GAS TRANSPORT IN NANO-POROUS HYDROPHOBIC MEDIA

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A new type of highly porous hydrophobic material with nano-size pores (in the range 20 – 100 nm) made from dispersed carbon blacks treated with PTFE by a special technology is developed in this laboratory[1]. The hydrophobic material is produced in a form of powder, from which tablets with various shape, thickness and size can be formed by pressing. This material is used successfully in electrochemical systems operating with gaseous reactants, such as gas-diffusion electrodes[2] for fuel cells, metal-air batteries and other electrochemical devices, developed in this laboratory. The same nano-porous material is also used in the recently designed biosensors[3] for phenol as a hydrophobic oxygen-permeable carrier on which the enzyme-catalyst is immobilized.

These electrochemical systems possess complicated porous structure comprising two types of pores: hydrophobic pores, through which a fast transport of the reactant (in gas phase) is achieved and hydrophilic pores (filled with electrolyte), where the electrochemical reaction is taking place. The performances of such electrochemical devices can be improved significantly by the use of properly designed hydrophobic porous material ensuring an increased rate of reactant-gas transport.

Here are reported some theoretical and experimental results from the investigation of the mechanism of gas-transport in the nano-porous hydrophobic material.

The pore size distribution of the material obtained both by Mercury or electrolyte intrusion porometry show porosity ca. 50%; major part of the pores radii in the range of ca. 30 nm and strongly hydrophobic surface (contact angle with water or water electrolytes ca. 118°– 124°).

The gas-permeability coefficient **K** is a measure of the rate of gas transport under a total gas pressure gradient. It can be obtained by measuring the gas flow **J** through a flat sample with thickness **L** under a total pressure difference $\mathbf{\Delta P = P_0 - P_L}$:

$$\mathbf{J} = \frac{\mathbf{K}}{kT} \cdot \frac{\mathbf{\Delta P}}{\mathbf{L}} \qquad /1/$$

where ***k*** is the Bolzmann's constant and T - the absolute temperature.
The gas-permeability coefficient **K** is a two terms sum: a viscous term $\mathbf{K}_\eta$ accounting the viscous flow of the gas (accepted as a viscous fluid) and Knudsen term $\mathbf{D_{1K}}$ accounting the Knudsen diffusion mechanism

$$\mathbf{K} = \mathbf{D_{1K}} + \mathbf{K}_\eta = \mathbf{D_{1K}} + \frac{\mathbf{B_0}}{\eta}\overline{\mathbf{P}} \qquad /2/$$

where η is the viscosity of the gas, $\mathbf{B_0}$ – parameter of the porous structure, $\overline{\mathbf{P}} = (\mathbf{P_0} + \mathbf{P_L})/2$ - the mean pressure in the sample; $\mathbf{D_{1K}} = \frac{4}{3}\overline{\mathbf{v}}.\mathbf{K_0}$, ($\overline{\mathbf{v}} = \left(\frac{8kT}{\pi m}\right)^{1/2}$) is the mean thermal velocity of the gas molecules, $\mathbf{K_0}$ is a constant characteristic of the medium, i.e. $\mathbf{D_{1K}} \sim \sqrt{T}$. The Knudsen diffusion mechanism takes into consideration the influence of the bouncing of the gas molecules with the walls of the porous system.

In Fig. 1 is presented the permeability coefficient **K** of oxygen as a function of the mean gas pressure $\overline{\mathbf{P}}$ experimentally obtained for a sample of porous material from acetylene black wetpoofed with 35% PTFE. The experimental linear dependence is in agreement with the expression /2/. The intercept with the abscissa corresponds to the Knudsen term $\mathbf{D}_{1K}$. The value obtained is 2,89.10^{-2} cm^2/s.

The slope of the straight line is small, so that the ratio $\mathbf{K}_\eta / \mathbf{D}_{1K}$ at mean gas pressure 1 atm. is small ($\approx$ 0.1) which means that the gas flow is predominantly achieved by Knudsen diffusion and the viscous flow is quite negligible. At normal conditions (1 atm, 25° C) the mean free path $\bar{\lambda} = kT/\pi\sigma^2\overline{\mathbf{P}}$ of the air molecules ($\bar{\lambda} \approx 100$ **nm**) is greater than the mean pore radii ($\bar{\mathbf{r}} \approx 20 - 50$ nm), so that in the investigated material is fulfilled the condition ($\bar{\lambda} >> \bar{\mathbf{r}}$) needed by the Knudsen diffusion mechanism of gas transport.

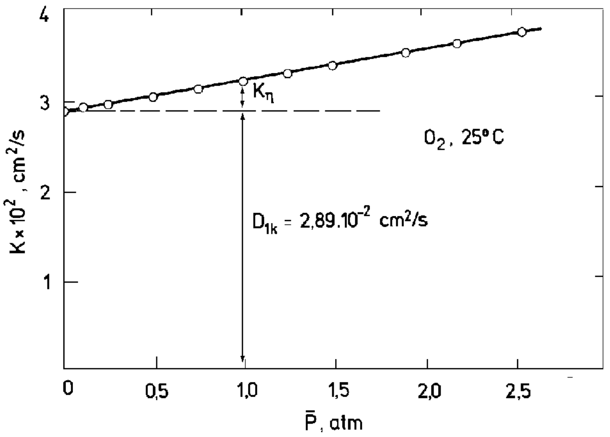

Fig. 1

Gas diffusion in the nano-porous hydrophobic material under partial pressure gradient and at constant total pressure is theoretically and experimentally investigated. The "dusty-gas model"[4,5] in which the porous media is presented as a system of hard particles with spherical form uniformly distributed in the space is used. In the model equations these particles are accepted as gas molecules with infinitely big mass. In the case of gas transport of two-component gas mixture (i = 1,2) the effective diffusion coefficient $(D_i)_{eff}$ of each of the components is connected with the corresponding Knudsen diffusion coefficient $D_{i,K}$ and with the effective binary diffusion coefficient $(D_{1,2})_{eff}$ by the Bosanquet relation:

$$(\mathbf{D}_i)_{\mathbf{eff}}^{-1} = \mathbf{D}_{\mathbf{iK}}^{-1} + (\mathbf{D}_{1,2})_{\mathbf{eff}}^{-1} \qquad /3/$$

in which $(\mathbf{D}_{1,2})_{\mathbf{eff}} = (\varepsilon/\mathbf{q}).\mathbf{D}_{1,2}$, where $\varepsilon/\mathbf{q}$ is the porosity/tortuosity factor of the porous media and $\mathbf{D}_{1,2}$ is the ordinary diffusion coefficient. After taking into account that $\mathbf{D}_{1,2}$ is inversely proportional to the gas mixture total pressure **P** ($\mathbf{D}_{1,2} = \mathbf{D}_{1,2}^{(1)}/\mathbf{P}$, where $\mathbf{D}_{1,2}^{(1)}$ is ordinary diffusion coefficient at unit total pressure – e.g. 1 atm). It can be obtained:

$$(\mathbf{D}_1)_{\mathbf{eff}}^{-1} = \mathbf{D}_{\mathbf{1K}}^{-1} + [(\varepsilon/\mathbf{q}).\mathbf{D}_{1,2}^{(1)}]^{-1}.\mathbf{P} \qquad /4/$$

In Fig. 2 are presented the reciprocal values of **$(D_1)_{eff}$** of oxygen in a sample of the nano-porous hydrophobic material as a function of the total pressure of gas mixture (oxygen-nitrogen) when the oxygen concentration in the mixture is 21%. Oxygen gas flow was measured by electrochemical methods. The obtained linear dependence is in agreement with /4/. From the intercept of the straight line with the ordinate the value of the Knudsen diffusion coefficient can be determined. It must be underlined that the value of Knudsen diffusion coefficient obtained by these diffusion measurements ($2{,}86.10^{-2}$ cm^2/s) is in very good coincidence with the value obtained by the gas permeability measurements.

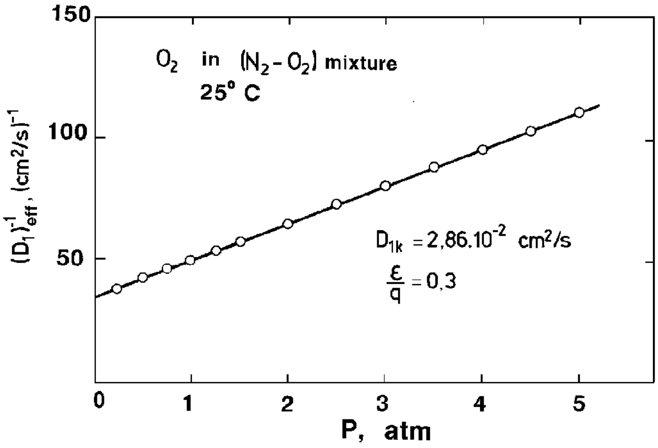

Fig. 2

It can be concluded that the predominating mode of gas transport in the investigated nano-porous hydrophobic material is Knudsen diffusion, so that the diffusion is the main mechanism of gas transport in electrochemical systems based on such material and operating with gaseous reactants. Even in the case when pure reactant gas is used, in the pores of the material are present not only the reactant gas molecules but also water-vapour molecules of the electrolyte. Additionally, during the long-term operation with “pure gases”, the gas-impurities in them can play a role of a second gas component influencing the transport. Actually, the performance of porous electrochemical systems operating with gaseous reactants is influenced by the simultaneous diffusion of the reactant gas, water-vapour molecules and the gas-impurities in the reactant (oxygen, nitrogen and water-vapour. in the case of air gas-diffusion electrodes).

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