

Composite Membranes of Cellulose Acetate and Zirconium Dioxide: Preparation and Study of Physicochemical Characteristics

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The composite membranes of zirconium oxide–cellulose acetate were prepared in a two-step procedure combining the phase-inversion method and deposition-hydrolysis technique. The first step allowed the preparation of membranes with different morphologies, and the second step allowed a highly dispersed metal oxide to be deposited on the membranes. The XPS O1s binding energy indicated that the interaction between the oxide and the cellulose matrix is probably of hydrogen bonding type. Phosphate retentions were 75 and 90% for the composite membrane in permeation experiments. The water fluxes for a pressure of 1.7 atm were $(3.7 \pm 1.7) \times 10^{-2}$ and $(13.0 \pm 2.1) \times 10^{-2}$ mL min⁻¹ cm⁻². The membranes are very stable under continuous use. Regeneration of the membrane using NaOH 0.01 M eluent solution did not decrease significantly, ca. 10%, the membrane efficiency. The great advantage of these membranes is the low operational pressure required to obtain high phosphate retention.

Introduction

Polymer–oxide composite materials have been used as multitask materials, where the polymer mechanical properties are combined with the chemisorptive and catalytic properties of the oxide. Many studies of these materials in wastewater treatments,^{1,2} chemical purification and separations,^{3–5} support for enzymes,^{6–8} and ceramic precursors⁹ have been made.

Fibers of cellulose have been coated with ZrO₂ or TiO₂ by dipping the fibers in the metal solutions.^{1,10–12} In this process the oxides are dispersed on the surface of the fibers as particles or thin films. Depending on the solvent and the precursor used, the resulting composite

materials may be used as adsorbent for chemical separations and as support for enzyme immobilization.^{2,4–9,13}

The preparation and properties of the zirconium oxide/cellulose composite membrane are described in this work. The main objective was to develop an alternative procedure for the preparation of this material incorporating the advantages of the phase inversion method to prepare membranes with the alkoxide deposition–hydrolysis method. The morphology, the oxide dispersion in the polymer and the polymer–oxide interaction were studied.

The selective retention of phosphate ion by zirconium oxide has been examined in natural waters.^{1,4} This was the reason to use zirconium oxide to cover the cellulose acetate. The serious environmental problems related with algae's proliferation caused by the presence of phosphate chemical species in natural waters motivated the investigation the polymer/oxide composite membrane in the retention of phosphate ion from aqueous solutions.

Experimental Procedures

Composite Preparations. The materials were prepared by a two-step procedure. The polymeric membrane was first prepared by the phase-inversion method,^{14–19} from two differ-

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Table 1. Incorporation of the Zr in the Membrane

samples	imm. time/min	Zr/wt %
Ac/Zr/S1	3	0.16 ± 0.05
Ac/Zr/S1	6	0.59 ± 0.05
Ac/Zr/S2	6	0.51 ± 0.05
Ac/Zr/S1	9	0.33 ± 0.05
Ac/Zr/S1	12	0.32 ± 0.05
Ac/Zr/S1	20	0.25 ± 0.05

ent casting solution compositions (in weight percent) S1: 13% cellulose acetate (Rhodia Co., substitution degree equal to 2.45), 27% acetate acid, and 60% dry acetone; S2: 11% cellulose acetate, 23% acetic acid, 43% dry acetone, and 23% distilled water. The membranes were prepared by casting a polymer solution on a glass plate, in a fume hood, and allowing the solvent to evaporate at room temperature for approximately 30 s. The film-covered glass was then immersed in a water bath. In the second step, the membranes were immersed in 2.2 wt % Zr(PrO)₄ propanol solutions and then immersed in 9 × 10⁻⁴ M HNO₃ aqueous solution, in order to hydrolyze the metal alkoxyde.

Caution: Acetone is toxic and flammable, and acetic acid is an irritant and toxic. Zr(PrO)₄ propanol solutions are toxic and flammable. All the steps of this procedure **must be** made in a fume hood. Use of gloves is recommended. The waste of the propoxide deposition is treated with HNO₃ acid solution, and the zirconium oxide formed is filtered.

The contact time of the membrane with the Zr(PrO)₄ was controlled in the preparations since it determines the quantities of incorporated metal. Table 1 summarizes the results obtained for Ac/Zr/S1 membrane. After 6 min of immersion, a decrease of the incorporated metal oxide was observed because of metal oxide detachment from the surface at higher loading. The membranes Ac/Zr/S1 and Ac/Zr/S2 having 0.51 and 0.59 Zr wt %, respectively, were used throughout this work.

Phosphate Permeation. The permeation of the membrane by phosphate ions was determined. Concentrations of 2 and 2.5 ppm of the phosphate solutions at pH 5.8 were used. The solutions were pumped through the membrane at a pressure of 1.7 atm and 298 K. The phosphate ion retention by the membrane was determined by using

$$R(\%) = (1 - C_d/C_a) \times 100$$

where C_d is the phosphate concentration of the solution after passing through the membrane and C_a is the initial phosphate solution concentration. The phosphorus concentrations in the solutions were determined by the conventional phosphomolybdic method.

Cross-Polarization Magic Angle Spinning ³¹P Nuclear Magnetic Resonance. The nuclear magnetic resonance was obtained on a Bruker AC/P 300 spectrometer with a solid-state probe. The ground samples were put in a zirconia rotor at 4500 Hz spinning rate. The chemical shift was referenced to 85% phosphoric acid signal.

X-ray Photoelectron Spectroscopy (XPS). The XPS measurements were carried out on a McPherson spectrometer at a pressure of 2 × 10⁻⁷ Torr. The binding energies were referenced to the hydrocarbon C1s binding energy at 284.6 eV, used as the internal standard. The confidence interval of the binding energies is ±0.3 eV. The binding energy peaks were deconvoluted using the Gaussian functions and a least-squares curve-fitting program. The atomic ratios were calculated using the Scofield cross sections and the area under the deconvoluted peaks. The confidence interval is ±20%.²⁰

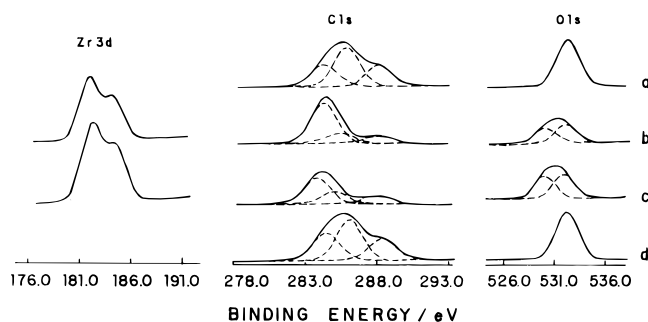


Figure 1. C1s, O1s, and Zr3d XPS peaks of pure cellulose acetate membrane (a), Ac/Zr/S1 (b), Ac/Zr/S2 (c), and Ac/Zr/S1 used after 5 turnovers and reactivated with NaOH 0.01 M (d).

Table 2. XPS Binding Energies for Pure and Composite Membranes

samples	binding energies/eV					atomic ratios Zr/O ^b
	O ^a	O ^b	C ^a	C ^b	C ^c	
Ac ^a	532.6		288.6	284.6	284.6	
Ac/Zr/S2	532.0	530.1	288.6	285.7	284.6	0.5
Ac/Zr/S1	532.1	530.3	288.8	285.8	284.6	0.5
Ac/Zr/S2 ^b	532.5		288.5	286.5	284.6	

^a Pure membrane. ^b Composite membrane after 5 turnovers.

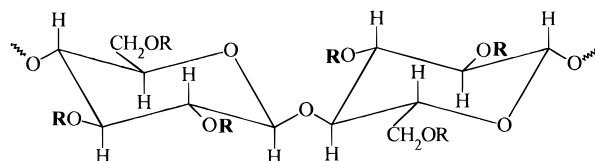


Figure 2. Monomeric unit of cellulose acetate, where R = CH₃CO-, acetyl, or -H group.

Zirconium Analysis. The quantity of zirconium in the matrix was determined using an X-ray fluorescence equipment from Tracor Northern X-ray fluorimeter equipped with an energy-dispersive solid-state detector.

Scanning Electron Microscopy. The micrographies were obtained by using a JEOL JSM T300 scanning electron microscope using a secondary electrons detector for topographic images or a Tracor Northern Series II X-ray energy-dispersive spectrometer (EDS) for X-ray mapping.

Transmission Electron Microscopy. The transmission electron micrographies were obtained by using a ZEISS CEM-902 microscope. The membranes were embedded in an Med-cast Quick-Mix epoxy resin (Ted Pella, Inc.) and cured at 318 K during 6 h and at 333 K during 18 h. The resulting blocks were cut in a Leica cryoultramicrotome to supply an ultrathin cross section (ca. 80 nm) for TEM observation.

Results and Discussion

XPS. The C1s XPS features of the pure cellulose acetate and of the composite membranes show an asymmetric shape which by deconvolution resulted in three Gaussian peaks (Figure 1). The C1s binding energies of the pure cellulose acetate and the composite membranes are listed in Table 2.

For the pure cellulose acetate, the C1s binding energies can be assigned as follow: the peak at 286.3 eV is due to the carbon atoms in the C—O—H and C—O—C moieties (C^b) and at 288.6 eV due to the carbon atom in O—C=O and O—C—O moieties (C^a).²¹ The line peak at 284.6 eV is due to the reference carbon of the hydrocarbon (C^c) and —CH₃ carbons of acetyl groups in Figure 2. For samples Ac/Zr/S1 and Ac/Zr/S2 the C^b binding energies are shifted to 285.8 and 285.7 eV, respectively, upon coating the fiber surface by the oxide.

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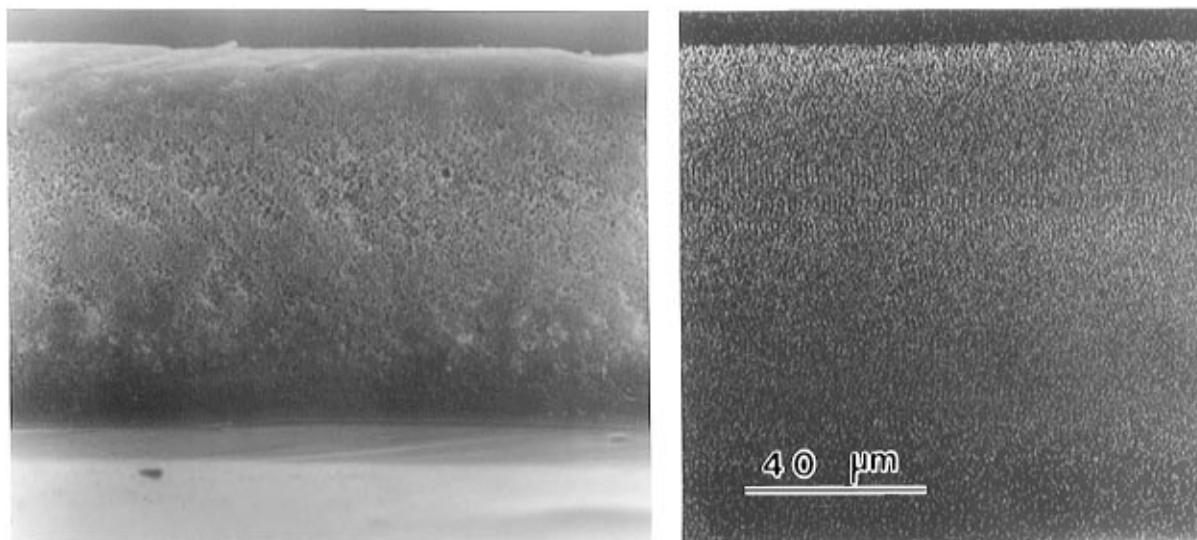


Figure 3. Scanning electron micrographs of Ac/Zr/S1: (A, left) by secondary electron image (SEI); (B, right) Zr X-ray emission dot map obtained with X-ray fluorescence microprobe; zirconium are the white points. The scale is the same for both micrographs.

The O1s binding energy peak appears as a symmetric band for the pure polymer and as an asymmetric band for the composite polymer (Figure 1). Upon deconvolution of the band in the second case, two peaks can be distinguished, 530.3 and 532.1 eV for Ac/Zr/S1 and 530.1 and 532.0 eV for Ac/Zr/S2. The lower energy peak is assigned to the ZrO_2 O1s binding energy (O^b) and the other to the cellulose oxygen atom (O^a).^{21,22} It is important to note that O^a 1s binding energy in the composite membrane is lower than that observed in the untreated cellulose acetate. This shift to lower energy indicates that in the composite membrane O^a has a higher electronic density than in the untreated membrane. This shift could be to the hydrogen bonding interaction, $-\text{O}^a\text{H}\cdots\text{O}^b\text{Zr}$, where $-\text{O}^a\text{H}$ is the nonacetylated group of the cellulose acetate bonded to the cellulose acetate matrix.²³ This interaction is possible because the oxygen atom on zirconium is basic (isoelectric point of ZrO_2 is 6.7²⁴). The present conclusion is similar to that suggested by Kennedy et al.²⁵

The zirconium $3d_{3/2}$ and $3d_{5/2}$ binding energies for Ac/Zr/S1 and Ac/Zr/S2, both observed at 184.8 and 182.4 eV, are the same as those quoted for ZrO_2 ²² and ZrO_2 supported on α -cellulose.¹⁰ The composition of the coating metal oxide for both composite materials agree with the ZrO_2 formulae since the atomic ratio Zr/O^b is 0.5 ± 0.1 (Table 2).

Micrography. The scanning electron micrographs of the membranes Ac/Zr/S1 and Ac/Zr/S2 are shown in Figures 3A and 4A, respectively. The Ac/Zr/S1 membrane shows a dense skin on the top side and a relative homogeneous pore distribution over all membrane cross sections. The average pore dimensions are about $3 \mu\text{m}$ and the average membrane thickness is about $90 \mu\text{m}$. The Ac/Zr/S2 membrane shown in Figure 4A has an

asymmetric morphology characterized by a dense skin supported on a finger pore structure. The total average thickness of this membrane is approximately $150 \mu\text{m}$.

The zirconium oxide distribution in both membranes appears in Figures 3B and 4B as dot map patterns indicating the uniform dispersion of oxide in the polymeric matrix. Oxide agglomeration was not observed within the magnification range used to obtain the micrographs. Figure 5 shows a TEM micrograph of the Ac/Zr/S1 membrane. The higher magnification of the membrane cross section shows a porous structure embedded in an epoxy resin (marked E). The darker points in this micrograph (marked O) reveal a uniform distribution of very small oxide particles in the membrane polymeric matrix.

Phosphate Permeation. The permeation experiments of the phosphate ions (2.5 ppm solutions) through the membranes were carried out for both Ac/Zr/S1 and Ac/Zr/S2 composite materials using a pressure of 1.7 atm. The resulting fluxes were $(3.7 \pm 1.7) \times 10^{-2}$ and $(13.0 \pm 2.1) \times 10^{-2} \text{ mL min}^{-1} \text{ cm}^{-2}$, for Ac/Zr/S1 and Ac/Zr/S2, respectively, and $(55.0 \pm 5.5) \times 10^{-2} \text{ mL min}^{-1} \text{ cm}^{-2}$ for the pure S1 cellulose acetate membrane. The phosphate retention in these conditions was 90 and 75%, respectively, while for untreated membrane no retention was observed. The difference observed in these retentions can be accounted for the contact times of the solution with the solid phase. The higher contact time for the Ac/Zr/S1 membrane due to a more dense structure, as was shown before, resulted its higher retention.

Since the rejection is observed only for the composite membrane, clearly the adsorption sites on zirconium oxide surface are responsible for the phosphate retention. However, it is known that other factors contributing to the retention may arise by repulsion of the ions in the solution phase surface by the electrically charged species adsorbed on the surface.¹⁵ Qualitative information of how of both effects can contribute on the membrane permeation was obtained by CP MAS ^{31}P NMR spectrum of phosphate adsorbed on the composite membrane. Figure 6 shows two peaks with chemical shift at -22.2 and 5.2 ppm corresponding to the species $\text{Zr}(\text{HPO}_4)_2$ and HPO_4^{2-} respectively.²⁶⁻²⁸ The retention is therefore a result of the adsorption of part of

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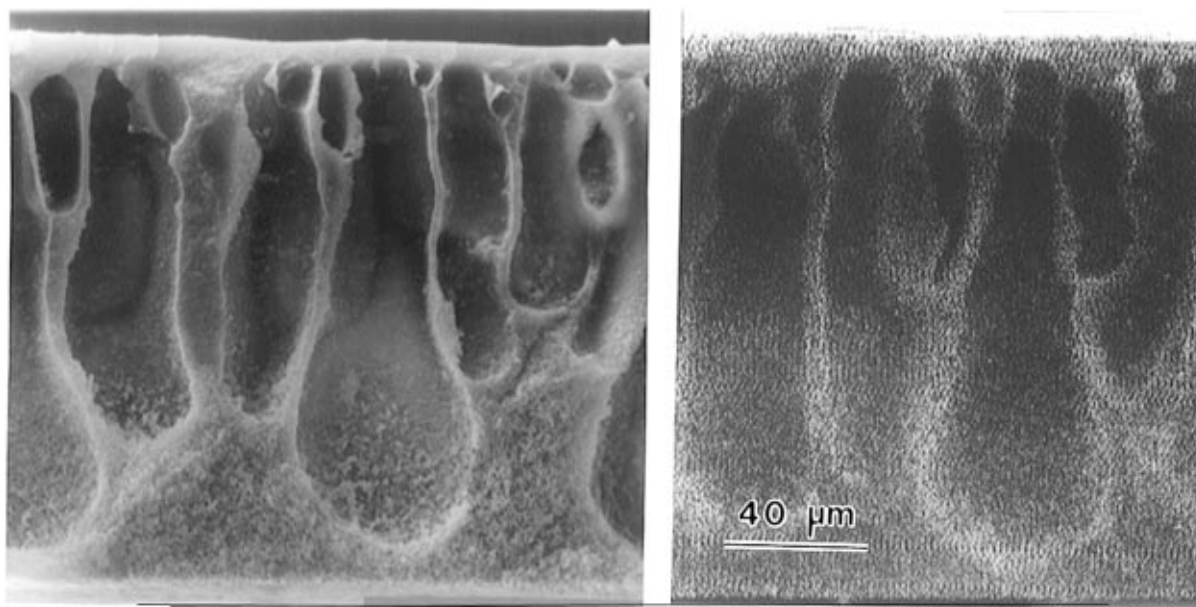


Figure 4. Scanning electron microographies of Ac/Zr/S2: (A, left) by secondary electron image (SEI); (B, right) Zr X-ray emission dot map obtained with X-ray fluorescence microprobe; the white points are zirconium. The scale is the same for both microographies.

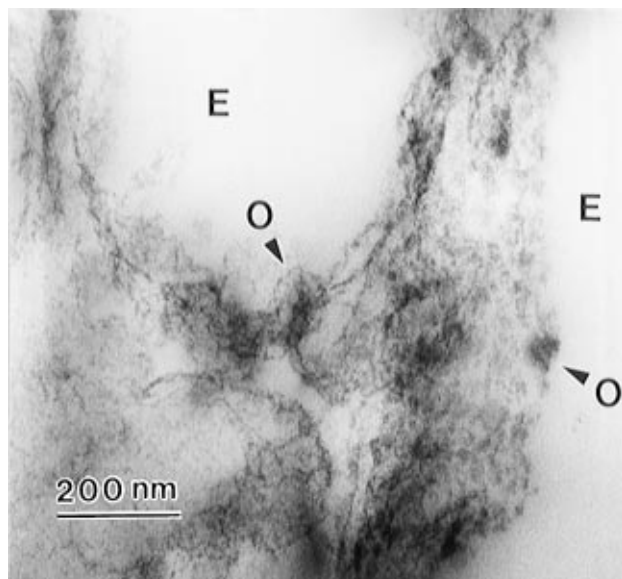


Figure 5. TEM micrography of Ac/Zr/S1, where E is the epoxy resin and O is the oxide particles.

phosphate ion by chemically bonding to the surface forming the species $\equiv\text{Zr}-\text{O}-\text{PO}_3\text{H}^-$, where $\equiv\text{Zr}$ stands for the Lewis acid site on the zirconium oxide surface, and part on the surface retained by the Donnan exclusion mechanism as HPO_4^{2-} species. Because pure cellulose acetate does not show any ^{31}P NMR peak, HPO_4^{2-} species must be absorbed on the $\equiv\text{Zr}-\text{OH}_2^+$ and $\equiv\text{Zr}-\text{OH}$ sites that are present on the solid-solution interface. Therefore, the retention of phosphate in the conditions used in these experiments is related to the presence of zirconium oxide on the cellulose acetate membrane. The composite membrane works based on both mechanisms: chemical adsorption and Donnan exclusion phenomena.

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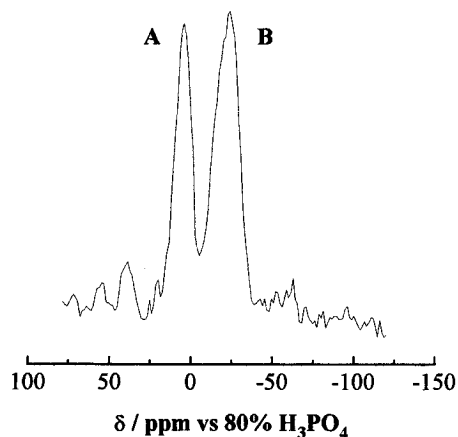


Figure 6. CP MAS ^{31}P NMR of composite membrane after phosphate permeation experiment, (A) HPO_4^{2-} -adsorbed species and (B) $\text{Zr}(\text{HPO}_4)_2$ -formed species.

Stability of the Composite Membrane. The composite membrane is chemically very stable. Passing the solution in conditions described in the experimental part the rejection coefficients were 90 and 75% for Ac/Zr/S1 and Ac/Zr/S2, respectively, under continuous operation for 70 h. Elution of the sorbed phosphate was made by passing NaOH 0.01 M solution followed by 10^{-3} M HNO_3 , since NaOH can react with titanium phosphate liberating the phosphate ion.²⁹ After treatment with NaOH, the membrane was submitted to an XPS analysis after five turnovers. The Zr 3d binding energy peak was not observed (Zr/O = 0; see Table 2). However, it does not mean that all zirconium atoms in the matrix were leached by the eluent solution, but only those at the surface of the matrix. It must be remembered that XPS technique probes an average depth of ca. 3 nm. The rejection capacities of both membranes were reduced only ca. 10% after the chemical treatment for regeneration of the membrane. The EDS analysis showed one peak at 2.09 keV for Ac/Zr/S1 and Ac/Zr/S2 membranes due to the Zr atom, indicating that ZrO_2 trapped inside

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the polymer matrix is not leached by the alkali treatment.

Conclusions

The two-step procedure for the composite membrane preparation allows the control of the membrane morphology and to obtain metal oxide highly dispersed in the cellulose acetate polymeric matrix.

The composite ZrO_2 /cellulose acetate membranes have been easily prepared by this procedure. They have

shown a good performance on the retention of phosphate ions from an aqueous solution as a result of the morphology and oxide dispersion.

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