots of the dry membrane at room temperature (just the bound water was remaining). The contact angle was determined as an average value of five measurements.

2.1.5. Limiting current density

In order to determine the diffusion of the limit current, we conducted measurements of the potential difference variation as a function of injected current intensity, which allowed us to determine the current–voltage characteristics in a steady state, and to therefore measure/deduct the current limit.

That said, we used a cell called "Guillou's cell" [13], which geometry ensure perfect orthogonality of the current lines with the face of the membrane faces (Fig. 1).

2.2. Structural characteristic by SEM and EDX

Samples used for the structural investigation were vacuum dried overnight at 40°C, before measurements. SEM image were obtained from Pt/Pd coated

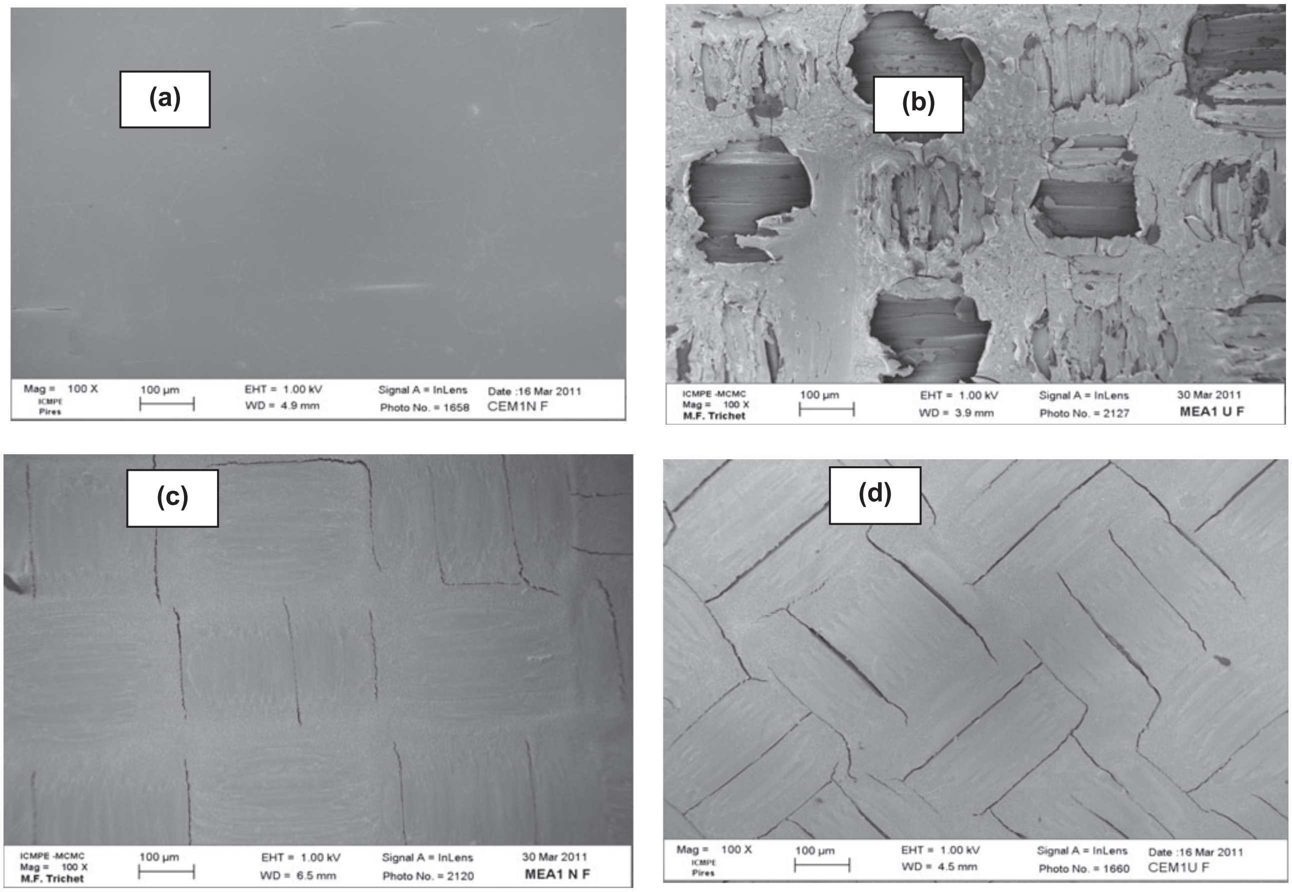

Fig. 2. SEM micrographs of new and used CEM ((a) and (b)) and new and used AEM ((c) and (d)).

Table 1
Static and dynamic characteristics of the studied membranes: exchange capacity (E_C), water content (%W), thickness (T), contact angle (θ°), and limit current ($I_{\lim}$)

	CEM		AEM	
Membranes	CEMN	CEMU	AEMN	AEMU
E_C (meq g^{-1} of dry IEM)	2.66	0.77	1.45	0.23
%W	28.2	23.7	28.7	40.3
T (μm)	176	160	148	344
θ (°)	38 ± 2	79 ± 2	69 ± 2	52 ± 2
$I_{\lim}$ (mA cm^{-2})	14.0	14.6	12.1	6.1

samples with an accelerating tension of 3 keV using a LEO 1530 microscope. The surface elemental composition of the samples was also determined by EDX spectroscopy with a 10 mm germanium diode as an X-ray detector (I_{mix}, Princeton Gamma-Tech) attached to the SEM equipment.

3. Results

The SEM pictures of new and used membranes are shown in Fig. 2. As it can be seen, the surface of new Neosepta® membranes is smooth and homogeneous. The surface of used CEM presents some "scales" showing that the membrane becomes fragile. The surface of used swollen membrane is smooth, but when the membrane dries, the scales appear.

The surface of AEM shows important structural defects. Formed cavities are large enough that the reinforcing cloth is exposed. Evidently, such strong deterioration of membrane structure should be accompanied without less significant changes in membrane properties [10].

The main equilibrium and transport characteristics of the IEMs under study are listed in Table 1.

This table shows that the exchange capacity of the two types of membranes decreased significantly after two years of use in the ED process. There was a significant variation in the contact angle values of the CEM and in the ion-exchange capacity. However, there was a moderate decrease in the water content and the membrane thickness, and a slight increase in the limiting current. The AEM seems to be the most affected, as shown by the decrease in the exchange capacity, the contact angle and the limiting current, accompanied by a sharp increase in water content and thickness.

The contact angle of CEM increased significantly after the ED operation, thus showing that the membrane became less hydrophilic. This is consistent with the decrease in the water content. The loss of water and the increase in surface hydrophobicity apparently arose from the reduction in the concentration of active functional sites resulting from their detachment.

For the AEM membrane, the decrease was more significant. This is confirmed by a sharp increase in the water content and in the membrane thickness. Taking into account that the ion-exchange capacity decreased, this effect might be due to the sorption of highly hydrophilic substances, which could be organic acids with hydrophilic groups such as carboxyl and hydroxyl ones.

4. Discussion

Analysis of current–voltage curves is made according to the model of Lee et al. [14]. These authors based on the evolution of three parameters (limiting current density, limiting current density ratio R3/R1, and plateau ΔV) concluded the presence or absence of fouling in the IEMs.

Fig. 3 shows general current–voltage curves, which are divided into three distinctive regions. Region I is

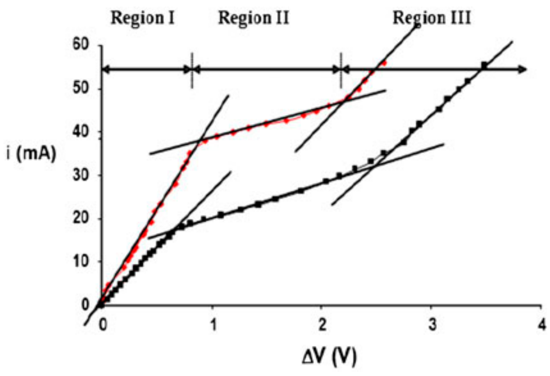

Fig. 3. Example of operating curves current potential according the model of Lee et al. [14].

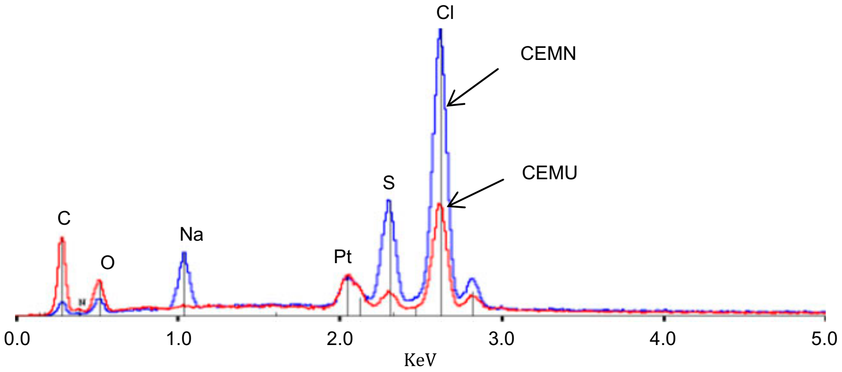

Fig. 4. EDX analysis of the new and used CEM.

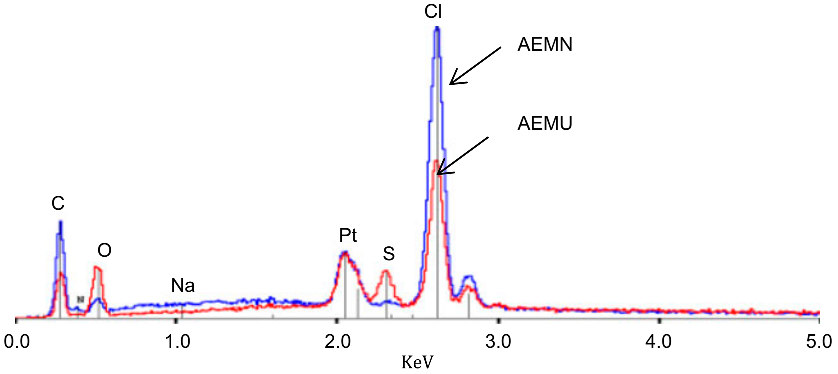

Fig. 5. EDX analysis of the new and used AEM.

the Ohmic region, which is governed by the Ohm's law. As the current density increases, the concentration depletion on the membrane surface occurs, which is referred to as the limiting current region in the Region II. The limiting current density is the maximum current density to transfer all ions through the ion-exchange membrane. A plateau is observed in the current–voltage curve in this region. The slope of the curve increases again and eventually reaches an asymptotic value in the Region III.

We have found that all the three indicators point to the confirmation of a significant fouling of the AEM. This fouling was a consequence of the overlay of organic ions on the surface of the membrane thus causing a decrease in the contact angle values. For the CEM, the slight increase of the I_{lim} indicated no fouling on the membrane surface. The strong change in its exchange capacity can be explained by a loss of functional sites.

To confirm these findings an elemental analysis was performed. According to the spectra of Figs. 4 and 5 there was a presence of an organic fouling from the treated solution (increase in peak oxygen and sulfur), and there was a loss of functional sites ($-SO_3^-$ of the CEM as shown by the decrease in peaks corresponding to sulfur (Fig. 4).

From Fig. 5, we observe a significant decrease in the intensity of the nitrogen peak of AEMs. This decrease is due to loss of some quaternary ammonium functional sites. This observation is entirely consistent with the measurements of the exchange capacity which significantly decreased.

5. Conclusion

This paper provides an insight into the understanding of ageing of a CEM and an AEM used in ED processes for the food industry involving organic acids.

However, the CEM is generally more robust and resistant than the anion-exchange counterparts. The structure and properties of CEM end AEM vary in different ways. The CEM become denser, their water content and thickness decrease, and the surface becomes more hydrophobic. Apparently, it is due to the loss of hydrophilic ion-exchange sites.

For the AEM, the surface hydrophilicity increases since its water content and its thickness increase essentially in the course of ED. This behavior can be explained by sorption of organic colloidal particles within membrane nanopores. As these particles are generally hydrophilic, they attract water which leads to higher swelling. However, the higher swelling of AEM leads to the rupture of some bonds and polymer chains. As a result, structure macro-defects (fissures, cavities, and caverns) filled with external solution appear in the membranes

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