CARBON GAS DIFFUSION ELECTRODES PROMOTED WITH SILVER AND OPERATING ON AIR OR OXYGEN IN ALKALINE MEDIUM. PHYSICAL PARAMETERS OF ELECTRODES AND THEIR COMPONENTS

Karel Smrček[a], Martin Wedell[a], Jiří Mrha[b] and Miroslava Musilová[b]

[a] ČKD Polovodiče, 140 03 Prague and
[b] J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 102 00 Prague

From the ratio of hydrophobic to hydrophilic pore volumes determined after a long-term exposure of the gas or active layer to water, the strong hydrophobic nature of the teflonized carbon black contained in carbon-based gas diffusion electrodes was confirmed. This material proves better than Teflon in Teflon-bonded active carbon electrodes, whose hydrophobicity is adversely affected on heating and the mechanical strength of the layer decreases. Measurement of the penetration of water and rate of flow of oxygen revealed that the teflonized carbon black ensures two essential functions of the gas diffusion electrode: feeding the active layer with oxygen and prevention of flooding of the gas pores.

Our preceding work[1] dealt with double-layer electrodes operating on oxygen or air in alkaline medium with either active carbon or active carbon promoted with silver as catalyst. It turned out that the electrode activity depends on the following factors (assuming a high and constant hydrophobocity of the gas layer and gas pores in the active layer): *i*) the ratio of the drowned to the gas-filled pores in the active layer; *ii*) the rate of mass transport in the gas-filled pores; *iii*) the resistivity of the active and gas layers.

The first factor is controlled by the mass ratio of the hydrophilic (catalyst) to the hydrophobic (teflonized carbon black) component of the active layer. The second factor is important in the case where the electrode operates on air[2], while the third one plays a role at high current loads. In the present work attention has been paid to all the three mentioned factors.

EXPERIMENTAL

The electrode layers were prepared from teflonized carbon black[3], active carbon HS-4 of a particle size under 60 μm either pure or promoted with 5—30% silver (denoted as catalysts 95/5 through 70/30)[1]. Silver in electrodes without active carbon was prepared by reduction of an aqueous suspension of a silver salt[4]. The gas layer was prepared from teflonized carbon black[1] without a current collector. The active layer was prepared from a mixture of this material with active carbon either pure or promoted with silver as described earlier[1]. The active carbon–PTFE system

was prepared by deposition from a PTFE suspension "Soreflon"[5,6]. The corresponding layer without a collector was made by rolling and, eventually, subsequent pressing at a chosen pressure. Such a layer was additionally heated at 340°C for 15 min. Electrodes with the pure silver catalyst were provided with a Teflon gas layer[7-9].

Structural characteristics of the layers were derived from measurements of the true and apparent densities and the rate of flow of oxygen. Thus, the ratio of the drowned and gas-filled pore volumes, which is related to the three-phase interface, was calculated from a) the true density, γ_t, determined by weighing on the air and in xylene, b) the apparent density, γ_a, determined from the mass and geometric dimensions, and c) the "water density", γ_w, determined by weighing on the air and after soaking with water for a sufficiently long time, thus imitating the conditions of operation of the electrode. The difference between the densities γ_t and γ_w is related to the difference in wettability of the semihydrophobic structure by xylene and water[10].

The fraction of hydrophobic pores, ε_{phob}, can be expressed as the ratio of the volume of dry pores, V_{phob}, to the volume of the electrode layer, V

$$\varepsilon_{phob} = V_{phob}/V . \tag{1}$$

The volume of the electrode layer consists of the volume of the solid phase, V_s, and of the volumes of dry (V_{phob}) and wetted (V_{phil}) pores, $V = V_s + V_{phob} + V_{phil}$. The individual volumes can be expressed as functions of the measured densities. Thus,

$$V = q/\gamma_t , \tag{2}$$

where q denotes mass of the sample. The "water density" is defined as

$$\gamma_w = \frac{q}{q - q_w} \gamma_0 = \frac{q}{V_s + V_{phob}} , \tag{3}$$

where q_w is the sample weight in water and γ_0 is the density of water. Since $V_s = q/\gamma_t$, we obtain

$$V_{phob} = \frac{(\gamma_t - \gamma_w) q}{\gamma_w \gamma_t} . \tag{4}$$

Finally, by substituting into Eq. (1) we obtain

$$\varepsilon_{phob} = \frac{(\gamma_t - \gamma_w) \gamma_a}{\gamma_t \gamma_w} . \tag{5}$$

Alternatively, the apparent density can be expressed from the definition of total porosity ε'

$$\varepsilon' = 1 - \gamma_a/\gamma_t \tag{6}$$

so that

$$\varepsilon_{phob} = \frac{\gamma_t - \gamma_w}{\gamma_w} (1 - \varepsilon') . \tag{7}$$

The fraction of wetted pores is simply

$$\varepsilon_{phil} = \varepsilon' - \varepsilon_{phob} . \tag{8}$$

The rate of flow of oxygen through the gas layer or through the electrode without current collector was measured by means of a device consisting of an overpressure cell, needle valve, manostat, and a gas burette. The porous layer in the overpressure cell was acted upon by a chosen overpressure of oxygen and the outlet was connected with a gas burette whose lower part was filled with water containing a saponate detergent. The time of passage of a bubble through a certain volume of the burette was measured. By a choice of this volume, the sensitivity was maintained the same with different porous samples, whose cross section was 10 cm^2.

The electric conductivity of the porous layers was measured by a modified four-electrode method on samples of 10 cm^2 surface area; the measuring electrode distance was 1 cm and the voltage signal was automatically detected and evaluated by a calculator[11].

RESULTS AND DISCUSSION

Ratio of Electrolyte- and Gas-Filled Pores

The measured three kinds of densities, total porosity, fractions of wetted and dry pores, and the percentual content of dry pores with respect to the total porosity for the studied samples are given in Table I. It is seen that the (total) porosity of the gas layer is equal to that of the active layer with the least silver content (catalyst 95/5) and it decreases somewhat with increasing content of the relatively little porous silver catalyst. The content of dry pores in the gas layer is much higher than that of the wetted ones. Of course, pores that are wetted only at their ends are not distinguished from those which are completely wetted. The strong hydrophobicity of the gas layer is evidenced also by the permeability measurements.

The fraction of dry pores in the studied active layers is considerably decreased by the presence of the hydrophilic catalyst regardless of its composition. This is because the increasing content of the nonporous silver catalyst was outweighed by the increasing fraction of the active carbon–silver mixture at the expense of the teflonized carbon black, so that the fraction of pores conducting the electrolyte in the active carbon was preserved.

Carbon electrodes are sometimes prepared from hydrophobized active carbon, therefore we studied the properties of the active carbon–PTFE system. The results are shown graphically in Figs 1 and 2. The samples were pressed either at the room temperature or at 340°C (softening point of PTFE).

It is seen from Fig. 1 that the porosity of the hot-pressed layer decreases with increasing pressing pressure up to about 30 MPa; at higher pressures the porous layer behaves as an elastic body. In the case of the cold-pressed layer, the porosity decreases nearly linearly with increasing content of PTFE, the slope of this dependence being independent of the pressing pressure. On heating, the porosity of the layer increases, evidence for sintering of the PTFE particles to aglomerates, whereby some active carbon particles originally blocked with Teflon are denuded. This interpretation is supported by the observed difference in hydrophobity of the active

layers prepared at the room temperature and at 340°C (Fig. 2). Such a large difference was not observed with the active carbon–teflonized carbon black system. The content of hydrophobic pores in the active carbon–PTFE layers prepared at 340°C begins to increase with the Teflon content only when this reaches about 40 mass %, whereas with samples prepared at the room temperature a content of 25 − 35% PTFE is sufficient for essential hydrophobization. It is interesting in this respect that the mechanical strength of the samples containing more than 20% PTFE is decreased.

TABLE I

Parameters of the cover and active layers

G^a	layer	γ_t g cm^{-3}	γ_w g cm^{-3}	γ_a g cm^{-3}	ε'	ε_{fob}	ε_{fil}	W^b %
—	cover	1·9732	0·8523	0·7412	0·624	0·494	0·130	79·2
3 : 2	active 95/5	1·0694	1·0694	0·7541	0·522	0·327	0·295	52·6
3 : 2	active 90/10	2·0176	1·1381	0·8172	0·595	0·313	0·282	52·6
2 : 1	active 80/20	2·1272	1·1924	0·8629	0·593	0·318	0·275	53·6
2 : 1	active 70/30	2·2225	1·2800	0·9237	0·584	0·3b6	0·278	52·4

^{a} Mass ratio of catalyst to teflonize carbon black; ^{b} fraction of hydrophobic pores.
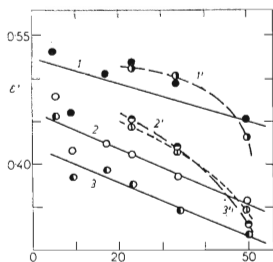

FIG. 1

Dependence of total porosity on PTFE content and pressing pressure. Nonheated layers: 1 Nonpressed; 2 30·8 MPa; 3 45·3 MPa; heated layers: 1' nonpressed; 2' 30·8 MPa; 3' 45·3 MPa
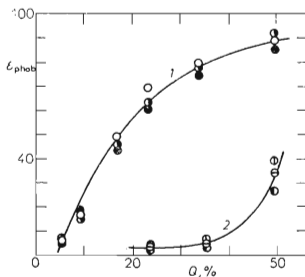
FIG. 2

Dependence of percent content of hydrophobic pores on PTFE content and pressing pressure. 1 Nonheated layers; 2 heated layers; ●, ◐ nonpressed; ○, ⊖ 30·8 MPa; ◑, ◒ 45·3 MPa

The mentioned aglomeration of PTFE is evidenced also by the measurement of the resistance (Fig. 3). With a low content of dry pores and low electric resistance of the active layer, the carbon particles must be held firmly by a network of sintered particles forming eventually chains. The volume ratio of the components is important, so that the effect of PTFE begins to be marked only at its high content. In this respect, the active carbon–PTFE system is distinguished from the silver–PTFE system.

Determination of Maximum Pore Diameter of Gas Layer

The gas layer of hydrophobic gas diffusion electrodes ensures uniform gas transport to the whole active layer. Constant hydrophobic properties of both layers are essential for their proper functioning. The maximum pore diameter must be such as to prevent penetration of the electrolyte during operation of the electrode.

Since the maximum pore radius cannot be found by mercury porosimetry, we used the method of water penetration through the porous layer, *i.e.*, measuring the overpressure at which the first drops of water appeared on the gas side. This overpressure is related to the corresponding pore radius as $p_k = (2\sigma \cos \Theta)/r$, where $\sigma = 7.275 \cdot 10^{-2}$ N/m and $\Theta = 121°$ at 20°C for the water–PTFE–air system[12]. With the three studied gas layers from teflonized acetylene black, studied by us, the mean value of the maximum pore radius was equal to $3.57 \cdot 10^{-6} \pm 8 \cdot 10^{-9}$ m. The corresponding mean water overpressure was $\bar{p}_k = 0.2127$ MPa which is higher than could be attained during operation of the electrodes. Thus, the gas layer excludes the possibility of penetration of the electrolyte.

If the water overpressure increases only by $5 \cdot 10^{-3}$ MPa (*i.e.*, to 0.2177 MPa), water begins to penetrate uniformly through the whole gas layer. This overpressure corresponds to the mean pore radius $\bar{r} = 3.46 \cdot 10^{-6}$ m. The similarity of both values of $\bar{r}$ is an evidence for the homogeneity of the porous structure.
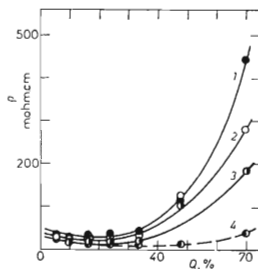

Fig. 3

Dependence of electric resistivity ϱ (mohm . . cm) on PTFE content and pressing pressure. Nonheated layers: *1* 12·3 MPa; *2* 30·8 MPa; *3* 60·6 MPa; heated layers: *4* at all pressures used

Penetration of Oxygen through the Gas Layer and Whole Electrode

The gas flow through the pores of the gas layer of the hydrophobic electrode at a certain overpressure can serve as a measure of the ability to feed the active layer with the electroactive gas, since it enables us to calculated the maximum attainable current which could be withdrawn from the electrode on the assumption of a full utilization of the gas. In the gas flow can be calculated theoretically and compared with the measured one, some conclusions concerning the porous structure can be drawn.

The gas flow through a capillary of length L and radius r can be calculated from an equation derived by Knudsen[13] which can be written in the form[14]

$$N = \frac{r^2(p_0 + p_1)}{16RT\eta}\left(1 + \frac{64}{3\pi}\frac{1}{r}\frac{1 + \sqrt{(2\pi)}\,r/1}{1 + 1\cdot235\sqrt{(2\pi)}\,r/1}\frac{p_0 - p_1}{L}\right), \qquad (1)$$

where N is expressed in mol/m^2 s units; l (m) is the mean free path of the gas molecules, η (Pa s) its dynamic viscosity, p_0 and p_1 (Pa) the pressure at the inlet and outlet. The velocity of flow, U (m/s), of the gas through a porous layer of thickness L, porosity ε and tortuosity factor f_p is for low overpressures $(p_0 - p_1 \ll p_0)$ given by the equation

$$U = \frac{r^2}{8\eta}F\left(\frac{1}{r}\right)\frac{\Delta p}{L}\frac{\varepsilon}{f_p}, \qquad (2)$$

where $F(1/r)$ stands for the terms in parentheses in Eq. (1), and $\Delta p = p_0 - p_1$. Equation (2) can be put into the more usual form

$$U = K\,\Delta p/L, \qquad (3)$$

where K is called the permeability coefficient.

Experimental values of U for oxygen are shown graphically in Fig. 4. With porous PTFE membranes, the linear dependence (3) holds good up to an overpressure of $0\cdot1$ MPa. It is therefore sufficient to measure the U values at lower overpressures (of the order of kPa) and to extrapolate them to higher overpressures. Straight line *1* in Fig. 4 corresponds to the flow of oxygen through the gas layer, straight lines *2* and *3* to the flow through the whole electrode (without the collector nets); the latter values are naturally lower. The values of the coefficient of proportionality, k, in the equation $U = k\,\Delta p$ are given in Table II.

To calculate the highest attainable current, the pressure difference Δp along the thickness of the porous layer must be known. With self-breathing electrodes, operating at atmospheric pressure and at a low water vapour tension, the value of Δp is close to $0\cdot1$ MPa. The calculated values of U and the corresponding maximum current

TABLE II
Characteristics of oxygen flow through cover layer and complete electrodes

System	In dry state					In wet state			
	k^a	U_1	i_{max}	ε'	ε_p	k^a	U_2	i_{max}	U_2/U_1
Cover layer (1)	$4.027 . 10^{-2}$	$3.948 . 10^{-3}$	6.83	0.624	0.09	$3.402 . 10^{-2}$	$3.478 . 10^{-3}$	6.02	0.881
Electrode (2)	$3.055 . 10^{-2}$	$3.004 . 10^{-3}$	5.21	—	0.6	$1.042 . 10^{-3}$	$8.158 . 10^{-5}$	0.14	0.027
Electrode (3)	$3.820 . 10^{-2}$	$3.691 . 10^{-3}$	6.39	—	0.08	$6.945 . 10^{-4}$	$6.011 . 10^{-5}$	0.104	0.016

[a] Constant (m s^{-1} MPa^{-1}) of the function $U = k\,\Delta p$.

densities i_{max} (A/cm^2) are also given in Table II. They are by an order of magnitude lower than in the case of porous PTFE membranes made for other electrodes[6,15], nevertheless they are still fairly high.

The hydrophobicity of the gas layer can be judged also by the change of the velocity of flow of oxygen after prolonged contact with water. This is seen from straight line *1'* in Fig. 4 and from the corresponding data in Table II. There is only a minor effect on the gas flow, evidence for only a slight wetting, probably only of the pore entrances. Changes due to wetting of the active layer are much more conspicuous (straight lines *2'* and *3'* and Table II).

A comparison of the calculated and measured U values enables one to estimate the fraction of permeable pores referred to the total porosity. We used the following values: $\Delta p = 1 \cdot 01 \cdot 10^5$ Pa, $r = 3 \cdot 5 \cdot 10^{-6}$ m, $L = 1 \cdot 46 \cdot 10^{-3}$ m, $\eta = 2 \cdot 41 \cdot 10^{-5}$ Pa s, $\varepsilon = 0 \cdot 62$, $f_p = 2$, and $l = 6 \cdot 3 \cdot 10^{-8}$ m.

The theoretical value of U for the gas layer is equal to $0 \cdot 0276$ m/s; the measured values are in Table II together with the fraction ε_p of permeable pores, participating in the gas transport. This value is, of course, lowered by the presence of the active layer (Table II). A comparison of the values of ε and ε_p may be helpful in evaluating the technology of the electrode preparation. A decreases of the gas permeability, however, need not have a negative effect on the electrode performance, since the gas transport rate may be sufficient thanks to the existence of pores that are not detected by the permeability measurement as they do not communicate with the electrolyte side of the electrode.

Electric Resistivity of the Layers

With carbon gas diffusion electrodes, a built-in metallic current collector is necessary to compensate for the considerable electric resistance especially of the active layer.
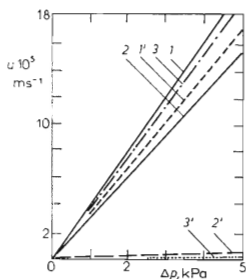

Fig. 4

Measured velocity of flow of oxygen as function of overpressure. Three layers in the dry *1—3* and wet state *1'—3'*

This is due to imperfect contacts among the active carbon or carbon black particles, their disordered structure, to the presence of Teflon as binder and waterproofing agent, and eventually various adsorbed substances. Some relevant data for active carbon–PTFE mixtures at various pressing pressures are shown graphically in Fig. 3. A shallow minimum of the resistivity is observed at $30-40$ vol.% of PTFE with thermally treated layers, and its position is different with thermally untreated layers. Sintering of PTFE particles doughtless plays a certain role. Resistivity values of up to several Ω cm were observed which could not be markedly decreased by the pressing pressure. They lead to considerable voltage losses, which must be eliminated

TABLE III

Resistivities of electrode layers

Layer type	Resistivity Ω cm	Note
1) Gas layer without collector	5·723	—
2) Gas layer with collector	0·01603	On the collector-free side
3) "Carbon" active layer	1·232	carbon black 3 : 2, no coll.
4) Catalyst 95/5	1·109	catalyst and teflonized carbon black 3 : 2, no coll.
5) Catalyst 90/10	1·047	as preceding
6) Catalyst 80/20	1·140	catalyst and teflonized carbon black 2 : 1, no coll.
7) Catalyst 70/30	1·569	as preceding
8) Whole electrode "carbon" catalyst	$9·364 . 10^{-5}$	catalyst and tefl. carbon black 3 : 2, coll. both sides
9) Whole electrode catalyst 50/50	$1·219 . 10^{-4}$	catalyst and tefl. carbon black 4 : 1, coll. both sides
10) Catalyst silver	$2·453 . 10^{-4}$	hot pressed at 4 NPa, 340°C, no collector
11) Catal. mixt. of Ag and active C	$4·553 . 10^{-3}$	as preceding; ratio of components 4 : 1
12) As preceding	$1·422 . 10^{-3}$	hot pressed at 4 MPa, 340°C, porous Ag coll.

by using a nickel-plated iron net of mesh size 1·0 mm and wire thickness 0·3 mm as a current collector.

Comparable values were measured with layers used in the present work (Table III, lines *1*, *3*, and *7*). The resistance of both the active and the cover layers drops after applying the collector. With the gas layer, measured on the collector-free side, the resistance drops by two orders of magnitude (Table III, line 2); and if the collector is applied onto both sides, the resistance drops by 4 − 5 orders of magnitude and is comparable with that of the metallic net.

The use of a current collector is necessary not only with the mentioned electrodes but also with electrodes whose active layer is prepared from a mixture of silver and carbon powders (Table III, line *11*). Only when the active layer is from powdered silver with 15% PTFE, its resistivity is so low that no current collector is necessary (Table III, line *10*).

REFERENCES

1. Musilová M., Mrha J., Wedell M., Smrček K.: This Journal, in press.
2. Iliev I., Gamburtsev S., Kaisheva A., Mrha J.: J. Appl. Electrochem. *5*, 291 (1975).
3. Iliev I., Gamburtsev S., Kaisheva A., Vakanova E., Muchovski I., Budevski E.: Izv. Ortd. Khim. Nauki, Bulg. Acad. Sciences *7*, 223 (1974).
4. Beran J.: Czech. 171 774.
5. Mrha J., Musilová M., Jindra J.: This Journal *36*, 638 (1971).
6. Jindra J., Mrha J.: This Journal *36*, 957 (1971).
7. Smrček K., Beran J., Jandera J.: Proc. 4th Internat. Symp. Fuel Cells, Anwerpe 1972.
8. Beran J., Smrček, Jandera J.: Czech. 149 395.
9. Beran J., Smrček K., Jandera J.: Czech. 159 414.
10. Volfkovich J. M., Skolnokov E. I.: Elektrokhimiya *15*, 8 (1979).
11. Škaloud M.: Unpublished results.
12. Fow H. W., Zisman W. Z.: J. Colloid Sci. *7*, 109, 428 (1952).
13. Záviška F.: *Kinetická teorie plynů*. Published by Vědecké vydavatelství, Prague 1951.
14. Micka K.: Private communication.
15. Smrček K., Ministr Z.: *Porometrie a její použití*. Českoslov. věd. techn. společnost, Prague 1979.

Translated by K. Micka.