



Vacuum Metallization of Ultrafiltering Polymer Membranes

KEYWORDS

polymer membranes, ultrafiltration, vacuum metallization, modification, phase inversion.

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ABSTRACT *We studied the performance of the composite ultrafiltration membranes which are vacuum metallized, using magnetron sputtering of an aluminum alloy. For the sake of good adhesion between the polymer membrane and the metal coating is performed prior to modification of the polymer surface of the membrane. It has been shown, as the influence of the time of sputtering on the alloy and the selective transport properties of the membranes and the effect of the additional metal oxide sublayer.*

Introduction

Vacuum metallization is based on evaporation (sputtering or by ion bombardment) and a metal vapor condensation on their membranes. In general the condensation process occurs at the membrane surface and forming a metal coating can be regarded as being made up of the following individual steps: seeded, growth and aggregation of seed islands, fusion of individual grains island to touch them; formation of „net“ coverage, formation of a thick coating, and a further increase of the coating. Vacuum metallization of membranes is meant to change transport characteristics, and selective membranes, which make them applicable to the solution of specific optimization problems. The other modes of vacuum metallization (exposure times) led to the formation of a metal layer on the polymer surface of the membrane, which is decisive for the characteristics of the membranes, the role of second selective layer already formed membrane. (Lu AH et al.,2005).

Experimental

Used ultrafiltering membranes are type 60000. One method for the preparation of polymer membranes is the phase inversion (Kim et al.,2002; Kobayashi et al., 1997). The membranes are formed in laboratory conditions through a phase-inversion method, more popular as the methods of Loeb (Loeb S., et al. 1962). In order to activate the polymer's surface and to increase the adhesion connection between the polymer membrane and the metal cover is made a preliminary modification with alkaline solutions of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Lipin, Yu. et al.1977).

The metal covers are obtained in a vacuum installation BUP-5 (Russia), by spreading aluminum alloy Magnetron spread is done of the alloy target with a starting vacuum in the chamber $P_H = 1 \cdot 10^{-3}$ Pa working gas medium Ar with purity 99,99% under the pressure of $P_p = 4 \cdot 10^{-2}$ Pa and a specific power of spreading $N_p = 5,7$ W/ cm^2 . The time of precipitation of the cover is 5,10,15,20 and 25 s. The power of the continuous current source feeder of the electric current from 0 A up to 10 A.

In order to define the working characteristics of the metal membranes is used a laboratory module " Sartorius" type SM – 165 (England). To define the selectivity of the membrane against the calibrator is defined with the help of UV/VIS spectrophotometer " Unican - 8625" (France) with the length's wave 280 nm.

Results and Discussion

Initially, the polymer membrane surface was activated with a solution having the following composition: 50 g/l $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 90 g/l $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, 75 g/l NaOH. In these solutions the membranes remain from 2 to 3 hours, then washed with dis-

tilled water to remove unbound ions. (Sacher, E. 2002)

Selected exposure times aim to create a metallic coating that does not isolate selective membrane surface, but only to improve its stability and gave new properties of the membranes. (Ulbricht, M 2006). Naturally for processing a single polymer membrane structure can decrease its permeability to enhance selectivity or increase the stability of the polymer relative to the applied pressure. It depends on the polymer surface, the nature and stability of the polymer, pre-modification of the membrane: the exposure time in the vacuum metallization, distribution and adhesion of the metal coating, and other factors. These basic relationships were planned in the study in order to obtain membranes with high mechanical resistance and various separation properties.

Figure 1 shows that with an increase in the times of deposition of thin layers on the membranes from 5 s to 25 s the water permeability decreases.

With increasing time of deposition of the aluminum alloy of the sprayed target killing a large number of atoms entering the selective layer of the membrane. This suggests thickening of this layer, leading to a string of metallic water permeability of membranes.

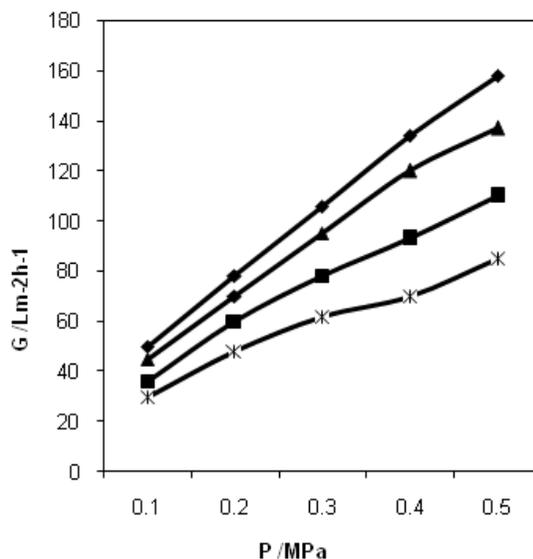


Fig.1. Water permeation flux of the membranes, vacuum metalling without sub-layer, oxide: ▲-5 s, ■-15 s, * -25 s, ♦-pure membrane.

This is confirmed by the results of a study of the selectivity and productivity of the membranes compared calibrants Albumin (fig.2).

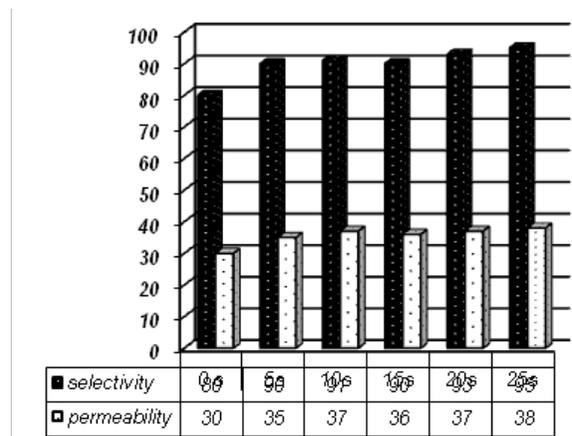


Fig.2. Selectivity and permeability towards Albumin (under 0,3 MPa) of polymer membranes, vacuum metalling without sub-layer

Studies of the various references relating to the application of ultra-thin layers on polymer using magnetron sputtering of pure metals or alloys showed that successful metallization of polymers besides activation of the polymer surface with different solutions may be used and the application of an additional metal oxide sub-layer on the polymer in the very process of vacuum metallizing. This intermediate oxide layer enhances the strength of the adhesion bond between the polymer and the metal coating. It is formed of the same alloy in the same vacuum chamber, but the sputtering is performed in an environment of oxygen, rather than argon. When using oxide sub-layer to carry out several nanostructured layers that overlap and form a structural system. This system completely changes the diffusion layer of the membrane, which affects their basic parameters.

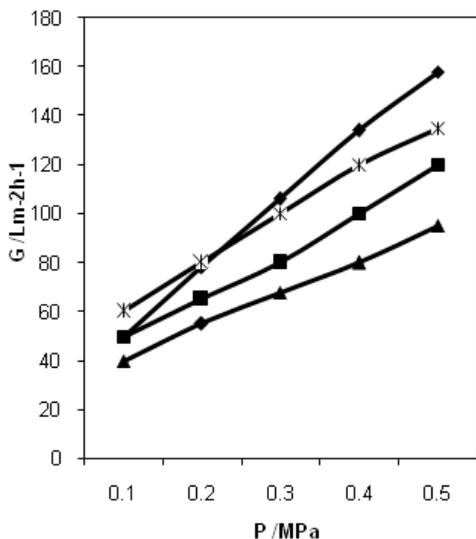


Fig.3. Water permeation flux of the membranes, vacuum metalling with sub-layer oxide: ▲-5 s, ■-15 s, ⋈-25 s, ◆-pure membrane.

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When the oxide sub-layer is absent the metalling atoms enter the porous structure and congest the diffusion layer.

When the time of exposure increase the density of that layer increase, and it lowers the waterpermeability of the membrane.

In that way they (the oxide atoms) build a barrier layer, which does not allow the aluminum atoms of the to enter the porous structure, and to block it. In this way, the structure of the membrane in the selective zone (fig.3) is characterized with the presence of the metalling layer without its registering in the porous structure. In practice, the usage of metal-oxide cover favours the setting up of two consecutively situated layers which define the positively changing characteristics of the membranes.

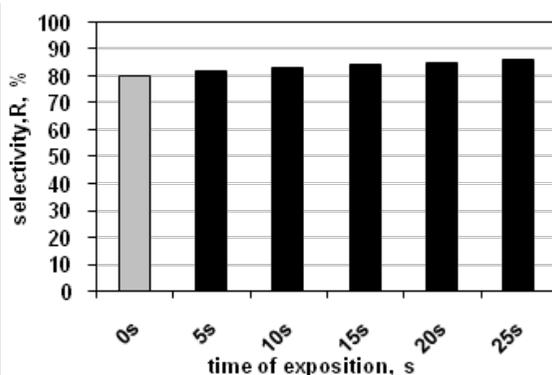


Fig.4. Selectivity towards Albumin (under 0,3 MPa) of polymer membranes, vacuum metalling with sub-layer oxide.

The time is enough to make a cover which increases selectivity of the membrane from 82 to 85%. We can suggest, that in practice a complete metal cover is not built. But the precipitation of the metal ions is done in the zones where an oxide pad is stored i.e. in practice it means that selectively are blocked the macropores of the membrane.

Conclusions:

1. The studies carried out showed that the method of vacuum metallization can be used for modification of polymer membranes to obtain structures and properties necessary for specific processes.
2. The whole procedure depends on the initial membrane structure, polymer type, method of preliminary treatment and the degree of emission metallization.
3. Followed the change in the selectivity of chemical metallic membranes to calibrant Albumin.