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Effect of ionizing radiation on a ceramic microporous membrane

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Abstract

Characteristic transport and interfacial parameters for a microfiltration ZrO_2/Al_2O_3 membrane (sample Z100S) were obtained from filtration, membrane potential and streaming potential measurements, which were carried out with the membrane in contact with different NaCl solutions, while membrane chemical surface was analyzed by XPS spectra. Electrical parameters indicate a weak electropositive character for the studied membrane.

Z100S sample was modified by gamma-irradiation (dose of 10 J/kg) delivered by a ^{60}Co Unit (membrane Z100S-Ir10). A comparison of the results obtained with pristine and irradiated samples shows: (i) ion transport numbers and electrical interfacial parameter (zeta potential) modification (anionic permselectivity increases from 9% for the untreated membrane to 23% for the irradiated sample); (ii) a decrease in the hydrodynamic permeability (around 10%); (iii) a reduction (18% approximately) in the atomic concentration of carbon, a non-characteristic membrane material element attributed basically to membrane manufacture. The presence of this element in the membrane structure could be directly related to the observed modifications, affecting the membrane behaviour as a result of the irradiation itself or associated to local heating effect.

Keyword: Membranes; Al_2O_3; Electrical properties; Impedance; Gamma-irradiation

1. Introduction

The development of inorganic membranes (metal and ceramic membranes) started at the end of the 1940s in connection with uranium concentration for power generating plants. Tubular composite membranes formed by a porous support and one or more layers of decreasing pore diameter plus an active or separating layer, which covered the internal surface of the tube, were used for diffusional gas separation.[1] Nowadays, flexible and flat ceramic membranes (similar morphology than polymeric membranes) for liquid filtration and new membrane processes (energy storage) are available.[2,3] The use of ceramic membranes for microfiltration and ultrafiltration solutions used in food and pharmaceutical industries is of great interest due to the fouling problems associated to those processes and solutions (adsorption or deposition of macromolecules on the membrane pores/surface), which strongly reduces the volume flow and makes necessary the use of hard chemical and high temperature in the cleaning procedures, causing the damage of polymeric membranes.[4] In fact, the ability of ceramic membranes to resist repeated sterilization cycles without damage is a basic point for their use when biotechnological species are involved since they assure longer operation life, which can compensate their higher cost. Since radiation (UV light and γ-radiation) are standard sterilization procedures in those systems, its possible effect on membrane characteristic parameters (transport and/or electrical parameters) and chemical modification should be well established in order to have a better knowledge of membrane–solution interactions and its performance under different working conditions.

In this work, transport and chemical surface characterization of a composite ZrO_2/Al_2O_3 flat membrane for ultrafiltration is carried out, and changes associated to membrane irradiation are considered. Chemical surface characterization was performed by X-ray photoelectron spectroscopy (XPS), while transport/electrical parameters such as hydraulic permeability, ion transport number, permselectivity and zeta potential were determined from volume flow, membrane potential and streaming potential, which were measured with the membranes in contact with NaCl solutions at different concentrations. The comparison of results obtained with untreated and irradiated

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samples allows the estimation of membrane changes caused by ionizing radiation.

2. Experimental

2.1. Membranes and solutions

A microporous ceramic membrane with planar geometry Z100S (CREAFILTER, Degussa, Germany) and composite structure formed by a fibrous stain steel network covered by a sublayer of Al_2O_3 particles plus an external layer of ZrO_2 was studied. Geometrical parameters submitted by the suppliers are[2]: average thickness of 80 μm and pore size of 100 nm.

Some membrane samples were treated with ionizing radiation delivered by a therapeutic ^{60}Co Unit (average photon energy of 1.27 MeV) as is described in Ref. 5, the irradiation procedure used permits us to ensure the dose received by the membrane. A dose of 10 J/kg was delivered, being the irradiation rate of 0.55 J/kg min; the irradiated sample will hereafter be named as Z100S-Ir10.

Electrochemical measurements were carried out with the membranes in contact with aqueous NaCl solutions at different concentrations ($10^{-3} \leq C(\mathrm{M}) \leq 10^{-1}$), at room temperature $t = (25.0 \pm 0.5)\,^{\circ}\mathrm{C}$ and standard pH (5.9 ± 0.4). Before use, the membranes were immersed for at least 8 h in a solution of the appropriate concentration.

2.2. Chemical and morphological surface characterization of membranes

Surface chemical characterization was carried out by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics PHI 5700 spectrometer with a non-monochromatic Mg Kα radiation (300 W, 15 kV, 1253.6 eV) as excitation source. High-resolution spectra were recorded at 45° take-off-angle by a concentric hemispherical analyser operating in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Charge referencing was done against aliphatic/aromatic carbon[6] (C 1s 285.0 eV). Survey spectra in the range 0–1200 eV were also recorded at 187.85 eV of pass energy. Software package used for data acquisition, analysis and atomic concentration percentages (A.C.) determination of the membrane surface elements are described in detail elsewhere.[7]

Micrographs of the membrane surface were obtained by a JEOL JSM-6400 scanning electron microscope; the samples were coated with a thin layer of gold before microscopy examination.

2.3. Hydrodynamic permeability and membrane potential measurements

Hydraulic permeability was determined from volume flux (J_v) measurements carried out in a tangential test-cell (Minitan S, Millipore), the membrane having an area of $59 \times 10^{-4}\,\mathrm{m}^2$. The applied pressure ranged between 2×10^4 and 10^5 Pa. Measurements were performed with water and NaCl solutions at four different concentrations ($0.005 \leq C(\mathrm{M}) \leq 0.1$).

The dead-end test cell used for membrane potential measurements is similar to that described elsewhere.[8] The electromotive force (ΔE) between both sides of the membranes caused by a concentration gradient was measured by two reversible Ag/AgCl electrodes connected to a digital voltmeter (Yokohama 7552, 1GΩ input resistance). Measurements were carried out by keeping the concentration of the solution at one side of the membrane (C_1) constant, and gradually changing the concentration of the solution at the other side (C_2) from 10^{-3} to 0.1 M. Measurements were made with two different C_1 values: 5×10^{-3} and 10^{-2} M.

2.4. Electrokinetic characterization of the membranes/solution interface

The electrical potential difference between both sides of the membranes due to the movement of the electrolyte solution under a pressure difference (ΔP) or streaming potential (ΔV_{st}) was measured with an EKA analyser (Anton Parr, GmBH, Graz, Austria). The equipment basically consists of: (i) a cylindrical cell with two Ag/AgCl electrodes provided of small holes to permit the solution flow through them and the membrane; (ii) a mechanical drive unit to produce and measure the pressure that drives the electrolyte solution ($10^4 \leq \Delta P(\mathrm{Pa}) \leq 3.5 \times 10^4$). Detailed description of EKA analyser and experimental procedure is made in Ref. 9. Measurements were carried out varying the NaCl concentration ($5 \times 10^{-4} \leq C(\mathrm{M}) \leq 0.01$). The streaming potential values presented correspond to the average of at least 10 measurements.

3. Results and discussion

Modification in membrane transport parameters associated to irradiation can be determined by measuring hydrodynamic permeability and membrane potential.[4] The hydrodynamic permeability, L_p, is the parameter commonly used for membrane characterization since it establishes the relationship between the pressure difference applied to a membrane, ΔP, and the water (or solution) volume flow, J_v, that is[4]: $J_v = L_p \Delta P$. Fig. 1a shows the volume flow versus applied pressure for Z100S and Z100S-Ir10 membranes at different solution concentrations; L_p was obtained from the slopes of the straight-lines shown in Fig. 1a and its variation with the NaCl concentration is shown in Fig. 1b. A reduction in L_p values for the irradiated sample can be observed, being the permeability ratio $L_p(\text{Z100S-Ir10})/L_p(\text{Z100S}) = (0.90 \pm 0.08)$, which indicates slight membrane modification as a result of radiation. It should be pointed out that a decrease in membrane permeability as a result of temperature treatment was also obtained in a previous work[8] with a similar ceramic membrane but low pore size (25 nm).

Membranes potential, $\Delta \Phi_{\mathrm{m}}$, is the electrical potential difference at both sides of a membrane separating two solutions of the same electrolyte but different concentrations (C_1 and C_2). For porous and weakly charged membranes, membrane potential can be considered as the diffusion potential ($\Delta \Phi_{\mathrm{dif}}$) due to the different mobility of ions in the membrane, and its expression

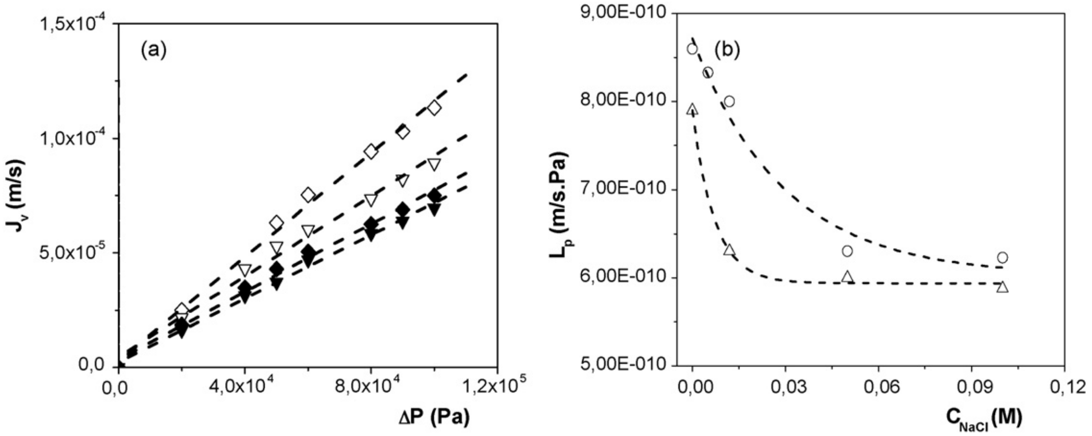

Fig. 1. (a) Volume flux (J_v) vs. applied pressure difference (ΔP). Membrane Z100S: (◇) water; (◆) feed solution 0.05 M NaCl. Membrane Z100S-Ir10: (▽) water; (▼) feed solution 0.05 M NaCl. (b) Variation of hydrodynamic permeability, L_p, with electrolyte concentration: (◯) membrane Z100S; (△) membrane Z100S-Ir10.

for 1:1 electrolytes and diluted solutions is[10]:

$$\Delta\Phi_m \approx \Delta\Phi_{dif} = \left(\frac{RT}{F}\right)[t_- - t_+]\ln\left(\frac{C_1}{C_2}\right) = \left(\frac{RT}{F}\right)[1 - 2t_+]\ln\left(\frac{C_1}{C_2}\right) \quad (1)$$

where t_i is the transport number of ion i in the membrane, z_i its valence (i = + for cation, − for anion); R and F are the gas and Faraday constants and T is the thermodynamic temperature. Ion transport number, t_i, represents the amount of current transported for one ion with respect to the total current crossing the membrane, $t_i = I_i/I_T$, that is, $t_+ + t_- = 1$ and $t_- - t_+ = (1 - 2t_+)$. Eq. (1) indicates a linear dependence between $\Delta\Phi_m$ and $\ln(C_1/C_2)$, and it allows the estimation of the ion transport numbers in the membrane from membrane potential at different concentration ratio. Membrane potentials, $\Delta\Phi_m$, were obtained from measured potential difference (ΔE) by subtracting the electrode potential[10]: $\Delta\Phi_e = -(RT/z_-F)\ln(C_1/C_2)$, that is: $\Delta\Phi_m = \Delta E - \Delta\Phi_e$.

Experimental membrane potential values as a function of $\ln(C_1/C_2)$ for Z100S and Z100S-Ir10 membranes at both constant concentrations studied are shown in Fig. 2. From the slopes of these straight-lines the average cationic transport number in the membrane $\langle t_+\rangle$ at each constant concentration was determined, and their values are indicated in Table 1. As can be observed, $\langle t_+\rangle$ values hardly depend on constant concentration but lower values for the irradiated sample were obtained. Moreover, lower cation transport number across both membranes than in solution was obtained ($t^{o}_{Na^+} t^{\circ}_{Na}{}^{+} \approx 0.385$), which may be due to the presence of a small positive charge in the membranes causing the exclusion of co-ions (cations). This effect is usually quantified by determining the membrane ionic permselectivity, $S(i)$, which is a measure of the selectivity of counter-ions (anions, in this case) over co-ions in a membrane, and it can be determined by[11]:

$$S(-) = \frac{t_- - t^{o}_{-}}{1 - t^{o}_{-}} \quad (2)$$

where t^{o}_{-} represents the anion transport number in solution. Ionic permselectivity values for both membranes are also indicated in Table 1, where the increase of $S(-)$ for the irradiated sample can be observed.

Membrane permeability and transport number results indicate changes in transport parameters across the membrane as a consequence of γ-irradiation, but both might be caused by a reduction in the pore size (morphological effect) without change in the membrane charge[12] (electrical modification). To elucidate this point an electrokinetic characterization of the pore wall/electrolyte solution by measuring streaming potential was carried out. Streaming potential (ΔV_{st}) is the electrical potential difference between the two ends of a capillary or channel

Table 1
Average membrane cation transport number, $\langle t_+\rangle$ and anionic permselectivity, $\langle S(-)\rangle$

Membrane	$\langle t_+\rangle$ C_1 = 0.005 M	$\langle t_+\rangle$ C_1 = 0.01 M	$\langle S(-)\rangle$ (%)
Z100S	0.353 ± 0.002	0.347 ± 0.006	9.1 ± 0.2
Z100S-Ir10	0.288 ± 0.003	0.302 ± 0.004	23.4 ± 0.6

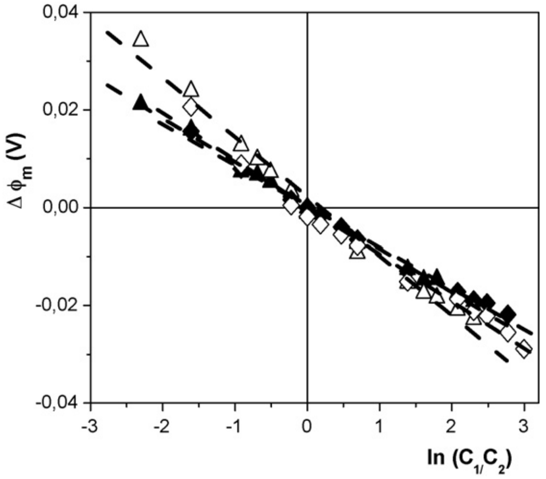

Fig. 2. Membrane potential vs. $\ln(C_2/C_1)$. C_1 = cte = 0.005 M: (◆) membrane Z100S, (◇) membrane Z100S-Ir10; C_1 = cte = 0.01 M: membrane Z100S (▲), membrane Z100S-Ir10 (△).

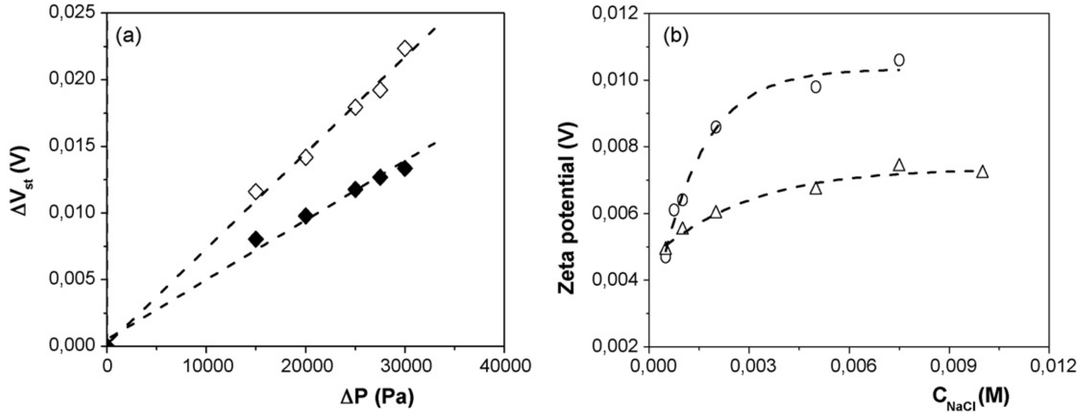

Fig. 3. (a) Streaming potential, ΔV_{st}, vs. applied pressure difference, ΔP, for membranes Z100S (♦) and Z100S-Ir10 (◊), at a given solution (0.002 M NaCl). (b) Zeta potential (ζ) vs. NaCl concentration: (△) membrane Z100S, (○) membrane Z100S-Ir10.

caused by the movement of an electrolyte solution by a pressure difference (ΔP) under steady state conditions (that is, $I = 0$).[13–16] Fig. 3a shows streaming potential-applied pressure linear relationships for both membranes, where differences depending on the sample can be observed. Zeta potential (ζ) or electrical potential at the shear plane can be determined by the Helmholtz–Smoluchowski equation[13] (for wide pore membranes) by using the slope, $(\Delta V_{st}/\Delta P)_{I=0}$, of the straight lines shown in Fig. 3a by:

$$\zeta = \left(\frac{\lambda_o \eta}{\varepsilon_o \varepsilon_r}\right)\left(\frac{\Delta V_{st}}{\Delta P}\right)_{I=0} \qquad (3)$$

where λ_o and η are the liquid conductivity and viscosity, respectively; ε_o is the permittivity of vacuum and ε_r is the relative dielectric constant of the electrolyte solution. Variation of zeta potential with salt concentration is shown in Fig. 3b for ZS100 and ZS100-Ir10 samples, where differences in the membrane/solution interface associated to electrical modification of the membrane matrix can be observed; this result indicates higher electrokinetic surface charge density for the irradiated sample.[13] It should also be pointed out that the positive values of zeta potential obtained for both membranes supports the positive effective charge attributed to Z100S and Z100-Ir10 samples from membrane potential results.

Membrane surface chemical modification as a result of membrane irradiation can be estimated from XPS measurements. Relative atomic concentrations (A.C.%) of the elements present in the surface of Z100S and Z100S-Ir10 samples were determined by XPS analysis and the percentages obtained are indicated in Table 2, which correspond to the average of three different samples. Other non-characteristic membrane elements (nitrogen, silica, etc.) were also found (A.C. < 0.5%), which are considered impurities associated to environmental contamination or membrane manufacturing processes[17] and they are not indicated in Table 2; however, due to the high atomic concentration percentage of carbon its value is also given in Table 2. The presence of this element on the membrane surface can partially be associated to environmental contamination but the use of organic compounds for membrane manufacture must also be considered.[17] As can be observed, there is a slight excess of oxygen in both samples according to the steochiometry (49.5% for Z100S and 50.5% for Z100S-Ir10), probably due to impurities. Although these results established the presence of ZrO_2 on the membrane surfaces, it does not form a layer covering the alumina support (as was indicated by the suppliers) but it could be mainly embedded into the alumina sublayer. Fig. 4 shows a SEM micrograph of the Z100S membrane surface which confirms this point.

Table 2
Atomic concentration percentages of different elements on the surface of ceramic ZS100 and ZS100-Ir10 membranes

Membrane	⟨C 1s⟩ (%)	⟨O 1s⟩ (%)	⟨Al 2p⟩ (%)	⟨Zr 3d⟩ (%)
ZS100	16.0 ± 1.5	51.6 ± 1.0	29.9 ± 0.8	2.5 ± 0.1
ZS100-Ir10	12.9 ± 1.0	54.2 ± 0.7	30.7 ± 0.7	2.2 ± 0.1

Fig. 5 shows a comparison of C 1s core level for Z100S and Z100S-Ir10 samples, where only slight differences in the intensity of peaks can be observed. The same behaviour was obtained with the other membrane surface elements, and the B.E. of the maxima are indicated in Table 2. In fact, the most

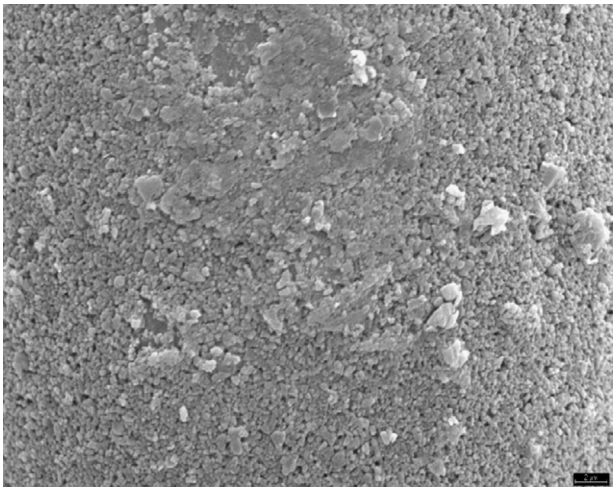

Fig. 4. SEM micrograph of the Z100S membrane surface (black line length = 2 μm).

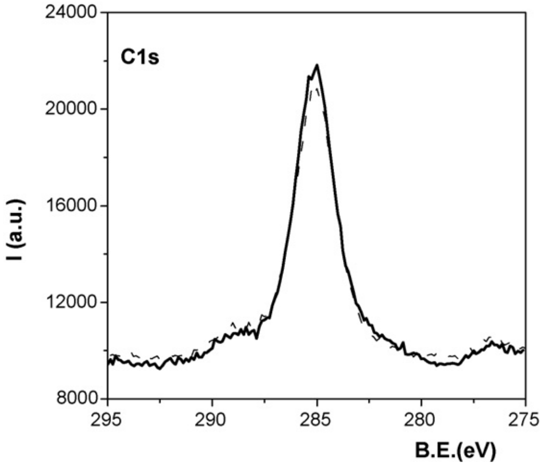

Fig. 5. C 1s core level for membranes Z100S (solid line) and Z100S-Ir10 (dotted line).

significant effect of membrane irradiation is the reduction in the carbon atomic concentration (around 18%), which is attributed to surface cleaning effect associated to radiation as was already reported for polymeric membranes.[17] Taking into account carbon atomic concentration percentage indicated in Table 2 and the binding energy (and symmetry) of the peak shown in Fig. 5, the permanent presence of an organic compound (particle binder or precursor) on the surface of the ceramic membranes can be assumed.

4. Conclusions

A flat and flexible microporous composite ceramic membrane (ZrO_2/Al_2O_3) for liquid filtration application has been characterized by XPS, transport parameters (hydraulic permeability and ion transport number/permselectivity) and membrane–solution electrical interfacial interactions (zeta potential). The weak electropositive character exhibits by the membrane makes it adequate for application in separation of positively charged macromolecules or cations.

Modification caused in the membrane by ionizing radiation (1.27 MeV average electron energy and a doses of 10 J/g) was established. Results show changes in membrane transport and interfacial parameters, which causes a decrease of diffusional permeability and an increase of membrane permselectivity, which indicates both morphological and electrical modifications, and it is of interest for application of ceramic membranes in filtration of biotechnological solutions in connection with membrane cleaning/sterilization procedures.

The presence of an organic compound on the membrane surface determined by XPS analysis could explain the reduction of hydrodynamic permeability for the irradiated sample by partial occlusion of pore size as a result of the radiation itself or the associated heating effect.

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