

SPONTANEOUS PENETRATION OF HYDROGEN AND OXYGEN THROUGH SEMIHYDROPHOBIC FUEL CELL ELECTRODES

Karel SMRČEK^a, Olga MARHOLOVÁ^a and Karel MICKA^b

^a ČKD Semiconductor Division, 140 00 Prague 4 and

^b J. Heyrovský Institute of Physical Chemistry and Electrochemistry, 102 00 Prague 10

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Spontaneous penetration of hydrogen or oxygen through porous Teflon membranes into water or KOH solution was studied by a new method based on the measurement of the minimum gas overpressure necessary for the penetration at various temperatures. The results were compared with measurements on hydrogen-oxygen fuel cells and are in qualitative agreement with theoretical studies. The penetration of gases into the electrolyte can be prevented by their humidification before introducing them into the cells.

The system gas-hydrophobic porous membrane-water (or aqueous solution) shows an anomalous behaviour, namely that at a sufficiently high temperature the gas penetrates spontaneously the pores of the membrane to form bubbles at the water side. This phenomenon was first observed on carbon cathodes provided with a porous Teflon layer on the air side^{1,2}. Other authors³ measured the resulting pressure gradient and rate of gas flow, influence of the pore size, quality of the gas, hydrostatic pressure, and temperature. From the effect of water vapour they concluded that the process is based on counterdiffusion of water vapour and gas in the pores. This concept was treated mathematically⁴⁻⁶ to obtain equations for the gas flow.

According to the results of our study of semihydrophobic air cathodes⁷, their maximum operating temperature in 7M-KOH is about 70°C; higher temperatures cause air to penetrate through the pores. A similar behaviour can be expected with hydrogen anodes, the rate of hydrogen diffusion being particularly high². The dependence of the spontaneous penetration on the temperature and the membrane structure, eventually the differences between the behaviour of a Teflon membrane and a complete electrode have not been studied in detail and form the subject of the present work with the aim to obtain basic informations for the construction of hydrogen-oxygen fuel cells with semihydrophobic electrodes.

EXPERIMENTAL

Porous Teflon membranes were prepared by leaching out a filler from a heat-treated rolled layer⁸. They were characterized by the capillary pressure p_k and the coefficient of permeability⁹ K . The value of p_k is equal to the overpressure of water necessary to penetrate the membrane to form a first drop on the air side, hence it is related to the radius of the largest pores r_k . The coefficient

of permeability K is defined by the law of Darcy⁹

$$q = K \frac{A \Delta p}{\eta d} \quad (1)$$

where q denotes the volume rate of flow of a gas of viscosity η through a membrane of thickness d and surface area A an overpressure Δp . The rate of flow was measured for nitrogen at an overpressure of 1.96 kPa and temperature 20°C ($\eta = 1.72 \cdot 10^{-5}$ Pa s according to ref.¹⁰). The values of d , r_k and K are given in Table I. For a bundle of parallel pores of equal radius, K is proportional to the square of the pore radius.

The spontaneous gas penetration through the membrane was, in contrast to the previous studies¹⁻³, investigated by a new method consisting in measuring the gas overpressure Δp necessary for penetration into the liquid phase at various temperatures. With increasing temperature, the value of Δp becomes gradually lower until the gas will penetrate without overpressure; the corresponding temperature will be denoted as the temperature of beginning spontaneous penetration.

The membrane sample was to this purpose fastened tightly in a metal cell dipped either in water or in a solution of 7M-KOH. At a chosen temperature, gas at a present overpressure was introduced to the membrane. The valve at the outlet from the gas compartment of the cell was either closed or opened. The overpressure necessary for the gas penetration was read on a manometer. The measurements started at the room temperature and highest overpressure, which was gradually lowered to find the equilibrium overpressure. This was measured with an accuracy to within ± 0.1 kPa. The temperature was measured with a digital thermometer HP 34740 A. In some experiments, the gas was humidified by bubbling through water in a tempered washbottle. Care was taken to prevent condensation of water vapour from the humid gas, which was led to the membrane.

TABLE I

Thicknesses, capillary pressures, maximum pore radii and permeability constants of selected Teflon membranes

Membrane No	d mm	p_k MPa	r_k m	K m ²
51	0.19	0.07	0.94	$4.17 \cdot 10^{-17}$
108	0.22	0.17	0.41	$2.92 \cdot 10^{-17}$
727	0.26	0.11	0.63	$7.21 \cdot 10^{-17}$
793	0.25	0.09	0.75	$3.51 \cdot 10^{-15}$
801	0.27	0.08	0.84	$2.37 \cdot 10^{-15}$
803	0.25	0.09	0.75	$1.35 \cdot 10^{-15}$
851	0.30	0.09	0.75	$4.37 \cdot 10^{-16}$

RESULTS AND DISCUSSION

Closed and Open System

The system Teflon membrane–water–gas behaves differently in two different situations: a) The gas flows from the membrane cell through the outlet into the atmosphere at a rate given by the hydraulic resistance and overpressure; the system is open. b) The gas outlet is closed, so that the gas cannot flow through the gas compartment along the membrane; this will be called the closed system.

With the open system, there is a temperature region in which the gas overpressure necessary to penetrate through the pores is equal to zero. With the closed system, this overpressure is nearly independent of the temperature and the spontaneous penetration does not take place. This difference is apparent from Fig. 1 describing the behaviour of hydrogen and oxygen; and it can be demonstrated by heating the open system to the temperature of spontaneous penetration and closing after a while the gas outlet, whereby the gas flow through the membrane is caused to stop within a second.

At the room temperature, the overpressure necessary for the gas to penetrate through the membrane is of the order of several kPa. With increasing temperature, it does not change until the temperature of spontaneous penetration is approached (Fig. 1). The temperature at which the overpressure necessary for penetration decreases to zero is equal to the temperature of spontaneous penetration of the gas through the membrane.

The differences between the behaviour of the closed and open system can be attributed to the known effect of water vapour³. With the open system, dry gas flows along the membrane surface, and at a sufficiently high temperature the gradient of water vapour partial pressure in the pores brings about the gas transport. With the closed system, the gas compartment becomes rapidly saturated with water vapour, whose partial pressure gradient thus decreases causing the gas transport to stop.

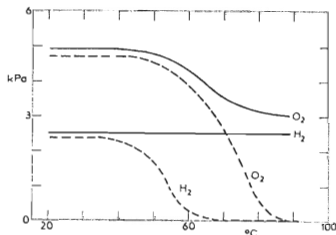


FIG. 1

Dependence of the penetration overpressures of hydrogen and oxygen on the temperature of water in contact with a porous Teflon membrane. Solid curves: closed system; dashed curves: open system. Membrane No 793

Differences Between the Behaviour of Oxygen and Hydrogen

It was stated by some authors² that hydrogen is transported through the pores into water more rapidly than oxygen, however the effect of the temperature was not studied. It turned out in our work that hydrogen penetrates through the membranes at lower temperatures and lower overpressure (Fig. 1), which is important for the construction of the hydrogen anode for fuel cells.

The different behavior of both gases is in agreement with theoretical predictions. Based on simplifying assumption, the following approximate equation was proposed for the stationary volume rate of flow of a gas⁴ in the considered system:

$$J = (D_{12}V_p/f_p d)(c_v^* - c_v^0 - c_g^0 \Delta p/p_0), \quad (2)$$

where V_p denotes porosity (relative volume of passable pores) of the membrane, D_{12} coefficient of binary diffusion in the system water vapour-gas, f_p tortuosity factor of pores, d membrane thickness, c_v^* volume concentration of saturated water vapour, c_v^0 and c_g^0 volume concentrations of water vapour and gas at the gas side of the membrane, Δp overpressure (difference of the pressures on both sides of the membrane), and p_0 atmospheric pressure.

A more exact theory⁶ is based on the consideration of two transport processes, diffusion and convection (Poiseuille) flow, where the transport parameters are functions of the effective pore radius r , tortuosity factor, f_p and porosity V_p . Since, however, these three quantities were difficult to determine in our case, we shall restrict ourselves to rough qualitative considerations based on Eq. (2).

TABLE II

Volume concentrations of saturated water vapour c_v^* above pure water and c_{ve}^* above 7M-KOH (ref.¹³), binary diffusion coefficients D_{12} (cm²/s) for O₂/H₂O and H₂/H₂O systems at 0.1013 MPa and viscosities η (Pa s) of oxygen and hydrogen (ref.^{6,10})

Temp., °C	25	35	45	55	65	75	85	95
c_v^* (H ₂ O)	0.0313	0.0555	0.0946	0.1553	0.247	0.380	0.571	0.705
c_{ve}^* (7M-KOH)	0.0177	0.0316	0.0541	0.0893	0.143	0.221	0.334	0.491
D_{12} (O ₂ /H ₂ O)	0.265	0.282	0.299	0.317	0.335	0.354	0.373	0.392
D_{12} (H ₂ /H ₂ O)	0.964	1.026	1.086	1.150	1.214	1.279	1.346	1.415
$10^2 D_{12} c_v^*$ (O ₂)	0.829	1.57	2.83	4.92	8.27	13.5	21.3	27.6
$10^2 D_{12} c_v^*$ (H ₂)	3.02	5.69	10.3	17.9	30.0	48.6	76.9	99.8
$10^5 \eta$ (O ₂)	2.00	2.03	2.06	2.09	2.13	2.16	2.19	2.22
$10^5 \eta$ (H ₂)	0.880	0.894	0.909	0.923	0.937	0.951	0.964	0.978

We shall assume that dry gas flows along the gas side of the membrane, *i.e.*, $c_v^0 = 0$, and that the pressure on both sides is the same, $\Delta p = 0$. Then, the product $D_{12}c_v$ is a measure of the diffusion flux of the gas (or water vapour) in the membrane pores. Since this flux must overcome the capillary pressure of water acting against it, the convective (Poisseeuille) gas flow in the opposite direction comes into play. If the membrane pores are sufficiently small, this convective flow is negligible and the bubbling effect takes place corresponding to the diffusion flux of the gas, hence roughly proportional to the product $D_{12}c_v^*$. The necessary data for oxygen and hydrogen are given in Table II, whence it follows that the ratio of the diffusion flux of hydrogen to that of oxygen is equal to 3.63 ± 0.02 . From the regression analysis, we find

$$D_{12}c_v^*(O_2) \approx 1.30 \cdot 10^8 e^{-5612/T}, \quad (3)$$

$$D_{12}c_v^*(H_2) \approx 4.51 \cdot 10^8 e^{-5598/T}. \quad (4)$$

From these equations, it follows that, *e.g.*, the flux of hydrogen at 65°C (338 K) should be equal to that of oxygen at a temperature by 28.4 K higher, which is in good agreement with the experimentally found temperature difference from the corresponding curves in Fig. 1.

To calculate the temperature at which the bubbling effect commences, it would be necessary to use the more exact theory⁶ and to take the capillary pressure in the pores into account.

Influence of Membrane Structure

The measured dependences of the penetration of hydrogen through membranes with equal values of p_k but different values of K are shown in Fig. 2. The corresponding curves for oxygen are similar but shifted along the temperature axis as can be seen from Fig. 1. The dependences of the overpressure Δp necessary for penetration into water at 20°C on the parameter K are similar for both gases (Fig. 3); Δp decreases moderately with increasing K . In the region of decreasing Δp , an inversed behaviour is observed: at lower K values the gas penetrates into water at lower overpressures (Fig. 2). However, this can be interpreted rather as a temperature effect, namely that the temperature of spontaneous penetration decreases with decreasing value of K , as is apparent from Fig. 2, the difference amounting to 10–15°C. This dependence is shown separately in Fig. 4.

The described effects can again be explained by considering two transport phenomena⁶, the convection and diffusion fluxes. With increasing pore radius (increasing value of K), the contribution of the convective transport increases in proportion to $r^2 dp/dx$, hence at higher values of K a lower overpressure is sufficient for the gas penetration; and at constant overpressure a higher temperature (higher concentration gradient of water vapour) must be applied if K increases.

Influence of Water Vapour

Since the gradient of the partial pressure of water vapour is the driving of the bubbling effect⁶, elimination of this gradient causes the bubbling to stop. This occurs in a closed system or at a temperature at which $c_v^* = c_v^0$. In our experiments, the gradient of the partial pressure of water vapour was changed by changing the humidity of the inlet gas. The results for hydrogen in an open system are shown in Fig. 5. Although the character of the dependence of Δp on the temperature remains preserved, the water vapour present in the inlet gas causes the overpressure for the gas penetration to become appreciably higher, and this even at relatively low temperatures of saturation. Moreover, spontaneous bubbling is prevented.

Influence of KOH Solution

Solutions of potassium hydroxide have a higher surface tension than water, *e.g.*, in 7.2M-KOH $\gamma = 9.25 \cdot 10^{-2}$ N/m against $7.28 \cdot 10^{-2}$ N/m for pure water at 20°C (ref.^{11,12}). The vapour tension above a solution of 7M-KOH used in fuel cells is appreciably lower than above pure water¹³ (the volume concentrations in Table II were obtained by dividing the vapour tension with 0.1013 MPa, *i.e.*, the atmospheric pressure). Both these phenomena cause the gas flow through the membrane into the solution of KOH to start at a higher temperature than when pure water is used.

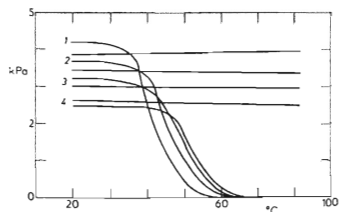


FIG. 2

Influence of the membrane structure on the penetration overpressure for hydrogen. Straight lines correspond to closed system, curves to open system. Membrane No 1 851; 2 803; 3 801; 4 793

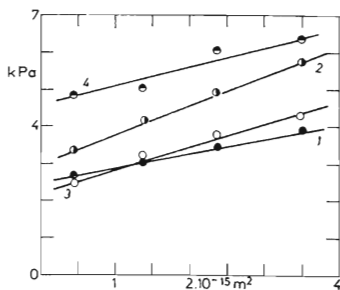


FIG. 3

Dependence of the penetration overpressure on the permeability of membranes. 1, 2: closed system; 3, 4: open system; 1, 3: hydrogen; 2, 4: oxygen; $p_k \approx 0.1$ MPa, 20°C

The measurements of the hydrogen flow indeed showed a difference in the expected sense (Fig. 6), although only several degrees (according to Table II, the difference between the saturated vapour concentrations above 7M-KOH and pure water corresponds to a temperature difference of slightly more than 10°C).

The Behaviour of the Complete Electrode

The dependences described above form a basis for studying the behaviour of complete electrodes. Our interest was focused on the anodes, since hydrogen penetrates more

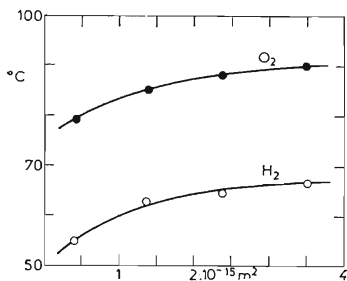


FIG. 4

Dependence of the spontaneous gas bubbling temperatures on the permeability of membranes

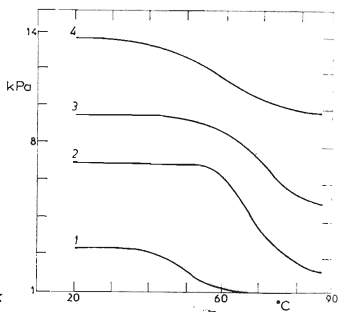


FIG. 5

Influence of water vapour on the hydrogen penetration overpressure. Membrane No 793. open system. 1 Dry hydrogen; 2 saturated with water vapour at 20°C; 3 at 70°C; 4 at 90°C

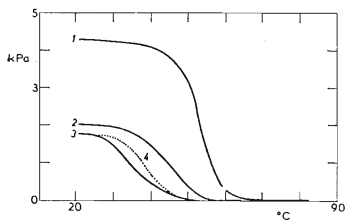


FIG. 6

Dependence of the penetration overpressure of hydrogen on the temperature. 1 Teflon membrane in water; 2 Teflon membrane with silver collector in water; 3 complete electrode in water; 4 complete electrode in 7M-KOH. Open system

easily than oxygen. These consisted of a cover layer formed by a porous Teflon membrane of 0.4 mm thickness, covered with a finely porous semihydrophobic silver collector layer of 0.2 mm thickness, and this in turn was covered with a semihydrophobic porous catalytic layer of 0.4 mm thickness. The layers were joined by rolling and heat treatment. The behaviour of hydrogen on the membrane, membrane with collector, and complete electrode is illustrated in Fig. 6.

It is seen that by combining the layers the overpressure necessary for gas penetration into water is gradually lowered; the same applies to the temperature of spontaneous penetration. This is in accord with the above-mentioned experimental findings. By combining the layers, the gas permeability is lowered, which leads to a decrease of the temperature of spontaneous penetration.

The mentioned changes are rather important as they lead to difficulties during operation of semihydrophobic hydrogen anodes in an open system. Fortunately, the situation is much improved by humidifying the inlet gas; this brings about changes which are as marked as in the case of hydrogen penetration through the sole membrane (Fig. 5). The increase of the temperature and overpressure necessary for the penetration of hydrogen through the electrode is sufficient to enable normal operation of the semihydrophobic hydrogen anode in a fuel cell.

Our measurements thus provide additional information about the spontaneous gas penetration through semihydrophobic porous electrodes in fuel cells or hydrophobic porous membranes. The trouble-free functioning of fuel cells requires to ensure a certain concentration of water vapour in the inlet gases, which was verified by a long-term operation of fuel cell modules in the temperature range 70–80°C.

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