

ON THE EFFECT OF VARIOUS ACTIVE CARBON CATALYSTS ON THE BEHAVIOUR OF CARBON GAS-DIFFUSION AIR ELECTRODES: 1. ALKALINE SOLUTIONS

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Summary

The electrochemical behaviour of carbon gas-diffusion air electrodes in alkaline solutions was investigated. Electrodes with defined structural and hydrophobic properties were chosen as a suitable system for comparing the electrochemical activity of different active carbon catalysts. The current-voltage characteristics of electrodes with 11 different active carbon catalysts were investigated when operating both with air and pure oxygen. The mass transport hindrances of the electrodes were studied in terms of $\Delta E(i)$ curves. Potential recovery transients of the electrodes were correlated with the electrochemical activity of the different active carbon catalysts. On the basis of the experimental results the active carbon sample with the most suitable structural properties was chosen as a proper carrier to be promoted with small amounts of metal catalyst. The electrode with active carbon promoted with small amounts of metal catalyst. The electrode with active carbon promoted with 1.5 mg/cm² silver loaded with 100 mA/cm² has a potential of -67 mV (*vs.* Hg/HgO) when operating with oxygen and -106 mV when operating with air at room temperature.

Introduction

The electrochemical behaviour of carbon gas-diffusion air electrodes in alkaline solutions is strongly affected by the original catalytic activity, by the porous structure of the active carbon catalyst and by the overall structure of the electrode. In order to compare the effect of various active carbon catalysts the same porous structure of the electrode must be used.

In the present paper the electrochemical performance of air electrodes with identical gas supplying layers and having the same construction of the

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active layer [1] is investigated in alkaline solution and the results obtained with different active carbon catalysts are compared. The construction of the active layer of these electrodes is very suitable for such comparison since the catalyst is not subjected to any treatment with wetproofing and binding agents.

On the basis of current-voltage characteristics both with air and pure oxygen $\Delta E(i)$ values* were obtained [2]. These values are a measure of the rate of mass transport in the porous structure of the electrode. The catalytic activity of the active carbon was estimated from the linear portion of the $E_{\text{oxygen}}(i)$ vs. $\log i$ curve which is observable at low current densities. As a measure of this catalytic activity the current density i_{-30} at a potential of -30 mV vs. an Hg/HgO reference electrode in the same solution was accepted.

Additionally the potential recovery transients after a period of current load were investigated. The 'relaxation' time (t) of these transients was correlated with the activity of the catalyst (i_{-30}) and iR -free polarization curves of the oxygen electrodes were obtained.

The most promising active carbon with respect to the rate of mass transport was chosen on the basis of the $\Delta E(i)$ curves as a suitable carrier and was additionally promoted with a small amount of very active metal catalyst.

Experimental

Double-layer, fixed-zone, Teflon bonded carbon electrodes with a gas supplying layer consisting of 100 mg/cm^2 carbon black XC wetproofed with 35% Teflon (Teflon dispersion GP-1) and an active layer consisting of a 30 mg/cm^2 mixture of the same wetproofed material XC-35 and active carbon (weight ratio 1:2.5) were used [1]. The electrodes were sintered at 350°C under a pressure of 200 kg/cm^2 .

Electrodes with 11 different kinds of active carbon (see Table 1) were investigated. In some cases the active carbon was promoted with silver using either NaBH_4 reduction [2] or adsorption of AgNO_3 followed by thermal decomposition [3]. Platinum was deposited only by the former method.

Round-shaped electrodes with a projected area of 10 cm^2 and with a thickness of 1.6 - 1.9 mm were prepared. The current collector (nickel-plated iron grid) was pressed on the gas side of the electrode.

Steady state current-voltage characteristics, using a half cell arrangement, were measured in a 7 N KOH solution at room temperature; using electrodes operating with air (air breathing electrodes without overpressure) and with pure oxygen (overpressure 1 cm of water). The potential (including

* $\Delta E(i) = E_{\text{oxygen}}(i) - E_{\text{air}}(i)$ is the difference between the steady state potential of an electrode operating with air and with pure oxygen at the same current density.

TABLE 1

List of used active carbons with their BET surfaces and corresponding electrode numbers.

Type of active carbon	Country of origin	BET surface (m^2/g)	Electrode No.
NORIT BRX	Netherlands	1559	1
V-10 H	Fed. Rep. Germany	573	2
ELORIT HR	Czechoslovakia	917	3
HS-4 < 60 μm	Czechoslovakia	915	4
HS-4 60 - 100 μm	Czechoslovakia	859	5
NORIT NK	Netherlands	635	6
NORIT FNX	Netherlands	675	7
P-33	German Dem. Republic	1109	8
NORIT RBL-2	Netherlands	654	9
EPA	France	482	10
GLÜKONORIT	Netherlands	479	11

the iR -drop) was measured against an Hg/HgO electrode in the same solution.

The potential recovery transients were recorded using a SERVOGOR RE 511 strip chart recorder.

The electronic conductivity of the active layers was measured on samples prepared under the same conditions as the electrodes, using the four probe method.

The amount of electrolyte soaked into the active layer of all samples was estimated titrimetrically after mechanical destruction of the electrodes.

All electrochemical data were obtained after curing the air electrodes at a current density of 50 mA/cm^2 for 15 hours and they are stable during the course of several thousand hours [1].

Results and Discussion

The current-voltage characteristics of oxygen electrodes with different types of active carbon catalyst are shown in Fig. 1. The corresponding i_{-30} values and the slopes, $dE/d \log i$, of the linear portion of the $E_{\text{oxygen}} - \log i$ curves are listed in Table 2.

From the experimental data it is seen that these slopes range from 36 to 60 mV. ELORIT HR (electrode 3) has a comparatively very high catalytic activity due to the ammonium chloride activation at 1000 °C [4] used in the production process. On the contrary, NORIT BRX (electrode 1) shows the lowest catalytic activity among the samples listed in Table 2. These two samples show a significant difference in the slopes of the oxygen current-voltage characteristics (see Fig. 1) at high current densities. As will be shown later, this difference is caused by a difference in the porous structure of the active carbon catalyst.

TABLE 2

i_{-30} and $dE/d\log i$ values of pure active carbon electrodes

Electrode No.	i_{-30} (mA/cm ²)	$dE/d\log i$ (mV)
1	1.35	35.7
2	1.8	48.8
3	11.5	56.8
4	1.5	48.7
5	1.15	41.5
6	3.4	59.9
7	6.0	54.3
8	1.7	40.0
9	5.25	58.0
10	6.2	54.0
11	3.3	48.6

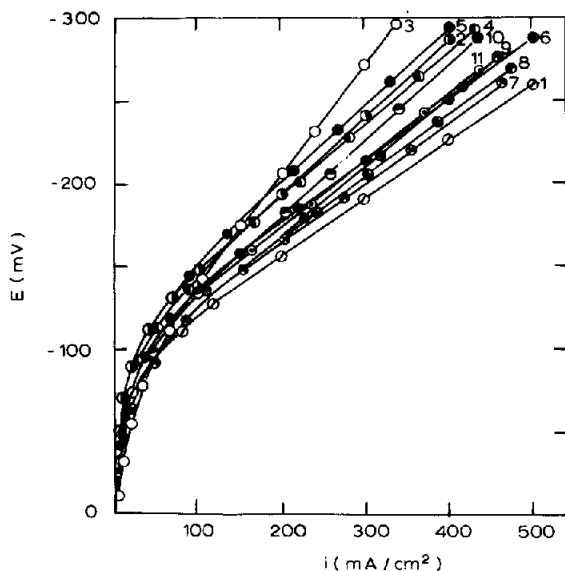


Fig. 1. Current-voltage characteristics of oxygen electrodes with the active carbon catalysts listed in Table 1.

The difference between samples 3 and 1 is more pronounced when air is used instead of oxygen (Fig. 2) and is mainly caused by the difference in transport hindrances as can be seen from Fig. 3.

Sample number 3 shows quite remarkable transport hindrances even at low current densities, 10 - 20 mA/cm². A similar shape of the $\Delta E(i)$ curve was obtained also with NORIT NK active carbon promoted with a small amount of silver, deposited by NaBH₄ reduction [2]. Therefore the results

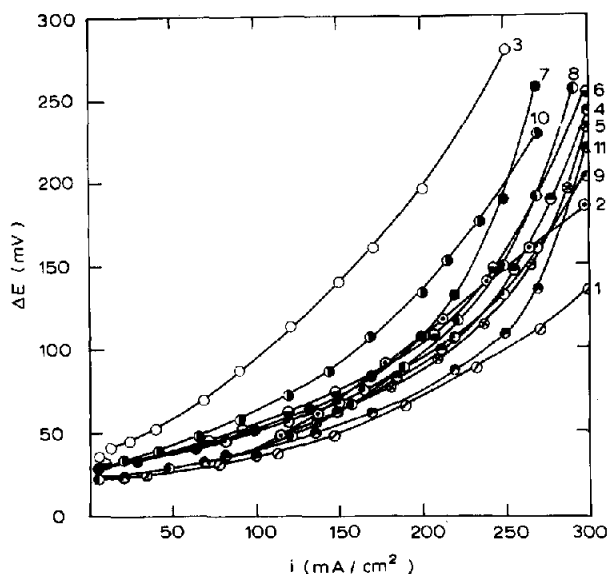


Fig. 2. $\Delta E(i)$ curves calculated from oxygen (Fig. 1) and air curves.

obtained with sample 3 can be interpreted on the basis of an active carbon catalyst with a loose network of very active sites additionally incorporated by the activation procedure.

On the contrary, sample 1 shows practically no transport hindrances in the range of current densities $<10 \text{ mA/cm}^2$.

In the $10 - 50 \text{ mA/cm}^2$ current density range the transport hindrances of sample 3 increase considerably, whereas the transport hindrances of sample 1 are negligible. This different behaviour could be explained on the basis of a different porous structure and by the nature of the catalyst in the active layer.

At high current densities ($>50 \text{ mA/cm}^2$) the transport hindrances in the gas supplying layer have an increasing influence on the rate of mass transport. The electrodes used in the present investigation had the same gas supplying layer. Therefore the same rate of mass transport through this layer is to be expected. The differences in the shape of the $\Delta E(i)$ curves should be attributed to the differences in the porous structure of the active layer, in our case to the differences in the porous structure of the active carbon catalysts.

From Fig. 2 it is seen that the transport hindrances in samples 1 and 3 increase at current densities $>50 \text{ mA/cm}^2$; the $\Delta E(i)$ curves of all other samples lie between these two extreme samples.

In order to obtain some additional information about the porous structure of active carbon catalysts embedded into the active layer the amount of electrolyte soaked into the active carbon after the electrochemical curing of the electrodes (24 h at 50 mA/cm^2 load followed by 48 h without load) was

TABLE 3

Correlation between the amount of electrolyte soaked into the active layer (V_{KOH}) and the reciprocal of the slope of the oxygen current-voltage characteristics $(\Delta E_{\text{O}_2} / \Delta i_{100-200})^{-1}$ in the 100 - 200 mA/cm² range

Electrode	V_{KOH} (ml)	$(\Delta E_{\text{O}_2} / \Delta i_{100-200})^{-1}$ ($\Omega^{-1} \text{ cm}^{-2}$)
1	0.53	2.8
2	0.32	2.2
3	0.20	1.3
4	0.24	2.1
5	0.27	1.9
6	0.27	2.3
7	0.275	2.4
8	0.36	2.5
9	0.25	2.3
10	0.24	2.15
11	0.28	2.35

estimated. This amount was compared with the reciprocal value of the slope of the oxygen current-voltage characteristics in the 100 - 200 mA/cm² range (see Table 3). There is a marked correlation between these two parameters. It can be therefore concluded that the slope of the oxygen current-voltage characteristics in the above mentioned current density range is mainly controlled by the resistance of the electrolyte network in the active layer.

The two extreme cases in Table 3 are again samples 1 and 3, sample 1 with the highest amount of soaked electrolyte and the lowest slope of oxygen current-voltage characteristic and sample 3 with the lowest amount of soaked electrolyte and the highest slope.

Samples 2 and 5 show a somewhat higher slope of oxygen current-voltage characteristics which can be attributed to the higher electronic resistivity of their electrolyte free active layers (8.53 and 4.11 ohm cm respectively). These resistivities are listed in Table 4 and it is apparent that samples 1 and 3 have approximately the same resistivity (1.88 and 1.31 ohm cm respectively). The corresponding resistivities of all other samples vary between 1.57 and 3.6 ohm cm.

In addition to the steady state current-voltage characteristics, the potential recovery transients for all electrodes with different active carbon catalysts were investigated after a period at various current loads. A typical potential recovery transient is shown in Fig. 3.

When the current load (i) is interrupted a rapid drop ($E_2 - E_1$) of the electrode potential, followed by an exponential-like transient, was observed. The rapid drop of the potential can be attributed to the iR drop since the ratio $(E_2 - E_1)/i$ is independent of i in the range 10 - 300 mA/cm². Using E_2 values, iR free oxygen current-voltage characteristics can be obtained (see Fig. 4). It is apparent that samples with the highest catalytic activity

TABLE 4

Electronic resistivities of electrolyte-free active layers

Electrode No.	Electronic resistivity (ohm cm)
1	1.88
2	8.53
3	1.31
4	3.3
5	4.11
6	1.68
7	3.6
8	1.56
9	2.2
10	1.57
11	2.88

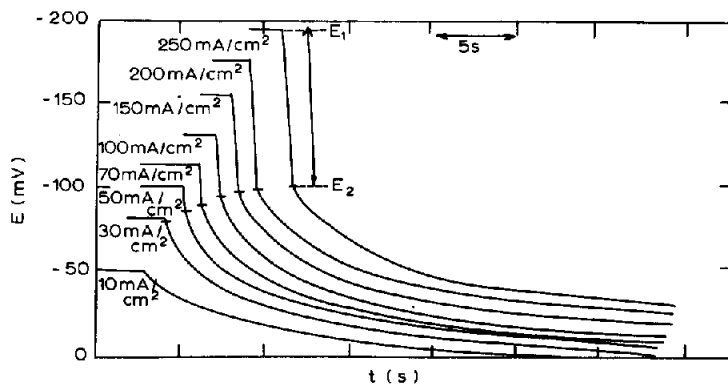


Fig. 3. Potential recovery transients of oxygen electrode (active carbon NORIT RBL-2).

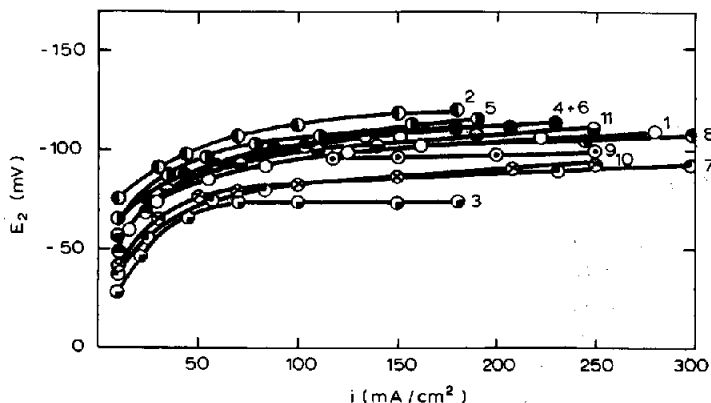


Fig. 4. iR -free current-voltage characteristics (calculated from potential recovery transients) of oxygen electrodes with the active carbon catalysts listed in Table 1.

have the lowest E_2 values at the same current density. In the case of samples with low catalytic activity the location of $E_2(i)$ curves is probably affected by the specific surface of the corresponding active carbon.

The log $E(t)$ vs. time (t) plot was used as an appropriate method to investigate the exponential-like part of the transients of all electrode samples. A typical example is shown in Fig. 5 (electrode 9). The curves obtained consist of two parts. The first part immediately following the rapid drop (iR) is probably connected with charge transport along the transmission line which represents the porous electrode [5]. Heterogeneous decomposition of hydrogen peroxide, diffusion of OH^- ions and water take place at the same time.

The second part of the log $E(t)$ vs. time (t) plot is linear (see Fig. 5). The slope of this part was accepted as a measure of the relaxation rate. This part is probably connected with the discharge of the double layer capacity.

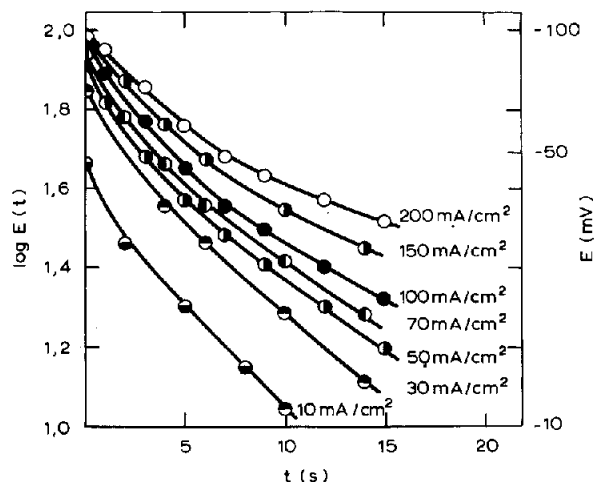


Fig. 5. Potential recovery transients (from Fig. 3) on a semi-logarithmic scale

The slopes ($d \log E(t)/dt$) obtained at a current density of 100 mA/cm^2 were plotted against i_{-30} value (see Table 5). A clear correlation exists for all samples and therefore it can be concluded that these slopes can be accepted as an additional measure of the electrochemical activity of various active carbon catalysts.

From all the above-presented data it can be concluded that NORIT BRX possesses the most favourable structural properties but has a low catalytic activity. This sample was therefore chosen as a suitable carrier to be promoted additionally by a catalytically active metal. In Fig. 6 oxygen current-voltage characteristics of electrodes with the same overall structure as for pure active carbon but with a small amount of silver or platinum are presented.

TABLE 5

Correlation between the slope of the linear portion of the potential recovery transient ($d \log E(t)/dt \times 10^{-2}$) and the catalytic activity (i_{-30}) of the active carbons listed in Table 1

Electrode No.	$d \log E(t)/dt \times 10^{-2}$ (s^{-1})	i_{-30} (mA/cm^2)
1	0.63	1.35
2	0.41	1.80
3	10.67	11.5
4	0.65	1.5
5	0.37	1.15
6	1.04	3.4
7	3.26	6.0
8	0.67	1.7
9	2.98	5.25
10	4.15	6.2
11	1.15	3.3

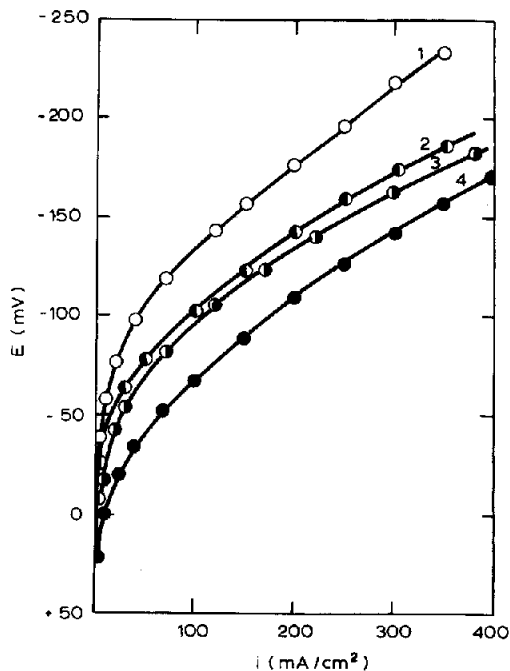


Fig. 6. Current-voltage characteristics of oxygen electrodes with NORIT NK active carbon catalyst promoted with metal catalysts: 1, pure NORIT NK; 2, NORIT NK + 5% Ag [3]; 3, NORIT NK + 5% Ag ($NaBH_4$ reduction); 4, NORIT NK + 5% Pt ($NaBH_4$ reduction).

Table 6 presents the corresponding i_{-30} values. In the case of NORIT BRX 1.5 mg/cm² of silver or 1.1 mg/cm² platinum were used. Electrodes with NORIT NK were promoted with 1.1 mg/cm² platinum or silver. From Table 6 it is seen that for both NORIT NK and NORIT BRX promotion with

TABLE 6

i_{-30} values and $dE/d\log i$ values of promoted active carbon electrodes.

Catalyst	i_{-30} (mA/cm ²)	$dE/d\log i$ (mV)
NORIT NK	3.4	59.9
NORIT NK +5% Ag(ads)	6.3	36.5
NORIT NK +5% Pt(BH ₄ ⁻)	46.0	43.3
NORIT NK +5% Ag(BH ₄ ⁻)	13.8	43.8
NORIT BRX	1.35	35.7
NORIT BRX +7% Ag(ads)	30.0	30.4
NORIT BRX +7% Ag(BH ₄ ⁻)	16.0	33.4
NORIT BRX +5% Pt(BH ₄ ⁻)	48.0	48.0

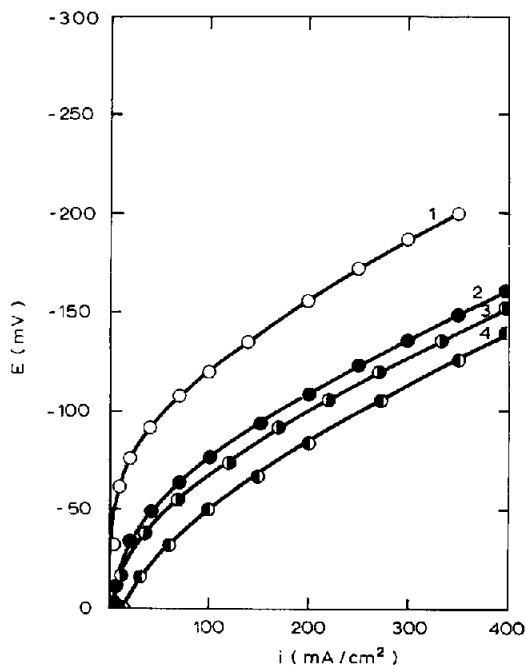


Fig. 7. Current-voltage characteristics of oxygen electrodes with NORIT BRX active carbon catalyst promoted with metal catalysts: 1, pure NORIT BRX; 2, NORIT BRX + 7% Ag (NaBH₄ reduction); 3, NORIT BRX + 7% Ag [3]; 4, NORIT BRX + 5% Pt (NaBH₄ reduction).

platinum is superior. It is noticeable that the slopes of the linear portion of the E vs. $\log i$ plots of metal promoted catalysts are somewhat lower than for pure active carbon catalysts.

The corresponding oxygen current-voltage characteristics for both active carbon carriers promoted with metal catalysts are shown in Figs. 6 and 7. The metal promotion improves the overall activity of the electrodes in the whole range of current densities.

The rate of mass transport in the case of NORIT NK was slightly improved by metal promotion (Fig. 8a). In the case of NORIT BRX the promotion with silver, using NaBH_4 reduction procedure, brings about an improvement in the rate of mass transport, whereas the promotion with silver by adsorption and thermal decomposition of AgNO_3 and with platinum, using the NaBH_4 reduction procedure, has a negative influence on the rate of mass transport (see Fig. 8b) at current densities $>100 \text{ mA/cm}^2$.

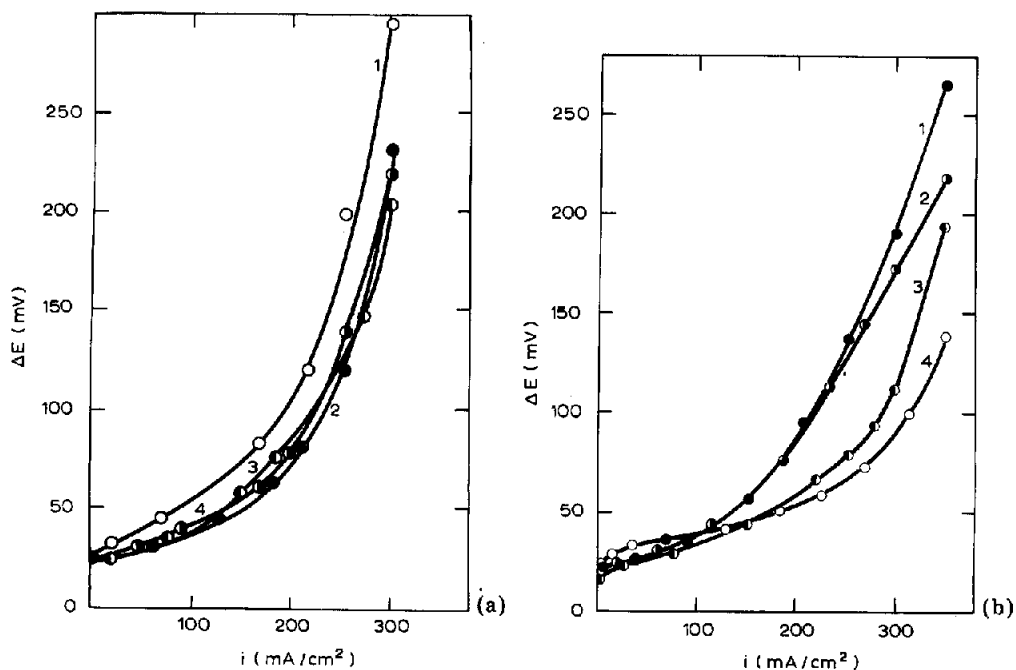


Fig. 8. $\Delta E(i)$ curves obtained from oxygen [(a) Fig. 6 and (b) Fig. 7] and air curves.

Conclusion

Different active carbons were used as catalysts in oxygen and air gas-diffusion electrodes in alkaline solution. It was shown that there exists a marked difference between these active carbon samples as far as their catalytic activity is concerned. Electrodes with these active carbons differ also in the rate of mass transport.

The overall electrochemical activity of the electrodes is influenced not only by the activity of the catalyst, but also by the rate of mass transport, especially when the electrodes are operating with air. At low current densities the catalytic activity of the active carbon controls the overall activity of the electrodes, whereas at high current densities the rate of mass transport becomes predominant. The slope of the oxygen current-voltage characteristics at high current densities is mainly influenced by the amount of electrolyte soaked into the active layer when active carbons with comparable electronic resistivities are used.

It was shown that the rate of potential recovery after interruption of the current load correlates with the catalytic activity of the active carbon.

When active carbon is promoted with silver or platinum, the electrochemical performance of electrodes is mainly controlled by the initial structural properties of the active carbon.

The investigation of these electrodes in acid solution is reported in Part 2 [6].

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