COMPOSITE INORGANIC MATRIX MODIFIED WITH ION-ECHANGER NANOPARTICLES

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ABSTRACT

The aim of the work was to elucidate a nature of charge-selective properties of macroporous composite inorganic membranes modified with nanoparticles of the ion-exchanger, namely hydrated zirconium dioxide. The membrane was found to be selective towards anions in acidic media: membrane potential was registered in the solutions containing 10-100 mol m^{-3} HCl. Overlapping of intraporous diffusion constituents of electric double layer cannot be provided under these conditions. The membranes have been investigated using methods of standard contact porometry, potentiometry, scanning electron microscopy. The method of transmission electron microscopy was used to research individual ion-exchanger as well as ceramic powder, which had been obtained by crumbling up of the non-modified ceramic matrix. Differential curves of volume and surface distribution have been factorized using Lorentz functions, each maximum has been related to either structure element both of the matrix and the ion-exchanger. Calculations according to homogeneous and heterogeneous geometrical models were carried out to make this relation. Structure of the ceramic matrix has been shown to be formed with particles of micron size. Particles of the ion-exchanger (6 nm) form aggregates. It was found that the empties between the aggregates of ion-exchanger nanoparticles are responsible for charge selectivity because the aggregates cork pores of the matrix. Maximal radius of pores caused by the aggregates has been estimated as 25 nm. This is in agreement with porometric data.

Key words: composite inorganic membranes, hydrated zirconium dioxide, nanoparticles, aggregates, standard contact porometry.

INTRODUCTION

Inorganic membranes can operate at high temperature and in aggressive media, moreover they are stable against fouling with organic matters [1-3]. Because of these remarkable properties the membranes are attractive for separation processes, particularly for electromembrane techniques [4]. However use of ceramic separators for electromembrane processes is limited by an absence

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of charge selectivity in rather concentrated solutions in spite of nanoporous active layer. This is due to extremely low ion exchange capacity (low charge density) of ceramics, since these materials are produced at high temperature [5], which does not provide retention of ion-exchangeable groups.

Ceramic membranes modified with nanoparticles of inorganic ion-exchanger, namely hydrated zirconium dioxide (HZD), were shown to demonstrate charge selectivity: they permit migration of counter-ions as well as electrolyte diffusion. At the same time migration of co-ions is not realized through these separators: the value of limiting current due to counter-ions is in a good agreement with the magnitude, which have been predicted theoretically from the approach for charge-selective membranes [6]. The aim of this work is to ascertain a cause of charge selectivity of composite inorganic membranes. The method of standard contact porometry, which allows us to determine pores whithin a wide interval of 0.3 nm – 300 μm, was applied for diagnostics of the membranes [7, 8].

EXPERIMENTAL

Ceramic membrane based on TiO_2 (*TAMI GBMH*), which contains no active layer, was investigated. The membrane was impregnated with ZrO_2 sol, which had been prepared from a 1 M $ZrOCl_2$ solution. ZrO_2 hydrogel was deposited inside the membrane with NH_4OH, then the sample was dried at ≈298 K and heated at 423 K [6]. Ion-exchange ability of the inorganic constituent retained under thermal treatment conditions. The modification procedure was repeated 7 times, after the last cycle the ion-exchanger layer was removed from outer surface of the membrane by means of ultrasonic activation. The samples were marked as TiO_2 (initial membrane, i.e. matrix) and TiO_2-HZD-7 (modified membrane).

HZD powder has been also obtained by means of hydrogel deposition from ZrO_2 sol, drying and heating at 423 K. The ion-exchanger was researched with a method of transmission electron microscopy using Leo 912 in-column CRYO EFTEM device. Ceramic powder, which had been obtained by mechanical treatment of the TiO_2 sample, was investigated by similar manner. SEM images of transverse section of the membranes was obtained using a ZEISS EVO 50XVP scanning electron microscope. Previously the transverse sections were polished, treated with ultrasound, dried at 373 K and covered with a thin gold layer using a SPI Module[TM] Sputter 12151-AX device at 100 Pa.

Before porometric measurements the membranes were heated at 423 K. The measurements were carried out by means of home-made porometer (Institute of Physical Chemistry and Electrochemistry of the RAS) at 100 MPa to provide a contact of the sample with the standard sample. Octane was used as a working liquid. Differential porogrammes (pore volume distribution, $\frac{dV}{d(\log r)}$,

where V is the volume) were factorized with Lorentz components using a PeakFit v. 4.12 computer program. Mathematical treatment of the porogrammes involved factorization within the intervals of pore radius (r) of 1×10^{-9}–1×10^{-7} and 1×10^{-9}–1×10^{-4} m and comparison of the data for peaks with a maximum at $\approx1\times10^{-7}$ m. Data adequacy is confirmed by coincidence of these maxima in two abovementioned diapasons and also high correlation coefficient (0.99). These procedure was necessary because the $\dfrac{dV}{d(\log r)}$ values are extremely low at 1×10^{-9}-1×10^{-7} m comparing with those found for the interval of 1×10^{-7}–1×10^{-4} m.

Bulk density of the membranes (ρ_b) was determined using a pycnometer method, particle density (ρ_p) was estimated taking into account geometrical parameters of the samples.

The membrane potential was measured using a divided cell. HCl solutions (10 and $15\div100$ mol m^{-3}) circulated through the chambers, Ag/AgCl electrodes were placed in each compartment. Transport numbers of counter-ions have been calculated from the integral equation for membrane potential similarly to [9].

RESULTS AND DISCUSSION

Insertion of HZD into the matrix caused increase of particle density, however no change of bulk density was found. Thus it is possible to confirm, that the bulk density of the ion-exchanger ($\overline{\rho}_{HZD}$) and the matrix are equal, this value was estimated as 4260 kg m^{-3}. Parameters of porous structure can be determined as follows. HZD volume per mass unit (m) of the composite membrane can be calculated approximately as $\dfrac{V(\rho_p - \rho_{p,0})}{\overline{\rho}_{HZD}m}$, where $\rho_{p,0}$ is the particle density of the initial matrix, V is the sample volume. Surface (S_0) and porosity (ε_0) and micropore volume of the ion-exchange constituent can be determined according to relative increase of membrane mass (*Table 1*).

Integral pore distributions of pore volume are plotted in Fig. 1. Rapid increase of pore volume at $r>1\times10^{-7}$ m indicates preferably macroporous structure of the membranes. However a presence of micropores is also visible: their volume can been found as intersection of the curves with ordinate axe. The volume of micropores was estimated as 3×10^{-7} (*TiO_2*) and 5×10^{-6} (*TiO_2–HZD-7*) m^3 kg^{-1}. Integral distributions of pore surface (S) demonstrate also mesopores: the most rapid increase of S value within the interval of 1×10^{-9}–1×10^{-8} m was found for the modified membranes.

Table 1 – Parameters of globular models for non-modified membrane and HZD layer inside matrix

Parameter	Homogeneous model		Heterogeneous model		
	Matrix	HZD	Globules	Matrix	HZD
ε_0	0.23			–	–
S_o, m^{2}kg^{-1}	820	$2.09\cdot10^5$	–	–	–
ε	–	–	I	0.02	0.42
			II	0.21	0.04
Globule packing	CFC or HXG	SC	I	CFC or HXG	SC
			II		
Number of contacts with neighbours	12	6	I	12	6
			II	12	6
$S_o \dfrac{\varepsilon_0}{\varepsilon}$, m^{2}kg^{-1}	–	–	I	8176	2.27×10^5
			II	201	3.88×10^4
$r_g\times10^9$, м	859	4	I	86	3
			II	3500	20
			III	–	(≈400)
$r_n\times10^9$, м	133 (204)	1 (≤1)	I	13 (8)	1 (≤1)
			II	542 (204)	8 (4)
			III	–	(190)
$r_c\times10^9$, м	355 (1730)	2 (2)	I	36 (39)	2 (2)
			II	1449 (1730)	13 (6)
			III	–	(331)

Experimental values identified according to porogrammes are shown in brackets. Packing: cubic face-centered (CFS), hexagonal (HXG), simple cubic (SC).

Micropores provide 10 (TiO_2) and 55 (TiO_2–HZD-7) % of total surface, which reaches 820 and 10430 m^2 kg^{-1} for the matrix and modified membrane respectively.

Differential distribution of pore volume $\left(\dfrac{dV}{d(\log r)} - \log r\right)$ gives more detail information about porous structure. Both homogeneous and heterogeneous globular models were applied to relate the maxima either to matrix or to ion-exchanger. The models give pairs of peaks in porogrammes: the first maximum corresponds to narrowing of pores between globules (pore necks), the second one is related to their widening (pore cavities) [10]. Parameters of the models are radii of globules (r_g, where $r_g = \dfrac{3}{\rho_b S_o}$), pore necks ($r_n$) and pore cavities ($r_c$),

the values of total surface and porosity are used. The magnitudes of r_n and r_c are calculated using special factors for each type of globule packing. In the case of TiO_2 membrane the model shows that particle of micron size are responsible for structure formation (see *Table 1*), this is in agreement with SEM microscopy data (*Fig. 2*). As seen, the spheres are distorted due to heating and pressure (these conditions are necessary for ceramics preparation), moreover irregular aggregates are formed during annealing.
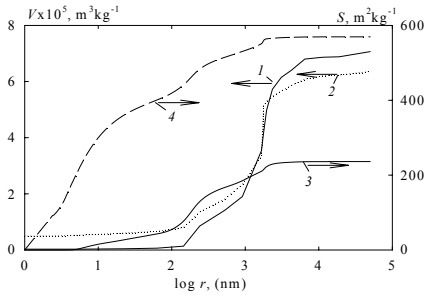
Fig. 1 – Integral distribution of pore volume (1, 2) and surface (3, 4) for TiO_2 (1, 3) and TiO_2-HZD-7 (2, 4) membranes
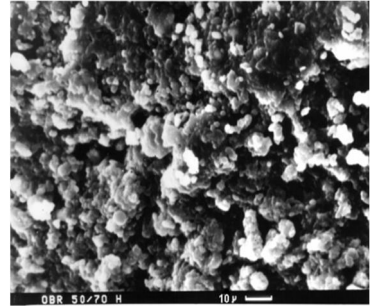
Fig. 2 – CEM image of transverse section of TiO_2 membrane

Analysis of location, width and intensity of stripes of the $\frac{dV}{d(\log r)} - \log r$ curves (Fig. 3) allows us to conclude, that the maximum at 2.04×10^{-7} m is related to pore necks, at the same time the peak at 1.73×10^{-6} m corresponds to cavities. Two maxima at $\log r = 0.5{-}2$ (nm) indicate the second type of globules. These spheres are much smaller than the particles, which are visible in SEM image.

Heterogeneous globular model was applied to identify the peaks. The model provides estimation of pore radius interval, which corresponds to each peak, using $\frac{dV}{d(\log r)} - \log r$ curves. Then the volume of pores, which are attributed to the peak, are found from integral distribution. The surface of each type of pores can be found as $S_o \frac{\varepsilon_0}{\varepsilon}$, where ε is the porosity due to particles, which form pores within the chosen interval of $\log r$.

Analysis of the porogramme for TiO_2 membrane allows us to identify smaller (particles I) and larger (particles II) globules (see Table 1). Particles II form pores, which give two maxima about 1.7×10^{-6} (pore cavities) and 2.2×10^{-7} (pore necks) m. Two maxima at 3.9×10^{-8} and 8.0×10^{-9} m correspond to pores caused by particles I.
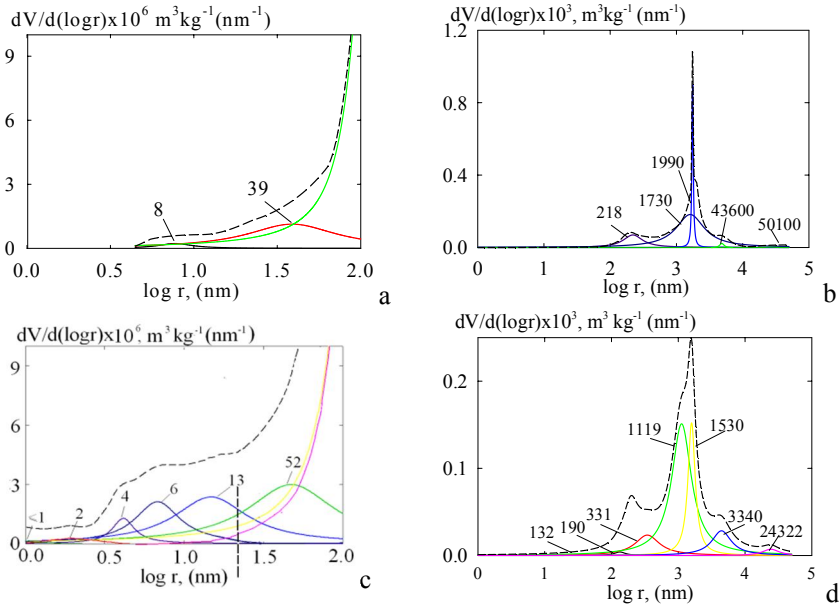
Fig. 3. Differential distribution of pore volume for *TiO₂* (a, b) and *TiO₂-HZD-7* (c, d) membranes. log r = 0÷2 (a, c) and 0÷5 (b, d) (nm). Dashed curves correspond to experimental data, solid curves are related to calculated peaks. Vertical line (c) points pores, which are responsible for charge selectivity

Three stripes at 3.0×10^{-6}, 4.4×10^{-6} and 5.0×10^{-5} m are outside the model, since their intensity decreases with increase of pore radius. These pores are evidently caused by irregular aggregates. Experimental r_n/r_g relation for particles II is larger comparing with calculated one probably due to distortion of the particles due to pressure and annealing. Compaction of the globules can lead to deviation from the globular model. No influence of pressure and annealing has been found for particles I: they are in a good agreement with the globular model.

Since a radius of globules is known, it is possible to calculate the amount of particles per mass unit taking into consideration the surface caused by these globules as well as the surface of a single sphere. The magnitudes of 5.4×10^{16} (particles I) and 1.2×10^{14} (particles II) kg^{-1} have been found, i.e. the relation of particle amounts is ≈ 450. At the same time the surface of the particle II is ≈ 1650 times larger than that for particle I. It means that the matrix structure is formed with particles II. Aggregates of particles I are placed on large spheres episodically. This consumption is confirmed by calculations according to homogeneous model and also by TEM image of the matrix powder (*Fig. 4*).

Two additional peaks   are   visible   in the case of modified membrane $(1\times10^{-9}$-3×10^{-9} m). These maxima are due to HZD layer inside matrix pores. Calculations according to homogeneous and heterogeneous models give nanosized particles, which evidently form structure of the ion-exchanger (particles I). Shift of the maxima at 4×10^{-9}-1×10^{-7} m towards larger r values indicates evidently aggregate formation (particles II). Similar regularity has been found for the peak at 3.9×10^{-8} m, this shows formation of more complex structure (particles III), unfortunately calculations of these particles is difficult due to overlapping of the stripes attributed to HZD and matrix. However their size can be estimated approximately from the peak at 5.2×10^{-8} м. Particles III are seen in TEM image obtained for the individual ion-exchanger (*Fig. 5*).

It should be stressed that the maxima related to the matrix are visible in the case of *TiO₂ -HZD-7,* though the peaks at $r>1\times10^{-7}$ м are shifted towards lower r values. This indicates macroporous structure of the modified membrane on the one hand and corrugation of macropores with HZD on the other hand.
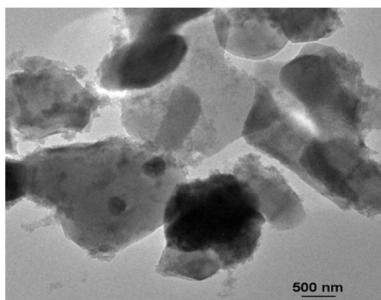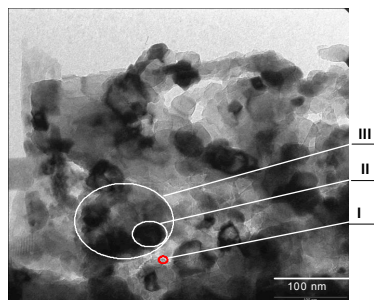

Fig. 4 – TEM image of matrix powder   **Fig. 5 –** TEM image of individual HZD

No membrane potential has not been registered during potentiometric measurements of the non-modified matrix. However the modified membrane demonstrates electrochemical activity in rather concentrated solutions: the transport numbers of counter ions ($t_{Cl,m}$) are higher than 0.5 (*Fig. 6*). Equation developed by Volfkovich has been applied to estimate a size of pores, which are responsible for charge selectivity [11]:

$$t_{Cl,м} = t_{Cl}\left(1+\frac{FrC}{k\eta}\right)\left(t_{Cl}+\frac{FrC}{k\eta}\right)^{-1},$$

where t_{Cl} is the transport number in a solution (0,18), k is the shape coefficient (k=2.8 for pores formed with globules), F is the Faraday constant, η is the charge density, C is the concentration of outer solution (average value of concentrations of the solutions from two sides of the membranes). The values of transport numbers were simulated using pore radius as a fitting parameter.

Calculated and experimental values do not coincide probably due to complex structure of the membrane.
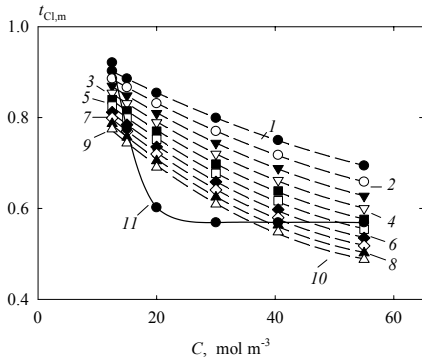

Fig. 6 – Transport number of counter ions as a function of solution concentration. Calculated data – 1-10, experimental data – 11. $r=(\times 10^9$ m) 20 (1); 21 (2); 22 (3); 23 (4); 24 (5), 25 (6); 26 (7), 27 (8), 28 (9), 29 (10)

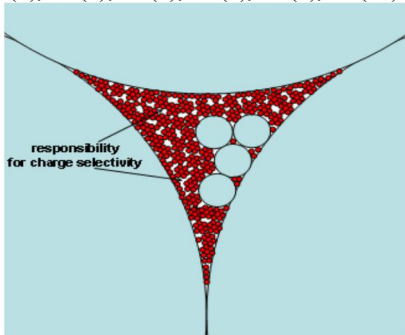**Fig. 7** – Structure of composite membrane

However statistical treatment gives the best correspondence at $r=2.5\times 10^{-8}$ m. This value is attributed to maximal size of pore necks, which are formed with particles II of the ion-exchanger (see Fig. 3c, these pores are marked with a vertical line). This correlation looks logical, since charge selectivity is determined by the largest pores. Thus charge selectivity of the composite membranes is caused by corking of matrix pores with aggregates of HZD nanoparticles. Necks of pores, which are formed with these aggregates, are responsible for electrochemical activity of the composite membrane in solutions of rather high concentration.

Structure of the composite membranes has been proposed based on results both of porometric and potentiometric measurements as well as SEM and TEM microscopy. The matrix is formed by large particles of micron size, the particles are distorted due to pressure and annealing. Aggregates of smaller particles are placed episodically on the largest globules (Fig. 7). Matrix pores are corked with aggregates of HZD nanoparticles. Pores, which are formed by particles III are not responsible for charge selectivity: they are evidently corked with particles II.

CONCLUSIONS

The method of standard contact porometry followed by porogramme factorization, calculations according to homogeneous and heterogeneous geometrical models and potentiometric measurements allow us to determine structure of composite membranes modified with HZD nanoparticles. It was found that the matrix is formed with particles of micron size, which are distorted due to

annealing and pressure. Aggregates of smaller particles are placed episodically on the surface of large globules, The ion-exchanger consists of nanosized particles (6×10^{-9} m), which form aggregates (4×10^{-8} m). These aggregates also form larger structure elements (8×10^{-7} м). The results are confirmed with SEM and TEM microscopy. Aggregates of nanoparticles of the second organization level form pores, which are responsible for charge selectivity, radius of these pores has been estimated as 25 nm. Charge selectivity of the membranes provides their use for electromembrane separation [6, 12].

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