OXYGEN CATHODES BASED ON CARBON PROMOTED WITH SILVER. I. SOME ELECTROCHEMICAL PARAMETERS OF THE ELECTRODES

Miroslava MUSILOVÁ[a], Martin WEDELL[b], Jiří MRHA[a] and Karel SMRČEK[b]

[a] *J. Heyrovský Institute of Physical Chemistry and Electrochemistry,*
Czechoslovak Academy of Sciences, 102 00 Prague 2 and
[b] *ČKD Semiconductors, 140 03 Prague 4*

A comparison of the electrochemical parameters of oxygen gas diffusion electrodes made of teflonized carbon black (the hydrophobic component) and of a catalyst — consisting either of pure silver or silver promoted active carbon (the hydrophilic component) — enabled to investigate the influence of the silver presence in this type of electrodes. The characteristics obtained with the pure and air oxygen permitted, in combination with other measurements, to explain the role of the silver catalyst. It was found that this catalyst has a positive effect on the electroreduction of oxygen but that it also, due to its structural properties, influences in a negative way the distribution of the gas and electrolyte filled pores — which, in consequence, leads to gas transport problems in the active layer. Comparative measurements, carried out with electrodes on the silver–teflon basis have supported the assumption that both the above types of pores influence the transport processes in the active layer. The measurements showed also the advantages of the silver–teflon electrodes with pure oxygen, as well as, their disadvantages when air oxygen was used.

After several years of stagnation, fuel cells have become again the subject of renewed, increasing interest. In the USA, this concerns first of all fuel cells based on the acid electrolytes, working at increased temperatures (phosphoric acid first-generation fuel cells[1]); in Europe the interest is still concentrated on the alkaline electrolytes (*e.g.* the ELENCO project[2] or a Swedish project[3] — solving simultaneously the production of hydrogen). A majority of studies and projects dealing with the alkaline medium still considers carbon electrodes to be one of the main alternatives for the air or oxygen electrodes.

A systematic research of electrodes consisting of a gas layer (teflon coated carbon black) and of an active layer (teflonized carbon black mixed with active carbon) enabled to optimalize the composition of these electrodes and, in this way, also the corresponding parameters obtained at different current loads[4-7]. The advantage of using the electric conductive gas layer was evident especially on electrodes with the decreased conductivity of the active layer, *i.e.* with electrodes in which the catalyst is formed by pure active carbon — with a small admixed amount of silver. The proper porosity and pore size distribution in this gas layer garantees a sufficient mass transport rate in the gas phase. The mass transport rate in the gas layer of such a type can be regulated mainly by the thickness of the layer, *i.e.* by the size of the teflonized carbon black doses. The optimum dosage[8] of teflonized carbon black — containing 35 weight % of PTEE — equalled 100 mg/cm^2 (the value relates to a 1 cm^2 geometrical area of the electrode).

As far as the active layer is concerned, the biggest attention was so far paid to the influence of the different size of particles of active carbon catalyst (the hydrophilic component of the active layer) and to the ratio: catalyst/teflonized carbon black (the latter representing the hydrophobic component[9]). In addition, the effect of the total size of doses of this mixture was studied on the various electrochemical parameters of the oxygen and air electrodes[9].

The use of the Ag-catalyst supported on an active carbon carrier resulted in improved activity of the oxygen electrode, but it also had a negative effect on the mass transport rate in the gas phase of the active layer[7,10-13].

The presented work investigates in more detail the catalytic system: silver/active carbon — from the aspect of its applicability in the active layer of the above type of electrodes. The work is aimed to clarify the role of the presence of silver, both with respect to electrocatalysis and to the mass transport in the porous system of the gas filled active layer.

EXPERIMENTAL

The double-layer hydrophobic electrodes used in the measurements were described in detail previously[5-12]. The gas layer is formed by teflonized carbon black (acetylene black P-1042, GDR, containing 35 weight % PTEE). The active layer consists of a mechanical mixture of teflonized carbon black and a powder catalyst — the latter present either in the form of pure active carbon HS-4 (MCHZ Ostrava, Czechoslovakia) or coated with silver. Silver was deposited by means of the method of active carbon impregnation, using treatment with a $AgNO_3$ solution of corresponding concentration, followed by silver reduction with hydrazine. The denotation of a catalyst (e.g. 95/5) signifies that the catalyst contains 95 weight % of active carbon and 5% of deposited silver.

The previously used factor of macroporosity β[8,12] characterizes the weight ratio of the hydrophobic particles forming the gas filled pores (teflonized carbon black) and the total dosage of the active layer (teflonized carbon black + a catalyst). This factor is defined by a relation

$$\beta = \frac{m_{TS}}{(m_K + m_{TS})},$$

where m_{TS} is the weight of teflonized carbon black and m_K the weight of a catalyst. Both weights are related to a 1 cm² geometric surface area of the electrode (mg/cm²).

The disc electrodes (with a 5 cm² effective geometrical area) used in the measurements were prepared by hot-pressing at 350°C, under a pressure 20 MPa. A nickel plated iron mesh was pressed-in from both sides of the electrodes. The dosage used in the gas layer was 100 mg/cm²; the corresponding values for the active layer are given separately, together with the results of the measurements.

The overpressures of oxygen and air equalled 100 Pa. The Hg/HgO system in a 7M-KOH solution was selected as a reference electrode. All our measurements were carried out in the same 7M-KOH solution, using a usual half-cell arrangement. All the given potentials refer to the above reference electrode. The polarization curves were recorded after 15 hours functioning of the electrodes, using oxygen, and working with current densities 100 mA/cm² at the laboratory temperature.

For a comparison, we used also disc electrodes (with a 5 cm² effective geometric area) in which

the gas layer was prepared of pure PTFE in a form of a porous sheet and the active layer consisted of a mixture of the silver powder and PTFE (refs[14−16]).

The amount of electrolyte in the active layer of the electrode was measured from the weight increment of the electrode — determined at the end of the measurement; (the measuremement lasted 7 days under a 100 mA/cm^2 load and was followed by 2 hours of rest period).

For greater simplicity and the possibility of comparison, the following electrochemical parameters were selected from the obtained experimental data: the current density i_{100} (mA/cm^2) of the oxygen electrode, at $E = -100$ mV; the absolute value of the potential change ΔE_{100} (mV) caused by replacement of the oxygen with air, at current density 100 mA/cm^2; the amount of electrolyte in the electrode — related to a unit weight of the active layer (m_E) and to a unit weight of the catalyst (m_E'). The voltage-current characteristics E/i obtained with pure and air oxygen enabled to calculate the "breathing curves" $\Delta E(i)$.

RESULTS AND DISCUSSION

Active Carbon as a Catalyst

Teflonized carbon black acts in the used electrodes as a binder but, at the same time, it forms in the gas layer and in the active layer a network of pores supplying both
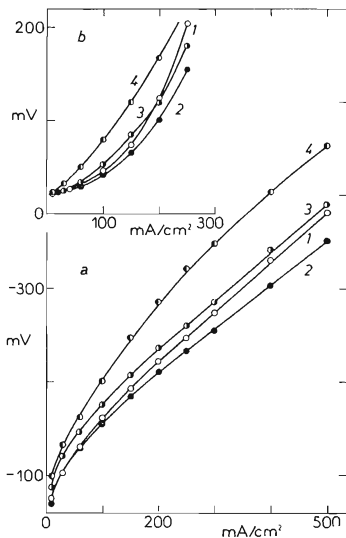

Fig. 1

a Current-voltage characteristics of the oxygen electrodes, with active carbon HS-4 as a catalyst. Total (catalyst + teflonized carbon black) dosage (in mg/cm^2): 1 20 + 10; 2 18 + 12; 3 15 + 15; 4 12 + 18; b $\Delta E(i)$ curves for the same electrodes

layers with pure or air oxygen. The role which teflonized carbon black plays as a binder is especially important in the case when the catalyst is formed by pure active carbon − since the bulk density of this catalyst is lower than the density of its mixtures with silver. Fig. 1a shows the polarization curves obtained with pure oxygen. Fig. 1b shows the "breathing" curves for four different ratios: carbon black/teflonized carbon black, in the active layer. From these curves it is possible to obtain the fundamental electrochemical parameters, which are summarized in Table I. The optimum mixture of active carbon and teflonized carbon black $(18 + 12 \text{ mg/cm}^2)$ represents a compromise between the electrochemical parameters of the electrode and the mechanical strength of its active layer (Fig. 1). The macroporosity factor of the above mixture equals $\beta = 0.4$.

From our measurements and the previously published papers[7−12], one can conclude that the electrochemical behaviour of the given electrode is in major part determined by the volume of the electrolyte and gas filled pores in the active layer and by the mutual ratio of the both types of pores.

The volume of the electrolyte filled pores can be affected by the content of carbon black in the active layer − as one can conclude from Table I. An information on the extent in which the gas transport is affected by the carbon black loadings, ranging betweeen $12−20 \text{ mg/cm}^2$ (the only hydrophilic component in the active layer) is shown in Fig. 1b. Transport problems appear not only at the very low contents of active carbon in the active layer, but also − and in a much more pronounced way − at the very high contents. The first case, $(\beta = 0.6)$, can be explained as a consequence of the very "diluted" structure of active carbon − and thus also of a sparse network of the electrolyte containing pores. On the other hand − the second case, $(\beta = 0.33)$, corresponds to a negative change in the network of the gas containing pores − which results in increased demands on gas transport in the "diluted" system of the gas pores. Also, one cannot neglect the increasing thickness of the active layer, as will be discussed later in connection with the catalyst 95/5.

The transport problems in the gas filled pores located close to the region of

TABLE I

Volume of the electrolyte filled pores

Dosage, mg/cm² HS-4 + teflonized carbon black	$20 + 10$	$18 + 12$	$15 + 15$	$12 + 18$
i_{100}, mA/cm²	27	28	19	11
ΔE_{100}, mV	46	40	52	79
m_E, g	0.79	0.70	0.55	0.42
m'_E, g	1.33	1.17	1.11	1.05

electrochemical reduction can be solved — on the basis of the earlier published paper[17−19] — also by changing the pore structure of the catalyst (pure active carbon) itself. Such a change must be aimed at increase of the volume porosity and the hydrophobicity of a catalyst — achieved — by the reduction of its hydrophilic surface oxides (H_2, 900°C — ref.[18,19]). In this way it was possible to prepare the active carbon in which 42% of total porosity was formed by the hydrophobic pores. The benefical effect of the increased proportion of gas filled pores directly within the active carbon particles leads (for air oxygen) to substantial reduction of the transport problems. The values of ΔE_{200} are visibly lower than the corresponding values obtained for the active carbon with low content of gas filled pores[19]. Also from paper[7] one can conclude that it is possible to regulate the content of electrolyte in the active layer (and in this way, also — the gas transport in the near gas pores), by using different types of active carbon.

From our experimental data it can be also concluded that in order to interpret some of the experimental data one needs neither to assume a partial penetration of the alkaline electrolyte into the hydrophobic structure of teflonized carbon black nor to assume the formation of a thin film of electrolyte — partially blocking the gas transport at $\beta < 0.35$. The assumption of the existence of a thin electrolyte layer in the hydrophobic structure — formed by teflonized carbon black — was used[9] also for interpretation of the observed inverse dependence between the size of the active carbon particles and the rate of gas transport (a coarser graining resulted into much lower transport rates with air oxygen).

In order to check the effect of the active carbon particle size on the electrochemical parameters of the oxygen and air electrodes, we have prepared electrodes with 18 mg/cm² loadings of active carbon and 12 mg/cm² loadings of teflonized carbon black in the active layer. Four different fractions of active carbon HS-4 were used: < 60 μm, $60−80$ μm, $80−100$ μm and the $1 : 1$ mixture of $(60−80)$ μm and $(< 60$ μm$)$ fractions. The obtained electrochemical parameters showed that the increase in size of the active carbon particles leads only to a relatively small decrease of the i_{100} values (and thus also of the content of electrolyte in the electrode) — while the corresponding ΔE_{100} values simultaneously increase. It is possible to conclude that the assumed necessity — to build-up a network with the optimum density of electrolyte filled pores in the whole volume of the active layer — was verified also for the active carbon samples with different particle size. The large size particles of active carbon (and thus also the corresponding active sites and electrolyte filled pores), form a "diluted" sparse structure causing transport problems in the vicinity of these particles.

The Active Carbon−Silver System as a Catalyst

We have examined the properties of electrodes using three different mixtures of the 95/5 catalyst with teflonized carbon black $(20 + 10; 18 + 12; 15 + 15$ mg/cm²$)$.

A survey of electrochemical parameters obtained in these measurements is given in Fig. 2. From the comparison of Fig. 2 and Fig. 1 (the latter corresponding to the pure active carbon catalyst), it is evident that the deposition of silver on active carbon leads to substantial increase of the i_{100} value, while the ΔE_{100} value remains practically unchanged. This fact suggest that in spite of the observed strong catalytic effect on the electroreduction of oxygen the rate of the gas transport is only very little affected.

In order to find out how far the electrochemical parameters of electrodes can be changed by the composition and by the total dosage of the mixture in the active layer, we have examined the following electrodes: a) electrodes with the constant content of a 95/5 catalyst (20 mg/cm^2) — with a variable amount of teflonized carbon/black $(10-30 \text{ mg/cm}^2)$ b) electrodes with a constant, $(3:2)$, ratio: catalyst $(95/5)$ teflonized carbon black — with the increasing dosage of this mixture in the active layer. The survey of electrochemical parameters obtained in these measurements is presented in Table II. Fig. 3 gives the i_{100} and ΔE_{100} values against the content of teflonized carbon black. On the last two dependences one can see that at the moment when the
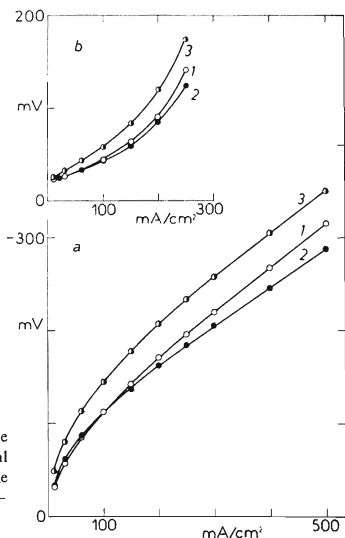

FIG. 2

a Current-voltage characteristics of the oxygen electrodes for the 95/5 catalyst. Total (catalyst + teflonized carbon black) dosage (in mg/cm^2): 1 $20 + 10$; 2 $18 + 12$; 3 $15 + 15$; b $\Delta E(i)$ curves for the same electrodes

content of teflonized carbon black exceeds the value 14 mg/cm^2 ($\beta = 0.4$), the i_{100} values begin to fall — while the E_{100} values are simultaneously increasing. Such behaviour indicates that — in analogy with the active carbon — also in the case of the 95/5 catalyst, the active sites become at $\beta = 0.4$ partially eliminated from participation in the current generating process — as it was discussed earlier in connection with

TABLE II
Survey of electrochemical parameters

Catalyst: teflonized carbon black	2 : 1	3 : 2	1 : 1	2 : 3
Dosage, mg/cm^2 95/5 + teflonized carbon black	20 + 10	20 + 13.4	20 + 20	20 + 30
i_{100}, mA/cm^2	82	80	61	45
ΔE_{100}, mV	44	44	58	77
m_E, g	0.73	0.61	0.44	0.23
m'_E, g	1.11	1.01	0.88	0.76

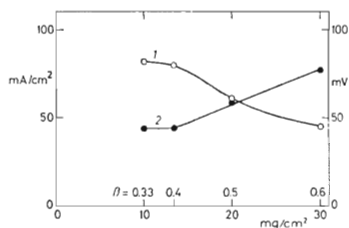| Catalyst: teflonized carbon black	3 : 2	3 : 2	3 : 2
Dosage, mg/cm^2 95/5 + teflonized carbon black	12 + 8	16 + 10.7	24 + 16
i_{100}, mA/cm^2	73	80	78
ΔE_{100}, mV	46	44	44
m_E, g	0.64	0.62	0.59
m'_E, g	1.07	1.04	0.99

FIG. 3

The effect of different teflonized carbon black content on the characteristics of electrodes with a 95/5 catalyst: 1 i_{100}; 2 ΔE_{100}; catalyst dosage 20 mg/cm^2

Fig. 1. The concept of gradual isolation of the active sites is also supported by the data showing the decreasing content of the electrolyte in the unit weight of the catalyst (Table II)

The experimental fact that at $\beta \geqq 0.4$, the active sites of the catalyst become to be blocked away from the current-generation process, is in good agreement with the earlier published values $(\beta = 0.35)$ — ref.[11,12]. In these papers, the blocking mechanism was attributed to the excessive thickness of the active layer and it was assumed that only a thin fraction of this layer ("active zone") — on the side of the electrolyte — takes part in the process. The thickness of this zone is comparable with the diameter of the catalyst particles $(30 - 100\ \mu m)$. The above described model is, however, based on results obtained with the Pt-PTFE type of electrodes[20-22]. In our case — with the carbon electrodes — the electrochemical parameters and the content of electrolyte in the active layer is only little affected by the increasing dosage in the active layer (Table II). It is clear that the information obtained for the Pt-PTFE system is not applicable for conclusions concerning the active layer of the carbon electrodes.

The Effect of the Increased Content of Silver Deposited on Active Carbon

On the basis of results obtained with the 95/5 catalyst — all subsequent measurements with the catalysts containing $(10-50\%)$ silver, used constant 30 mg/cm² doses of the catalyst in the active layer. The effect of the change of the catalyst/teflonized carbon black ratio was checked with each catalyst. These measurements included electrodes with the following silver catalyst compositions: 90/10, 80/20, 70/30, 50/50
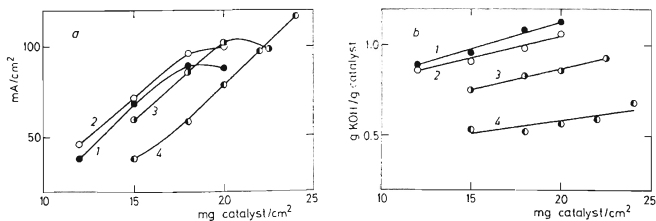

Fig. 4

The effect of different catalyst content (a) on i_{100} values and (b) the content of electrolyte: catalyst composition 1 90/10; 2 80/20; 3 70/30; 4 50/50; total (catalyst + teflonized carbon black) dosage 30 mg/cm²

and dosages: $12 - 24$ mg of a catalyst and $18 - 6$ mg of teflonized carbon black (per 1 cm² geometrical area of active layer). Fig. 4 shows, for the case of the above four catalysts, the effect of the increasing catalyst/ teflonized carbon black ratio — on the i_{100} value (Fig. 4a) and on the content of electrolyte in a unit catalyst weight (Fig. 4b).

It can be seen in Fig. 4a that all curves of the individual catalysts pass through a maximum, the magnitude of which slightly increases with the increasing amount of supported silver, while a position of the maximum is simultaneously shifted towards larger doses of that which catalyst. If we increase the doses of the catalysts with the $(10 - 30\%)$ Ag content — above 20 mg/cm², we change the optimum proportion between the gas and electrolyte filled pores in favour of the electrolyte pores — which leads consequently to a drop in the i_{100} values of the corresponding electrodes. For mechanical reasons we were unable to check with the 50/50 catalyst doses larger than 24 mg/cm². The increasing content of silver on the active carbon carrier has only a slight effect on the i_{100} values — assuming that the optimum ratio: catalyst/ /teflonized carbon black is kept unchanged.

The interpretation of the above dependences can be simplified by means of the dependence between the amount of electrolyte (per a unit weight of a catalyst) and the amount of a catalyst in the active layer. This dependence is shown in Fig. 4b for all the investigated catalysts. One can see that the electrolyte content increases with
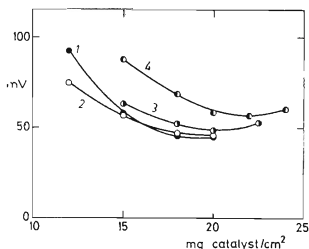
Fig. 5

The effect of different catalyst content on ΔE_{100} values; for the same electrodes as in Fig. 4
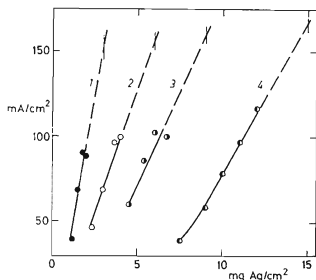
Fig. 6

The effect of different silver content on i_{100} values, for different catalysts: 1 90/10; 2 80/20; 3 70/30; 4 50/50; total (catalyst + teflonized carbon black) dosage 30 mg/cm²

the increasing amount of a catalyst in the active layer — on the other hand, the content of the electrolyte decreases with the increasing content of silver. Each of the studied catalysts requires therefore, at least to some extent, a special optimum proportion between the electrolyte filled and gas filled pores in the active layer. The catalysts with higher silver contents require lower dosages of teflonized carbon black, in order to compensate for the simultaneously observed negative effect of increasing silver amount, on the content of electrolyte in a unit weight of a catalyst. An establishment of the optimum ratio between the gas and electrolyte filled pores shows favourably in smaller transport problems in the gas phase (Fig. 5).

Comparison of Electrodes Using a Catalyst Made of Pure Silver or of Silver Deposited on the Active Carbon Support

Silver is a very efficient catalyst for the electroreduction of oxygen in alkaline solutions, however, for its effective functioning it must be introduced in the optimum way into the porous structure of active layer of the oxygen electrode. The decision, whether it is more preferable to use pure silver or silver deposited on an active carbon support, depends first of all on the power output requirements, as well as, on the economic aspects.

The advantage of electrodes using the silver deposited on the active carbon support can be seen in their relatively low price, a simple and highly reproducible way of their preparation and in their excelent electrochemical parameters — especially when used with air oxygen. The requirements on the mechanical strength in this type of electrodes do not permit — without lowering the level of the electrochemical parameters — to increase the content of the silver catalyst too much above 12 to 14 mg/cm^2. The amount 4 mg/cm^2 of Ag (of the catalyst 80/20) seems to be favourable not only because of economical reasons but also with respect to the obtained parameters.

This situation is evidenced in Fig. 6, showing a survey of the effect of various silver contents $(5-50\%)$ — for various catalyst/teflonized carbon black ratios — on the activity of electrodes for electroreduction of oxygen (i_{100}). If we extrapolate the dependences obtained for i_{100} (Fig. 6) — up to the theoretical maximum values (corresponding to the pure catalyst with no teflonized carbon black in the active layer), we obtain for i_{100} roughly the value $155-170$ mA/cm^2. The maximum value which can be reached practically varies for the individual catalysts between 90 to 120 mA/cm^2.

In order to find out whether it is possible to reach still higher i_{100} values, we have compared the catalytic system: silver/active carbon with the pure silver system. The use of pure silver requires a substantial increase of silver doses in the active layer, since the compact (*i.e.* non-porous) particles must form such a type of agglomerates

in the layer which would be able to build up a hydrophilic skeleton capable to distribute at least the minimum amount of electrolyte in the active layer. This "skeletal" type of silver prevails significantly over the "catalytic" silver in the total amount dosed — which increases the total dosage values to a level of several tens of mg of Ag/cm^2.

In the case of pure silver, the PTFE particles must act simultaneously as a binder, since they are able — even in small amounts — to guarantee the acceptable mechanical properties and the sufficient volume of the gas pores for the work with oxygen. With air oxygen — one can expect increased gas transport difficulties in the gas pores.
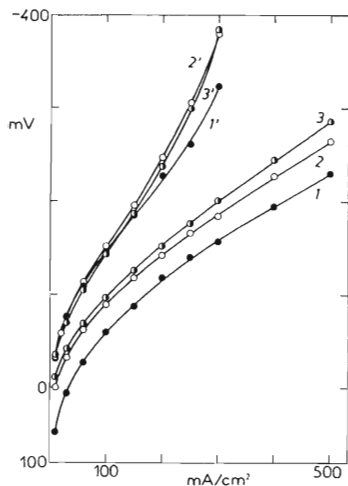

Fig. 7

The effect of different silver content on the current-voltage characteristics of the oxygen (1, 2, 3) and air electrodes (1', 2', 3'), for different catalysts: 1, 1' pure silver; 2, 2' catalyst 50/50; 3, 3' catalyst 80/20; same electrodes as in Table III
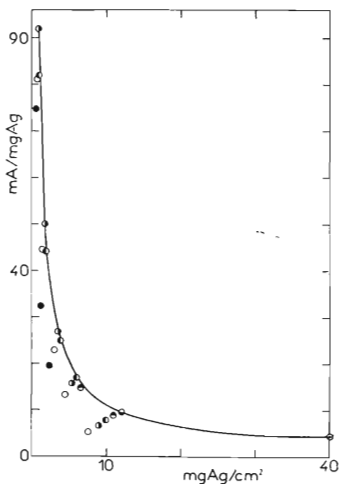
Fig. 8

The effect of different silver content on the current efficiency (mA/mg Ag) of all tested electrodes: catalyst/teflonized carbon black dosage (mg/cm²) ◒ 24/6; ◓ 22/8; ◑ 20/10; ◐ 18/12; ○ 15/15; ● 12/18. Pure silver/ PTFE: ⊙ 40/4

The above presented assumptions were verified on the electrode of a Ag-PTFE type, using $(40 \text{ mg Ag/cm}^2 + 4 \text{ mg PTFE/cm}^2)$ dosage in the active layer ($\beta = 0.091$). The results obtained with this electrode are compared in Fig. 7 and Table III with the parameters obtained for the electrodes based on the silver/active carbon catalyst. The last mentioned type of electrodes was represented by two sorts of electrodes: *a*) the "economical" version (catalyst 80/20; 4 mg Ag/cm²) and *b*) the electrode with a maximum silver content (catalyst 50/50; 12 mg Ag/cm²). The difference in a way, in which the electrolyte is distributed in these two types of electrodes (silver and silver/active carbon), can be seen in Table III. It is evident that the amount of electrolyte (per a unit weight of a catalyst) increases with the increasing relative proportion of the porous silver carrier.

In Fig. 7 one can see, for oxygen, the marked shift of the electrochemical characteristics of the pure silver electrodes compared to the silver − active carbon electrodes. In the last mentioned type of electrodes, the active carbon acts as an "active" catalyst support, *i.e.* it participates in the current-generation process − though − evidently with the different mechanism and kinetics.

The conclusion − according to which the electroreduction of oxygen on a silver − active carbon catalyst and on pure silver proceeds by two different mechanisms and with a different kinetics − is supported also by measurements showing the effect of the temperature at which the electrodes are operated, on the i_{100} values. *E.g.*, with pure oxygen, the increase of the electrolyte temperature from 28° to 70°C led − for the active carbon electrodes containing $(0-20\% \text{ Ag})$ M only to a $21-25\%$ increase of the i_{100} value. On the other hand, with the electrodes made of pure silver, a comparable increase of the electrolyte temperature resulted in the 95% increase of the i_{100} value.

TABLE III
Results obtained with Ag-PTFE electrode

Catalyst	ČKD	50/50	80/20
mg Ag/cm²	40	12	4
mg catal./cm²	40	24	20
i_{100}, mA/cm²	170	117	100
ΔE_{100}, mV	85	61	46
m_E, g	0.388	0.543	0.709
m'_E, g	0.425	0.680	1.060

On the characteristics obtained with the air (Fig. 7), one can clearly see the positive effect of porous structure of the catalyst support. With oxygen, the active carbon also acts as the "active silver support", however, its structure has a dominant effect on the electrochemical parameters − while its activity for the electrochemical reduction of oxygen is only of secondary importance. This has been proved in the earlier published results[7]. The comparison of the Norit NK and BRX activities has shown that in spite of the higher activity of Norit NK − for the case of the oxygen electrode − Norite BRX is a more suitable silver carrier due to its more favourable structural properties. The parameters of the air electrodes were evidently better with the silver supported on Norit BRX than on Norit NK.

The verification of the presumed uselessness of any additional increase of the silver content in the silver − active carbon type catalysts is illustrated in Fig. 8. The same figure shows also the large excess of "skeletal" silver over the "catalytic" silver. The curves connect points with the optimum results obtained with the individual types of catalysts and with their mixtures with teflonized carbon black.

REFERENCES

1. Kordesch K. V.: Progr. Batt. Solar Cells 2, 19 (1979).
2. Van den Broeck H.: Progr. in Batteries and Solar Cells 2, 204 (1979).
3. Lindström O., Nilsson T., Bursell M., Hönell Ch., Karlsson G., Sylwan Ch., Ahgren B. in the book: J. Thompson, Ed., *Power Sources*, p. 419. Academic Press, London, New York, San Francisco 1979.
4. Budevski E., Iliev I., Kaisheva A., Gamburzev S.: Bulgaria 16 152 (1971).
5. Iliev I., Gamburzev S., Kaisheva A., Vakanova E., Muchovski J., Budevski E.: Izv. Otd. Khim. Nauki, Bulg. Akad. 7, 223 (1974).
6. Iliev I., Gamburzev S., Kaisheva A., Vakanova E., Muchovski J., Budevski E.: Izv. Otd. Khim. Nauki, Bulg. Akad. Nauk 7, 233 (1974).
7. Iliev I., Mrha J., Kaisheva A., Gamburzev S.: J. Power Sources 1, 35 (1976/77).
8. Iliev I., Gamburzev S., Kaishava A., Budevski E.: Izv. Otd. Khim. Nauki, Bulg. Akad. Nauk 8, 359 (1975).
9. Iliev E., Kaisheva A., Gamburzev S.: Izv. Otd. Khim. Nauki, Bulg. Akad. Nauk 8, 367 (1975).
10. Iliev J., Mrha J., Gamburzev S., Kaisheva A.: J. Appl. Electrochem. 5, 291 (1975).
11. Gamburzev S., Kaisheva A., Iliev I., Budevski E.: Izv. Otd. Khim. Nauki, Bulg. Akad. Nauk 8, 433 (1975).
12. Gamburzev S., Kaisheva A., Iliev I.: Izv. Otd. Khim. Nauki, Bulg. Akad. Nauk 9, 220 (1976).
13. Mrha J., Musilová M., Iliev I., Kaisheva A., Gamburzev S., Jindra J.: Proc. Int. Conf. Electrochemical Power Sources, p. 148, Dům techniky Praha, Prague 1975.
14. Kaisheva A., Gamburzev S., Iliev I.: Proc. Conf. Electrochemical Power Sources, p. 174. Dům techniky Praha, Prague 1975.
15. Beran J., Smrček K., Jandera J.: Czech. AO 159, 413 (1975).
16. Smrček K., Beran J., Jandera J.: Quatrièmes Journées d'Etude des Piles à Combustible, Antverp 1972.

17. Johansson L. Y., Mrha J., Larsson R.: Electrochim. Acta *18*, 255 (1973).
18. Mokrousov L. N., Urisson N. A., Shteinberg G. V.: Elektrokhimiya *9*, 683 (1973).
19. Gamburzev S., Iliev I., Kaisheva A., Shteinberg G. V., Mokrousov L. N.: Ext. Abstr., Volume II, p. 303. ISE 28th Meeting, Varna—Druzhba, Bulgaria 1977.
20. Baranov A. P., Shteinberg G. V., Bagotzky V. S.: Elektrokhimiya *7*, 387 (1971).
21. Baranov A. P., Shteinberg G. V., Chirkov Yu. G., Bagotzky V. S.: Elektrokhimiya *8*, 1447 (1972).
22. Baranov A. P., Shteinberg G. V., Bagotzky V. S.: Elektrokhimiya *9*, 566 (1973).