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ULTRASTRUCTURE OF TiO_2 LAYER USED AS A SUPPORT FOR IMMOBILIZATION OF ENZYMES

The paper presents preliminary results obtained during examining the structure of TiO_2 layer under scanning electron microscopy (SEM). This layer is, in fact, the most active layer in a new generation of inorganic membranes, the so-called formed-in-place (FIP) "permanent" membranes. The water permeability of the "permanent" FIP membrane was tested and structural parameters of TiO_2 layer were calculated. This research should be considered as the first step towards the further investigations focused on the application of the membranes in biotechnologies.

1. INTRODUCTION

Ultrafiltration (UF) and microfiltration (MF) membranes are porous barriers used for the separation and concentration of proteins, colloids or particles in pharmaceutical, food or chemical industries. Such separation mechanisms are directly associated with the characteristics of the porous structure. In this case, selectivity depends mainly on the pore size.

Therefore, information on pore size, distribution and density at the membrane surface facing the feed are of the first importance for both membrane users and manufacturers.

From numerous technological solutions of the ultrafiltration membranes, wide application has been found for inorganic, especially formed-in-place (FIP) membranes.

Formed-in-place membranes were first tried successfully by MARCINKOWSKY and coworkers [1] by dynamic depositing Fe^{3+} and Zn^{4+} hydrous oxides on silver frits.

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Since then, such membranes have been made with a variety of charged polymers and metal oxide colloids on various kinds of porous supports such as carbon, polymers, ceramic and stainless steel. The membranes consist of a porous support on which a metal oxide gel and a molecular polymer or a polyelectrolyte are deposited (MENON [2]).

A "permanent" MF membrane developed in the U.S.A. was essentially a novelty in this membrane group. One can obtain it by applying a coating hydrous titanium dioxide to a porous stainless steel support. This porous titanium dioxide layer is permanently sintered with the support. The layer of sintered titanium oxide TiO_2 is the semi-permeable layer of the new membrane (SZANIAWSKI [3]).

The membrane is the subject of different studies which have been performed for several years in our research group. Recently, the tests for application of the above-mentioned membrane to the immobilization of enzymes are one of the problems to be solved. Based on the literature survey, the main requirements for the supports designed for the immobilization of enzymes have been established (HARTMEIR [4]). They are as follows:

high level of stability (both chemical and biological),
high level of mechanical durability (most important abrasion hardness),
large virtual structure,
high porosity.

Taking into consideration these requirements, there is the potential of using TiO_2 membranes in applications to immobilization of enzymes. There is a lack of detailed analysis concerning the physical identification of the surface structure. Hence, some tests for identification of the structure of this layer under scanning electron microscope (SEM) were carried out.

2. EXPERIMENTAL

2.1. SEM OBSERVATIONS

Tests have been carried out with samples taken from a new "fresh" membrane which has not been used in the research before.

Because of the lack of data in the available literature concerning preparation methods for this kind of membrane, our own methodology for scanning microscope observations has been developed.

It consisted of the following steps:

1. Samples of about 1 cm in length were cut using a power saw. Cutting caused excessive local heating. Therefore, in order to prevent drying of the sample while cutting, the cutting site was cooled by pouring deionized water over it continuously.

2. Samples cut in this way were again cut twice axially, while maintaining them wet, to get four quarters out of each centimeter section.

3. Wet samples were dried in dry air after water vapour removal for about 24 hours in a desiccator.

Samples prepared in this way were examined under the scanning electron microscope. The results of the observation are presented in the photographs 1–4.

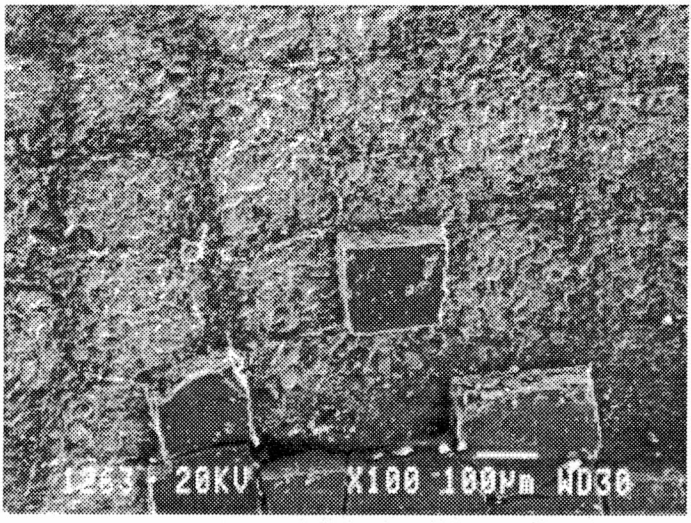

Fig. 1. General view of the "permanent" membrane surface before mechanical cleaning

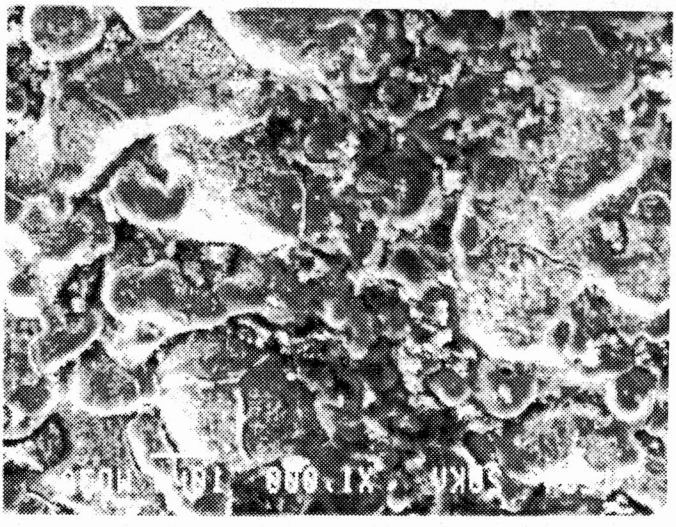

Fig. 2. Structure of the membrane surface (× 1000)

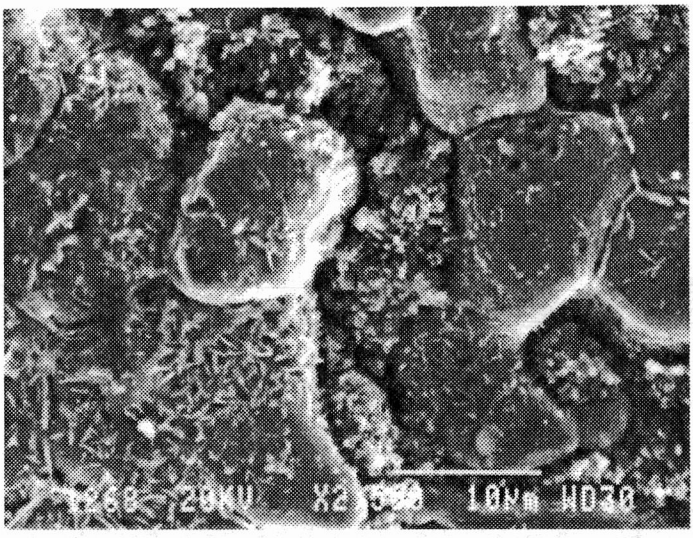

Fig. 3. Structure of the membrane surface (×2500)

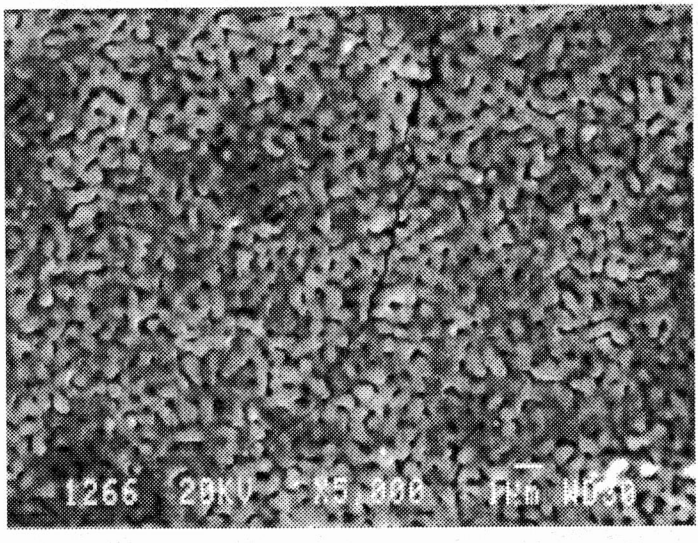

Fig. 4. Active centers of the "permanent" membrane

Photograph 1 presents a general view of the membrane surface after the process of active layer formation before mechanical cleaning. Irregular, black particles, which are easily seen in this photograph, are apparently formed during the coating of the steel surface with the dispersed TiO_2 particles. They form an excessive (nonactive) layer of the membrane which is removed in a mechanical way from the membrane before it is used.

Photographs 2 and 3 show the structure of the membrane surface. In these photographs, the cavities of the porous steel structure filled with hydrous titanium oxide are clearly visible. TiO_2 trapped in this way creates active pores which are involved in the separation processes.

The method of membrane formation (based on filling cavities) described above decidedly distinguishes "permanent" membrane from the other widespread FIP membranes formed with a metal oxide gel and/or molecular polymer layers (polyelectrolytes) on various types of porous supports.

The fibrous material which can be noticed in the photographs is some foreign material most likely generated at the membrane surface, while sintering or drying.

The porous structure of the TiO_2 can be seen in photograph 4.

The SEM photographs obtained allow for a preliminary estimation of average pore size, pore distribution on the membrane surface and porosity of the surface layer of the membrane. The pore dimensions determined roughly correspond, in principle, with the results obtained during hydraulic tests with a membrane manufactured by the same procedure as the sample that was investigated by SEM.

2.2. WATER PERMEABILITY TESTS OF THE "PERMANENT" MEMBRANE

Several relationships of water permeability versus pressure for the fresh, chemically washed membrane allowed calculation of the structural parameters of the membrane.

Based on the Hagen–Poiseuille equation for laminar flow in a pore:

$$J_v = \frac{n\pi r^4 \Delta p}{8\eta d} \tag{1}$$

where:

J_v – volume water flux through the porous layer of the membrane [m^3/m^2s],
n – number of pores per unit surface area [$1/m^2$],
r – pore radius [m],
Δp – transmembrane pressure difference [Pa],
d – thickness of the porous dynamic layer of the membrane [m],
η – water viscosity [Pa s],

the equation:

$$\varepsilon = n\pi r^2 \tag{2}$$

was used to reduce equation (1) and rearrange it to:

$$r^2 = \frac{8\eta d J_v}{\varepsilon \Delta p}, \tag{3}$$

η in eq. (3) was obtained from the literature as 5.988×10^{-3} [Pa s] at $T = 45$ °C; ε was assumed 0.65 which is appriopriate for random packing of spheres having the

same diameter, and d was assumed to be 0.5×10^{-3} [m] which is the normal thickness of the titania layer.

A series of tests was conducted. They consisted in measuring the steady state of water permeability and cleaning the membrane with 0.1 M NaOH followed by 0.1 M HNO_3 and repeating the test. The dependence of the volume flux on pressure for a series of five tests with the same membrane is shown in figure 5 as lines (1) through (5).

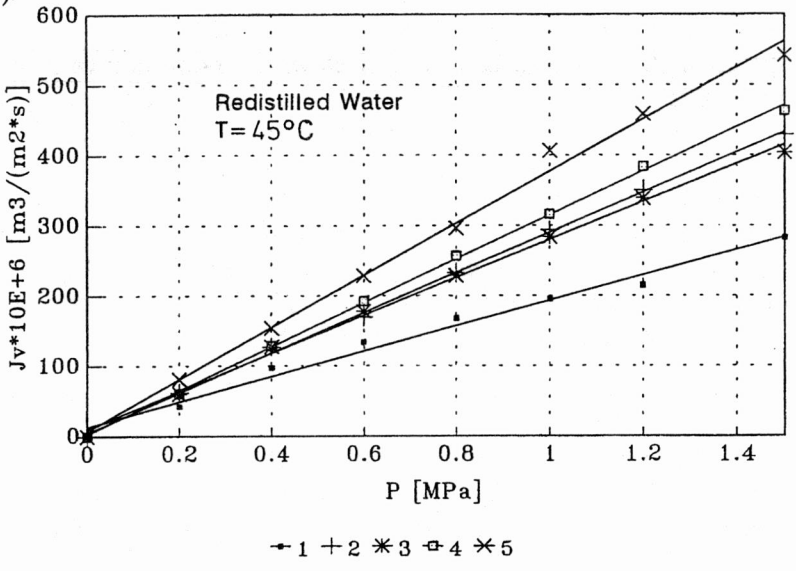

Fig. 5. Membrane water flux (J_v) vs pressure (P) for a series of permeability tests, (1) through (5), using the same membrane

Transport of water through the membrane clearly follows Darcy's law:

$$J_v = L_p \Delta p \tag{4}$$

where L_p is water permeability constant [m^3/m^2 s Pa].

Table

Calculated parameters for "permanent" FIP membrane

Material porosity [%]	Permeability constant L_p 10^{11} [m^3/m^2s Pa]	Pore density n 10^{-14} [$1/m^2$]	Thickness of TiO_2 layer d 10^3 [m]	Average pore radius r 10^9 [m] ([nm])
65	18	3.11	0.5	25.8 (26)
65	28	1.99	0.5	32.2 (32)
65	27	2.07	0.5	31.6 (32)
65	31	1.80	0.5	33.9 (34)
65	37	1.51	0.5	37.0 (37)

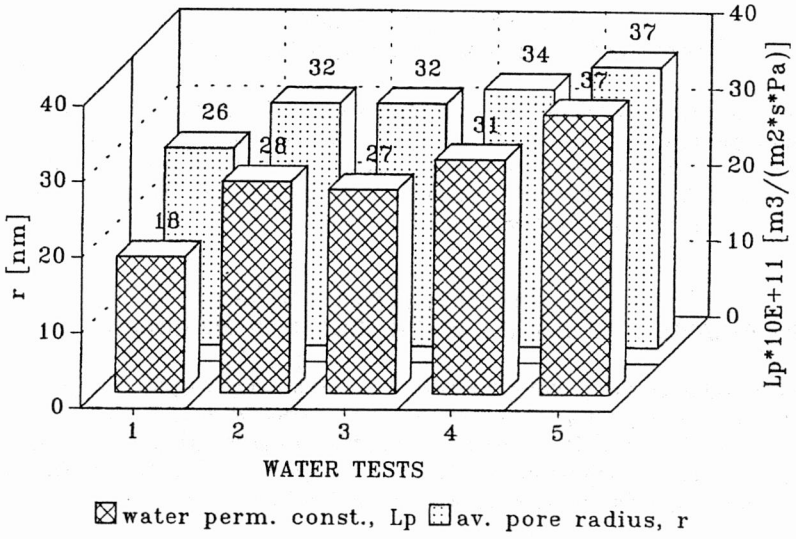

Fig. 6. Structure characteristics for the "permanent" FIP membrane obtained from the series of five permeability tests, using the same membrane

Water permeability constants which, in fact, are the coefficients of the slope of the lines representing permeability versus pressure, calculated on the basis of these tests, allowed the determination of an average pore radius r [nm]. Results of the calculation are presented in the table and figure 6.

These values for the average pore radius are close to the value expected from close-packed TiO_2 particles which gives an additional justification for the assumed values of d and ε.

3. CONCLUSIONS

It is worthwile to point out that the research performed is only the first step of the entire programme which will be focused on finding the possibilities of application of "permanent" membrane in the area of enzyme immobilization and protein fractionation.

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ULTRASTRUKTURA WARSTWY TiO_2 UŻYTEJ JAKO NOŚNIK UNIERUCHOMIAJĄCY ENZYMY

Przedstawiono wstępne wyniki badania struktury warstwy TiO_2 pod mikroskopem skaningowym. W rzeczywistości jest to najbardziej aktywna warstwa w nowej generacji nieorganicznych membran, tzw. membran trwałych. Badano przepuszczalność wody przez takie membrany i obliczono strukturalne parametry warstwy TiO_2. Przedstawiany artykuł powinien być traktowany jako wstęp do dalszych badań nad zastosowaniem membran w biotechnologii.

УЛЬТРАСТРУКТУРА СЛОЯ TiO_2, УПОТРЕБЛЕННОГО КАК НОСИТЕЛЬ, ОСТАНАВЛИВАЮЩИЙ ЭНЗИМЫ

Представлены предварительные результаты исследования структуры слоя TiO_2 под электронным микроскопом. В действительности это наиболее активный слой в новой генерации неорганических стойких мембран. Исследована проницаемость воды через такие мембраны и рассчитаны структурные параметры слоя TiO_2. Настоящую статью надо считать как введение в дальнейшие исследования применения мембран в биотехнологии.