

## ON THE EFFECT OF VARIOUS ACTIVE CARBON CATALYSTS ON THE BEHAVIOUR OF CARBON GAS-DIFFUSION AIR ELECTRODES: 2. ACID SOLUTIONS

J. MRHA\*, I. ILIEV, A. KAISHEVA, S. GAMBURZEV and M. MUSILOVA\*

Central Laboratory for Electrochemical Power Sources, Bulgarian Academy of Sciences, Sofia 13 (Bulgaria)

(Received October 31, 1975)

### Summary

The electrochemical performance of carbon gas-diffusion air electrodes was studied in acid solutions. Electrodes with defined structure prepared from 11 different active carbon samples were investigated when working with air and oxygen. The catalytic activity of these samples both in acid and in alkaline solutions was compared. The extent of mass transport hindrances was estimated in terms of  $\Delta E(i)$  curves. The effect of platinum and polymeric phthalocyanines as promoters on the overall electrochemical characteristics of oxygen and air electrodes was studied. In the case of oxygen electrodes at  $E = 700$  mV (*vs.* RHE)  $120$  mA/cm<sup>2</sup> were obtained with NORIT NK active carbon promoted with  $2.36$  mg platinum/cm<sup>2</sup> and  $30$  mA/cm<sup>2</sup> with P-33-active carbon promoted with  $13$  mg iron phthalocyanine/cm<sup>2</sup>. At low current loads the  $\Delta E(i)$  curves and the slopes of the linear portion of the  $E$  *vs.*  $\log i$  curves of oxygen electrodes reflect a different electrochemical mechanism and a different rate of mass transport for pure active carbon and active carbon promoted with the above-mentioned catalysts.

### Introduction

In Part 1 [1] the electrochemical performance of carbon gas-diffusion electrodes with different active carbon catalysts was investigated in alkaline solution. In the present paper the electrochemical behaviour of gas-diffusion electrodes with the same overall structure and the same active carbon catalyst as before [1] but in acid solution is described.

Current-voltage characteristics both with air and with pure oxygen were measured and  $\Delta E(i)$  values [1, 2] were calculated from them. From the linear portion of the  $E$  *vs.*  $\log i$  curves of oxygen electrodes at low current densities the catalytic activity of various active carbon catalysts was esti-

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\*Permanent address: J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague 10 (Czechoslovakia).

mated. The current density  $i_{700}$  at the potential + 700 mV vs. RHE was used as a measure of this catalytic activity.

In addition the electrochemical behaviour of carbon gas-diffusion electrodes with the catalytically active carbon NORIT NK promoted with platinum or phthalocyanines was studied and compared with that of electrodes with pure active carbon catalysts.

## Experimental

Double-layer, fixed-zone, Teflon bonded electrodes described previously and the same 11 types of active carbons were used [1]. A lead-plated expanded metal copper grid, pressed on the gas side of the electrode, was used as a current collector [3]. The characteristics of the electrodes were measured in 4.5 N  $H_2SO_4$  solution at room temperature. The autogen hydrogen electrode [4] was used as a reference electrode.

Current-voltage characteristics were measured after curing the electrode working with air at a current density of 5 mA/cm<sup>2</sup> for 15 h. The stability of these electrochemical characteristics with time is considerably lower than in alkaline solutions [1].

The  $NaBH_4$  reduction method [2] was used for the promotion of active carbon with platinum. Polymeric phthalocyanine with iron [5] or cobalt [6] as the central atom was deposited on the active carbon carrier NORIT NK using a precipitation method [7].

## Results and Discussion

In Fig. 1, the current-voltage characteristics of oxygen electrodes using 11 different active carbon catalysts are presented. Table 1 gives the  $i_{700}$  values obtained from the linear portion of the  $E$  vs.  $\log i$  curve of oxygen electrodes and also includes the corresponding slope of this portion of the curve and the  $\Delta E(i)$  values.

From Table 1 it follows that electrodes 6, 7, 10 and 12 have a relatively high catalytic activity. These electrodes also show a relatively good performance (see Fig. 1). The catalytic activity of electrodes 3 and 9 is comparable with that of the electrodes already mentioned but they show a poor performance at high current densities (see Table 1 and Fig. 1). In the case of electrode 3 the poor performance coincides with the extremely low volume of electrolyte (Table 2) soaked into the active layer as was the case also in alkaline solution [1]. Therefore, it could be concluded that the porous structure of this type of active carbon is not suitable for porous gas-diffusion electrodes at high current densities. The amount of electrolyte soaked into the active layer of electrode 9 is relatively high (see Table 2) and the performance of this electrode is quite normal [1] so that the porous structure of this active carbon could not be the main cause for its poor

TABLE 1

$i_{700}$ ,  $dE/d\log i$  and  $\Delta E(i)$  values for different active carbon electrodes.

Electrode No.	$i_{700}$ (mA/cm <sup>2</sup> )	$dE/d\log i$ (mV)	$\Delta E(i)$ (mV)
1	0.36	185	90
2	0.014	95	70
3	1.10	137	89
4	0.36	130	80
5	0.25	130	77
6	2.0	100	72
7	2.0	115	89
8	0.17	135	111
9	2.0	130	90
10	2.8	150	103
11	1.3	150	100

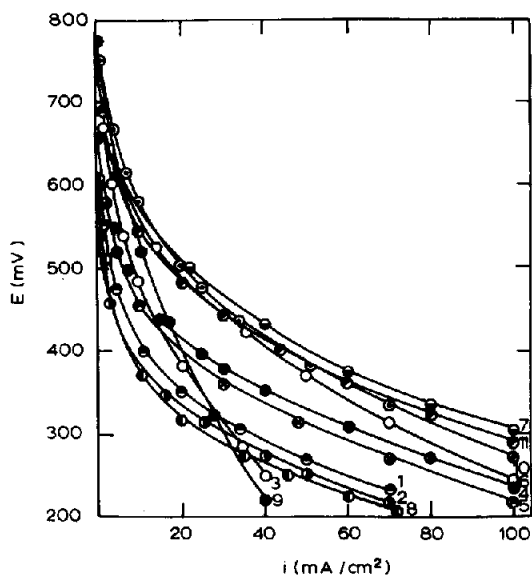


Fig. 1. Current-voltage characteristics of oxygen electrodes with active carbon catalysts ([1] Table 1).

electrochemical performance in acid electrolyte. During the electrochemical measurements an extremely high  $IR$  potential drop was observed when the current load was interrupted. After the electrochemical measurements it was observed that only spots on the surface of the active layer in contact with the bulk electrolyte were wetted. Therefore, the poor performance of electrode 9 can be explained by poor wettability of the surface of the active

TABLE 2

Volume of acid and alkaline [1] electrolyte soaked into the active layer with different active carbons

Electrode	$V_{H_2SO_4}$ (ml)	$V_{KOH}$ (ml)
1	0.56	0.53
2	—	0.32
3	0.15	0.20
4	0.33	0.24
5	0.36	0.27
6	0.27	0.27
7	0.33	0.275
8	0.44	0.36
9	0.31	0.25
10	0.23	0.24
11	0.32	0.28

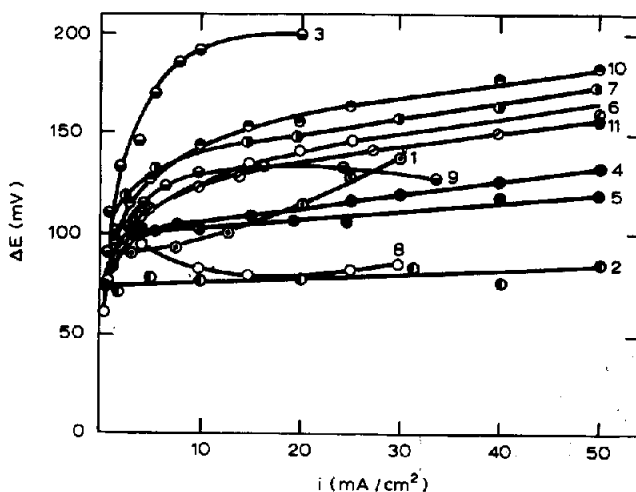


Fig. 2.  $\Delta E(i)$  curves calculated from current-voltage characteristics of oxygen (Fig. 1) and air electrodes.

layer which increases the resistance between the bulk electrolyte and the electrolyte soaked into the active layer of the electrode.

The general pattern described above does not change upon replacement of oxygen by air and the corresponding  $\Delta E(i)$  values are presented in Fig. 2. In comparison with an alkaline electrolyte [1] very high  $\Delta E(i)$  values were obtained at low current densities (see Table 1). For the electrochemical reduction of oxygen in acid solutions, when a two-electron process is considered, a  $\Delta E(i)$  value of  $\sim 81$  mV is to be expected at low current densities [8]. The experimentally obtained values range from 60 to 111 mV. Gener-

ally with rising current load a steep rise of  $\Delta E(i)$  values was observed (with the exception of electrodes 2 and 8), followed by a plateau-like region (from 10 to 50 mA/cm<sup>2</sup>). From the measurements in alkaline solutions [1] it can be concluded that no significant transport hindrances in the gas supplying layer of the electrodes are to be expected. The shape of the  $\Delta E(i)$  curves can be interpreted on the basis of a model consisting of an active layer with a catalyst with a loose network of active sites [1, 2].

From the experimental data obtained for active carbons it can be concluded that these catalysts have generally an insufficient activity to be used as catalysts for oxygen reduction in strong acid solutions. However, there is a correlation between the electrochemical activity of active carbons in alkaline ( $i_{-30}$  [1]) and in acid ( $i_{700}$ ) solutions (see Table 3), with the exception of electrode 3. This electrode has an extremely high activity in alkaline solution [1] but a relatively low activity in acid solutions (see Table 1).

The amount of electrolyte soaked into the active layer when the electrode is operating in acid solution is generally slightly higher than that when an alkaline electrolyte is used (see Table 2) with the exception of electrodes 1 and 6, where the two amounts of electrolyte are nearly equal.

Owing to the poor electrochemical activity of active carbon in acid solution the need for additional promotion of the carbon with a catalyst is more pronounced than in alkaline solutions. Therefore the electrochemical performance of electrodes with an active carbon catalyst promoted with platinum and an active carbon promoted with polymeric phthalocyanines with iron or cobalt as central atoms was investigated.

The corresponding data for electrodes with the catalyst NORIT and NK promoted with different amounts of platinum are shown in Figs. 3 and 4. It

TABLE 3

Correlation between the electrochemical activity of the same type of active carbon in alkaline ( $i_{-30}$  [1]) and in acid ( $i_{700}$ ) solutions

Electrode No.	$i_{-30}$ (mA/cm <sup>2</sup> )	$i_{700}$ (mA/cm <sup>2</sup> )
1	1.35	0.36
2	1.80	0.014
3	11.50	1.100
4	1.5	0.36
5	1.15	0.25
6	3.4	2.0
7	6.0	2.0
8	1.7	0.17
9	5.25	2.0
10	6.2	2.80
11	3.3	1.30

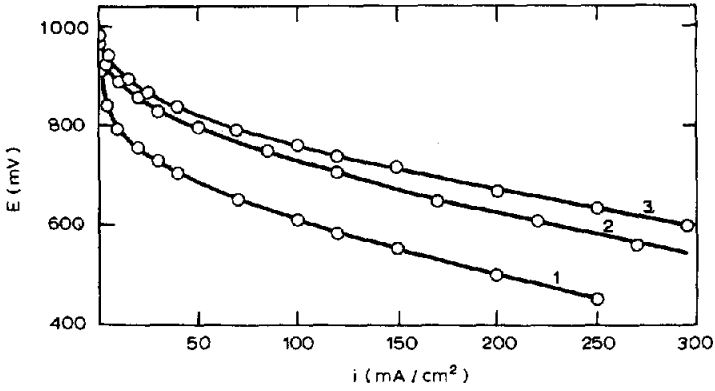


Fig. 3. Current-voltage characteristics of oxygen electrodes with NORIT NK active carbon catalyst promoted with different amounts of platinum: 1, 0.47; 2, 2.36; 3, 9.40  $\text{mg}/\text{cm}^2$ .

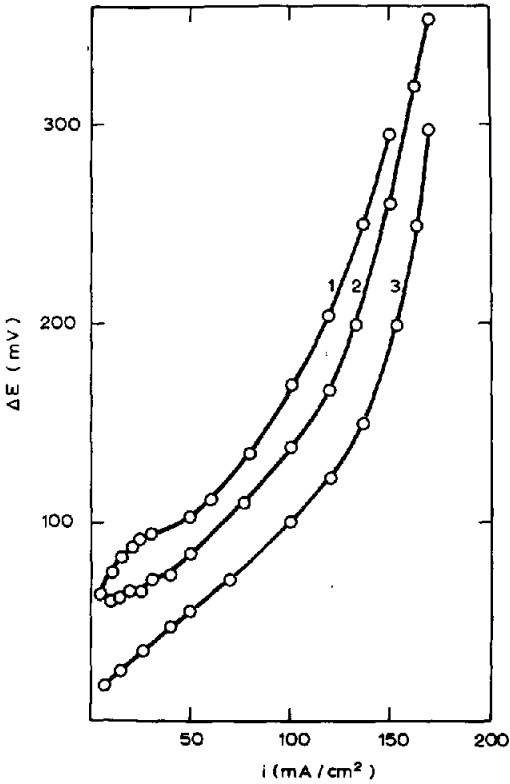


Fig. 4.  $\Delta E(i)$  curves calculated from current-voltage characteristics of oxygen (Fig. 3) and air electrodes.

TABLE 4

$i_{900}$ ,  $dE/d\log i$  and  $\Delta E(i)$  values for electrodes with catalyst NORIT NK promoted with different amounts of platinum.

Amount of platinum deposited on NORIT NK carbon electrodes (mg Pt/cm <sup>2</sup> electrode)	$i_{900}$ (mA/cm <sup>2</sup> )	$dE/d\log i$ (mV)	$\Delta E(i)$ (mV)
0.47	0.15	65	63
2.36	1.80	55	61
9.4	2.50	67	25

TABLE 5

$i_{800}$ ,  $dE/d\log i$  and  $\Delta E(i)$  values for electrodes with active carbons promoted with polymeric phthalocyanines.

Catalyst	$i_{800}$ (mA/cm <sup>2</sup> )	$dE/d\log i$ (mV)	$\Delta E(i)$ (mV)
NORIT NK +30% CoPc	4	50	37
P-33 +15% FePc	5	48	31
NORIT NK +30% FePc	40	60	38

can be seen that the electrochemical performance of electrodes improves with increase in the amount of platinum (see Fig. 3). From Fig. 4 it is seen that the transport hindrances decrease when the amount of platinum increases. The electrochemical activity ( $i_{900}^*$ ) and the slopes of the  $E$  vs.  $\log i$  curves of oxygen electrodes at low current density are listed in Table 4 together with the corresponding  $\Delta E(i)$  values. The experimentally obtained slopes range from 55 to 67 mV/current decade; such low slopes have been obtained earlier with platinum oxide electrodes 9. The experimentally obtained very low  $\Delta E(i)$  values at low current densities with 9.4 mg Pt/cm<sup>2</sup> (see Fig. 4) can also be explained by the presence of such an oxide.

The shape of the  $\Delta E(i)$  curves at current densities  $< 50$  mA/cm<sup>2</sup> is in accordance with a model with a loose network of very active sites [1, 2].

The results obtained with electrodes using active carbon promoted with polymeric phthalocyanines are shown in Figs. 5 and 6 and Table 5.

As far as the electrochemical activity ( $i_{800}^*$ ) is concerned iron phthalocyanine is superior to cobalt phthalocyanine under the same conditions (see Table 5). The experimentally obtained slopes and  $\Delta E(i)$  values with phthalocyanine

\* $i_{900}$  and  $i_{800}$  values were obtained from the linear portion of the  $E$  vs.  $\log i$  curve of oxygen electrodes at  $E = 900$  and  $800$  mV respectively.

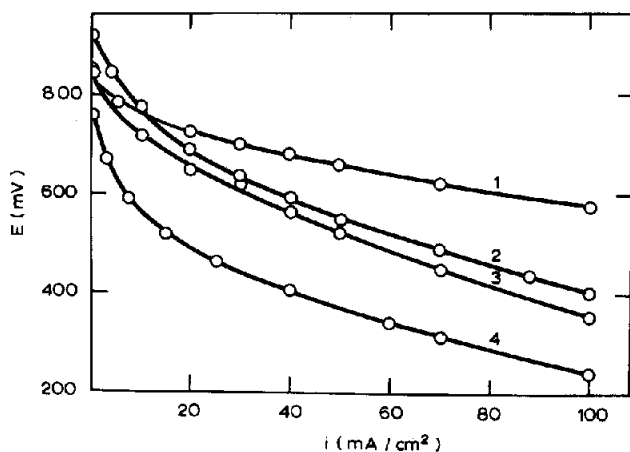


Fig. 5. Current-voltage characteristics of oxygen electrodes with active carbon catalyst promoted with polymeric phthalocyanines: 1, 73 mg/cm<sup>2</sup> active carbon P-33, 13 mg/cm<sup>2</sup> FePc, 43 mg/cm<sup>2</sup> XC-35; 2, 45 mg/cm<sup>2</sup> active carbon NORIT NK, 19 mg/cm<sup>2</sup> FePc, 26 mg/cm<sup>2</sup> XC-35; 3, 45 mg/cm<sup>2</sup> active carbon NORIT NK, 19 mg/cm<sup>2</sup> CoPc, 26 mg/cm<sup>2</sup> XC-35; 4, 21 mg/cm<sup>2</sup> active carbon NORIT NK, 9 mg/cm<sup>2</sup> XC-35.

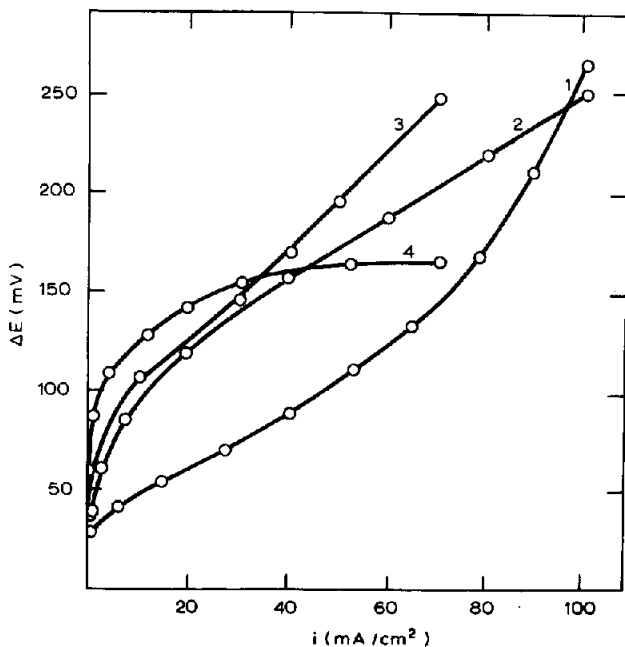


Fig. 6.  $\Delta E(i)$  curves calculated from current-voltage characteristics of oxygen (Fig. 5) and air electrodes.

cyanines at low current densities range from 48 to 60 mV current decade and 31 to 38 mV which are comparable with the data for electrodes with small amounts of platinum.



TABLE 6

$dE/d\log i$  and  $\Delta E(i)$  values for electrodes with NORIT NK and NORIT NK promoted with various catalysts

Catalyst	$dE/d\log i$ (mV)	$\Delta E(i)$ (mV)
NORIT NK	100	72
NORIT NK + 9.4 mg Pt/cm <sup>2</sup>	67	25
NORIT NK + 30% CoPc	50	37
NORIT NK + 30% FePc	60	38

From the results given in Table 5 it is clear that the catalytic activity of electrodes with catalyst NORIT NK +30% FePc is higher than that of electrodes with P-33 +15% FePc but at current densities  $>10$  mA/cm<sup>2</sup> the latter shows the better performance (see Figs. 5 and 6). This discrepancy can be attributed to the different structure of these two catalysts. The shape of the corresponding  $\Delta E(i)$  curves (see Fig. 6) supports this conclusion.

However, the electrochemical performance of oxygen electrodes in acid solutions is mainly influenced not only by the rate of mass transport (porous structure) but also by the electrochemical oxygen reduction mechanism which is more complicated than in alkaline solution [10]. From the experimental results it can be seen that a marked difference does exist between a pure active carbon catalyst and an active carbon promoted with platinum or polymeric phthalocyanines. This difference lies not only in the activity of the catalyst but also in the slope of the  $E$  vs.  $\log i$  plot of the oxygen electrode and the  $\Delta E(i)$  values at low current densities (compare Table 1 with Tables 4 and 5). These two values are connected with the mechanism of the oxygen reduction process. This mechanism is influenced by the mode of oxygen adsorption and by the hydrogen peroxide decomposition.

Table 6 summarizes the corresponding data for pure active carbon catalyst and an active carbon promoted with platinum or polymeric phthalocyanines. It is shown that a high slope and  $\Delta E(i)$  value correspond to pure active carbon. These values are lower for the same carbon promoted with catalyst. The slopes for three different types of catalyst (Pt, CoPc, FePc) deposited on the active carbon NORIT NK are nearly equal, but the  $\Delta E(i)$  value for platinum is lower. This low  $\Delta E(i)$  value can be interpreted in terms of the presence of platinum oxide.

## Conclusion

The results obtained with different active carbons in acid solutions show that generally the catalytic activity of all samples for the electrochemical reduction of oxygen is too low to be used as a catalyst for oxygen reduction in acid solutions. However, there exists a correlation between the

catalytic activity of the same active carbon in both acid and alkaline solutions. The amount of electrolyte soaked into the active layer of the electrode operating in acid is slightly higher than in alkaline solution. The shape of the  $\Delta E(i)$  curves at low current densities reflects a simultaneous influence of the electrochemical mechanism and of the mass transport on a loose network of active sites at the surface of active carbon and active carbon promoted with platinum or polymeric phthalocyanines.

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