INFLUENCE OF THE ELECTROLYTE CONTENT OF OXYGEN CARBON GAS-DIFFUSION ELECTRODES ON THEIR ELECTROCHEMICAL PERFORMANCE IN ACID SOLUTIONS

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

J. Heyrovsky Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences. Prague 10 (Czechoslovakia)

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Summary

Five different methods of Teflon deposition onto the carbon surface were used to study the influence of different electrolyte contents in the carbon gas-diffusion electrodes on their electrochemical performance in acid solution. It was shown that the electrolyte content can be controlled also by the addition of carbon black and by promotion of active carbon with platinum. Electrodes prepared in accordance with these five methods of Teflon deposition differ in electrolyte content over a wide range and therefore the rate of mass transport is considerably influenced especially when the electrodes are working with air. The catalytic activity of pure active carbon is relatively low but the current–voltage characteristics of the electrodes could be positively influenced in the range controlled by the rate of mass transport and ionic conductivity, using a suitable method of Teflon deposition and by the addition of carbon black. The electrochemical performance of electrodes with active carbon promoted with platinum can be improved by the presence of optimum electrolyte content in the electrode using a suitable method of Teflon deposition and the addition of carbon black.

Introduction

In a previous paper [1] the electrochemical performance of oxygen carbon gas-diffusion electrodes with different active carbon catalysts in acid solution was investigated. In the present paper the influence of the electrolyte content of the carbon gas-diffusion electrodes on their electrochemical performance, using either pure active carbon or active carbon promoted with platinum, was studied. The electrolyte content was regulated by the use of

*Permanent address: Central Laboratory for Electrochemical Power Sources, Bulgarian Academy of Sciences, Sofia 12 (Bulgaria).

various methods of Teflon deposition onto the carbon surface or by the addition of carbon black to the catalyst–Teflon mixture [2].

Air-breathing, fixed-zone, single- or two-layer electrodes were used [1]. Current–voltage characteristics both in pure oxygen and air were measured and on the basis of these characteristics $\Delta E(i)$ values* were obtained [3]. These experimental data were correlated with the electrolyte content. Furthermore the influence of the additional promotion with platinum was studied.

Experimental

Two types of round, fixed-zone, Teflon bonded carbon electrodes were investigated. Both types were pressed at ambient temperature using either pure active carbon Norit NK or active carbon Norit NK promoted with 10% platinum ($NaBH_4$ reduction). An active mass consisting of the same amount of active carbon or active carbon with platinum (64.3 mg/cm^2) and Teflon (7.1 mg/cm^2) was used in all cases.

Type A: single-layer electrodes with a geometrical area of 5 cm^2 and a thickness of about 1 mm pressed at 430 kg/cm^2 [4]. A gold grid was used as a current collector and was pressed into the electrolyte side of the electrode. A Teflon dispersion (Dupont 30-N) was used as a binding and wetproofing agent for the active mass.

Type B: double-layer electrodes with a gas supplying layer consisting of 50 mg/cm^2 carbon black wetproofed with 35% Teflon (Teflon dispersion GP-1) [5]. The electrodes were pressed at 200 kg/cm^2, their geometrical area was 10 cm^2 and total thickness about 1.3 mm. A lead plated copper grid current collector was pressed into the gas side of the electrode. Teflon dispersion GP-1 (~60% of Teflon) was used as a binding and wetproofing agent for the active mass.

The following five methods of Teflon deposition onto the carbon surface were used: (1) into a suspension consisting of the active carbon and water (weight ratio 1:8) the corresponding amount of non-diluted Teflon dispersion was added with stirring and the product was filtered, dried at 105 °C and milled; (2) similar to (1) but the weight ratio between the active carbon and water was 1:2; (3) similar to (1) but ethanol (1:8) was used instead of water; (4) an excess of ethanol was added with stirring to a suspension consisting of the active carbon and the corresponding amount of Teflon dispersion diluted with water (weight ratio between the active carbon and diluted Teflon dispersion was 1:8) and the product was treated as in (1); (5) Teflon was deposited onto the surface of carbon black and this powder was mixed with the corresponding amount of active carbon.

The same five methods were used also for active carbon with platinum.

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

In some cases the influence of the addition of carbon black to the active layer was also investigated. Carbon black (13 mg/cm^2) was additionally mixed with an already prepared mixture (methods 1 - 4) before the electrode was pressed.

Steady state current–voltage characteristics of the electrodes were measured at room temperature in 4.5 N sulphuric acid solution operating with pure oxygen and air (gas overpressure 1 - 3 cm water column). A half-cell arrangement was used in all experiments and the electrode potential E, including iR drop, was measured against a Hg/Hg$_2$SO$_4$ reference electrode in the same solution.

The electrolyte content in the electrodes was estimated from the weight difference of the electrode before and after the electrochemical treatment.

For the determination of the ionic conductivity of the single-layer electrodes (type A) a conventional method, which is suitable for ionic conductivity measurements of porous separators, was used [6].

All the electrochemical data for type A electrodes were obtained after working the oxygen electrodes at a current density of 10 mA/cm^2 for 15 h. The electrodes type B worked as air electrodes at a current density of 5 mA/cm^2 for 15 h.

Results and discussion

Figure 1 depicts two ranges where all the current–voltage characteristics of both types (type A and B) of oxygen electrode with methods (1) - (4) of Teflon deposition and with or without carbon black addition are located. The current–voltage characteristic of oxygen electrode type B (double-layer electrode) and method of Teflon deposition (5) lies between these two ranges. In Fig. 2 the influence of the electrolyte content on the potential of both types of oxygen electrode, with and without carbon black addition, at different current densities is presented.

A significant difference between the current–voltage characteristics for electrodes with and without carbon black addition is apparent. Electrodes type A and B with carbon black addition to the active layer show lower polarization especially at high current densities. This beneficial effect of carbon black can be attributed to the significantly higher electrolyte content in both types of oxygen electrode in the presence of carbon black. The electrolyte content in the absence of carbon black ranges between 0.24 and 0.64 g electrolyte/g electrode mass in the active layer (active carbon + Teflon). In the presence of carbon black the electrolyte content rises up to 0.69 - 0.87 g electrolyte/g electrode mass in the active layer (including carbon black), as can be seen in Fig. 2.

Concerning the influence of the methods of Teflon deposition (1) - (4), method (3) results, with both types of oxygen electrode, in the relatively highest electrolyte content and, as can be seen in Fig. 2(a), the lowest polarization values are obtained at the same current density. In the case of method
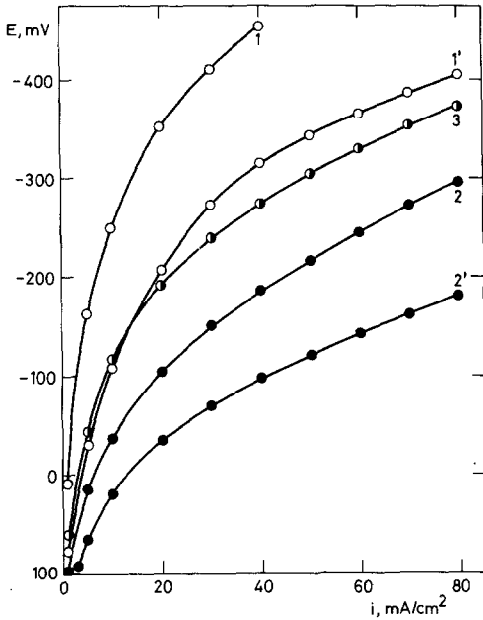
Fig. 1. Current–voltage characteristics of oxygen electrodes using five different methods of Teflon treatment of active carbon. Range of current–voltage characteristics of single- and double-layer electrodes method 1-4: 1-1', without carbon black; 2-2', with carbon black; 3, current–voltage characteristic of double-layer electrode method (5).
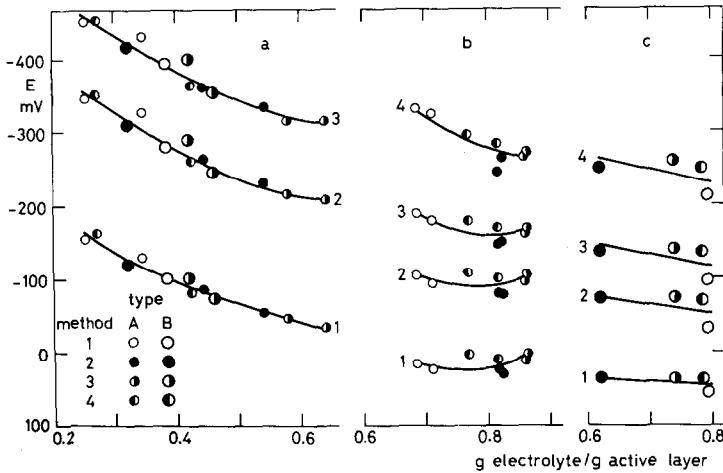

Fig. 2. Potential of single- (type A) and double-layer electrodes (type B) as a function of the amount of electrolyte (g) soaked in the active layer (g) at different current densities: 1, 5; 2, 20; 3, 40; 4, 100 mA/cm^2. (a) Method 1-4, types A, B, without carbon black; (b) method 1-4, type A, with carbon black; (c) method 1-4, type B, with carbon black.

(3) the Teflon particles are not uniformly deposited on the active carbon surface and the existence of Teflon agglomerates is to be expected [2]. This causes the electrodes prepared according to method (3) to have the relatively highest electrolyte content.

Teflon deposition using C_2H_5OH (method 3) does not give entirely reproducible results. The size of the Teflon agglomerates strongly depends on the rate of addition of the Teflon dispersion and on the mode and rate of stirring. This is apparent from previous results [2] where an extremely high electrolyte content was obtained in the electrode (0.98 g electrolyte/g electrode mass in the active layer) and the corresponding current–voltage characteristics of the electrode (without carbon black) is in the same range as electrodes with carbon black (Fig. 1) in the present paper.

Contrary to method (3), with other methods (mainly 1) a more or less uniform deposit of Teflon particles is most probable.

From the experimental data presented in Fig. 2(a) it is apparent that the electrolyte content controls the potential of oxygen electrodes at various current densities mainly in the range 0.23 - 0.64 electrolyte/g electrode mass in the active layer, where the corresponding shift of potential with rising electrolyte content is very pronounced. This range of electrolyte content corresponds to electrodes without carbon black addition.

In the range of electrolyte contents 0.62 - 0.87 g electrolyte/g electrode mass in the active layer (Figs. 2b and 2c), which corresponds to oxygen electrodes with carbon black addition, this influence is not so pronounced and the electrolyte content in this range can be considered to be the optimum.

The general pattern described above changes considerably upon replacement of oxygen by air. Figures 3 and 4 show the corresponding $\Delta E(i)$ curves for both types of electrode (types A and B) without (Fig. 3) and with (Fig. 4) carbon black addition. These curves were obtained from Fig. 1 and from the corresponding current–voltage characteristics obtained with air.

From Fig. 3 it follows that single-layer electrodes (type A) have generally lower $\Delta E(i)$ values than double-layer electrodes (type B) and this difference amounts to ~ 40 - 50 mV. Both groups of $\Delta E(i)$ curves are characterized by the same shape and they can be divided into two parts. The first part up to 10 mA/cm^2 is characterized by a steep rise of $\Delta E(i)$ values which cannot be explained by mass transport hindrances into the system of the gas supplying pores because of the extremly low current densities. This initial steep rise of $\Delta E(i)$ values reflects perhaps a strongly current dependent irreversible mechanism of oxygen reduction in acid solutions. The slope of the E vs. log i plot in the range of current densities up to 2 mA/cm^2 ranges between 100 and 130 mV/current decade, which values are approximately twice the values for the same active carbon promoted with platinum. These high values support the conclusion of a highly irreversible mechanism of the oxygen reduction.

The second part is distinguished by a plateau-like region which can be interpreted as a region in which a dynamic equilibrium of hydrogen peroxide concentration was established (the rate of hydrogen peroxide production is equal to its heterogeneous decomposition).
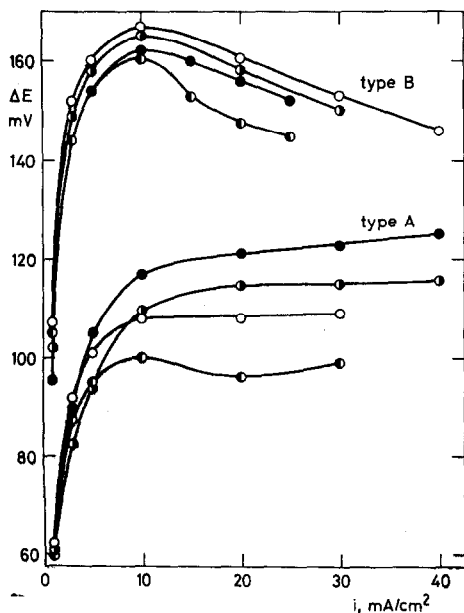
Fig. 3. $\Delta E(i)$ curves calculated from current–voltage characteristics of oxygen (Fig. 1) and air electrodes, without carbon black. Single- (type A) and double-layer electrodes (type B). O, method (1); ●, method (2); ◑, method (3); ◒, method (4).
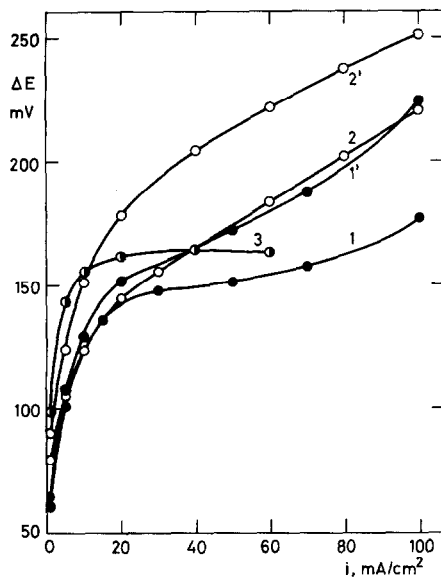
Fig. 4. $\Delta E(i)$ curves calculated from current–voltage characteristics of oxygen (Fig. 1) and air electrodes, with carbon black. Range of $\Delta E(i)$ curves of electrodes method 1-4: 1-1′, single-layer electrodes; 2-2′, double-layer electrodes; 3, $\Delta E(i)$ curve of double-layer electrode method (5).

    Contrary to the oxygen electrodes, in the case of air electrodes the higher electrolyte content is connected for both types of electrode with somewhat higher $\Delta E(i)$ values. The highest electrolyte content with type A electrodes corresponds to method (3) of Teflon deposition and to some extent also to method (2), with type B electrodes the highest electrolyte content corresponds to method (3) of Teflon deposition (see Fig. 2a) and with these electrodes the highest $\Delta E(i)$ values were obtained (see Fig. 3). This can be interpreted as a negative effect of higher electrolyte content on the rate of mass transport to the reaction zone through a somewhat reduced volume of gas supplying pores. Uneven deposition of Teflon particles on the active carbon surface [method (3) and to some extent method (2)] gives no guarantee of a sufficient rate of gas transport to the reaction zone.

    The difference in $\Delta E(i)$ values between the two types of electrode (type A and B) could also be explained both by a somewhat higher gas transport hindrance in the case of electrode type B, caused by a rather different mode of preparation of these electrodes, and their different initial working conditions (oxygen, electrodes type A; air, type B).

    Figure 4 presents the region where the corresponding $\Delta E(i)$ values of both types of electrodes with carbon black addition and methods (1) - (4) of

Teflon deposition are placed. There exists a marked difference in the shape of the $\Delta E(i)$ curves of these two types of electrode and also between electrodes without (Fig. 3) and with (Fig. 4) carbon black addition, especially in the region of current densities higher than 10 - 15 mA/cm^2. Using the model of gas diffusion electrodes [7] and the similarity of the porous structure of electrodes used in alkaline and acid solutions, we can explain this difference by the diffusion transport hindrances into the drastically reduced pore volume (by factor 1.5 - 3) in the active layer filled with electrolyte, caused by a rise of electrolyte content when carbon black was added to the electrodes.

   Double-layer electrode (type B) and Teflon deposition by method (5) is characterized by a relatively low electrolyte content and therefore by a higher volume of pores filled with gas. On this basis its position in Fig. 1 and the shape of $\Delta E(i)$ curve in Fig. 4 could be explained by a relatively low transport hindrance in the gas phase using air. A relatively high polarization using oxygen could be explained by the low electrolyte content and consequently a low transport rate in the liquid phase. Teflon particles are very uniformly spread among the carbon black particles and therefore the electrodes are more hydrophobic.

   The electrolyte content in the single-layer electrodes (type A) is related to the ionic conductivity of electrodes aged by electrochemical treatment in the electrolyte for at least 20 h (Fig. 5). The part of the curve which corresponds to the lowest electrolyte content can be extrapolated to the origin. The steep rise of the curve in Fig. 5 ($\sim$0.65 g electrolyte/g electrode mass in the active layer) corresponds to the highest electrolyte content in electrodes without carbon black addition and at the same time to the lowest electrolyte content in the electrodes with carbon black (see Figs. 2a, 2b and 5).

   In Fig. 6 current–voltage characteristics of oxygen electrodes type A (single-layer electrodes) with active carbon promoted with platinum, with and without carbon black additon are presented. Teflon was deposited on the carbon surface using methods (1), (2), (4), (5). Method (3) was also used but due to the poor mechanical stability of these electrodes the corresponding results have not been considered. For comparison, the ranges of current–voltage characteristics of electrodes from pure active carbon, with and without addition of carbon black, are also presented in Fig. 6.

   From the experimental data it is seen that all the curves for active carbon promoted with platinum have lower polarization and the slopes of the linear portion of these characteristics are considerably lower (1.2 instead of 2.2 ohm cm^2).

   Contrary to the behaviour of the pure active carbon the effect of the method of Teflon deposition is not so marked, this is caused by the relatively narrow range of electrolyte content (0.47 - 0.62 instead of 0.24 - 0.64 g electrolyte/g electrode mass in the active layer). The corresponding influence of the electrolyte content on the potential of oxygen electrodes with and without carbon black at different current densities is seen in Figs. 7a and 7b. To show the beneficial effect of platinum promotion, a comparison of electrodes promoted and not promoted with platinum at the same electrolyte content,
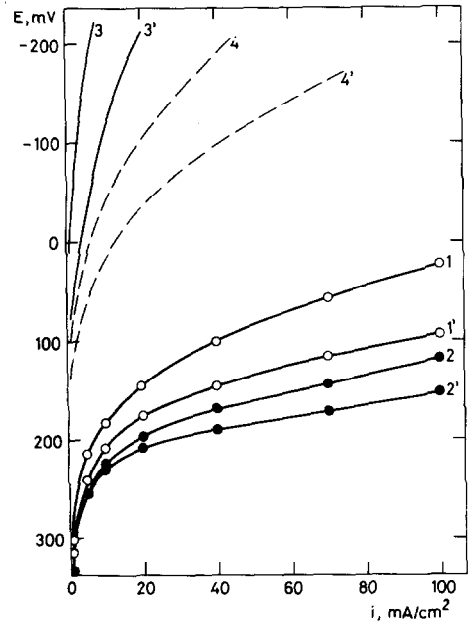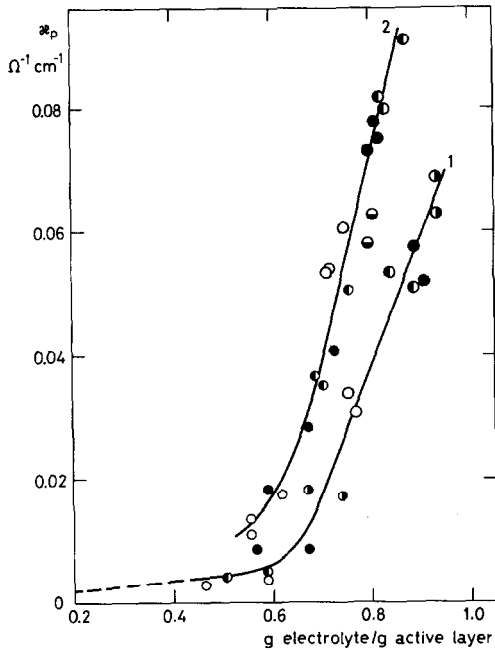
Fig. 5. Specific ionic conductivity κ_p of single-layer electrodes with pure active carbon (curve 1) and with active carbon promoted with platinum (curve 2). ○, method (1); ●, method (2); ◕, method (3); ◑, method (4); ◒, method (5); (small-size points refer to electrodes without carbon black addition, large-size points to electrodes with carbon black addition).

Fig. 6. Current–voltage characteristics of oxygen electrodes with active carbon promoted with platinum. Range 1-1′, method 1, 2, 4, without carbon black; range 2-2′, method (1), (2) and (4), with carbon black; (ranges 3-3′ and 4-4′ correspond to ranges 1-1′ and 2-2′ in Fig. 1).
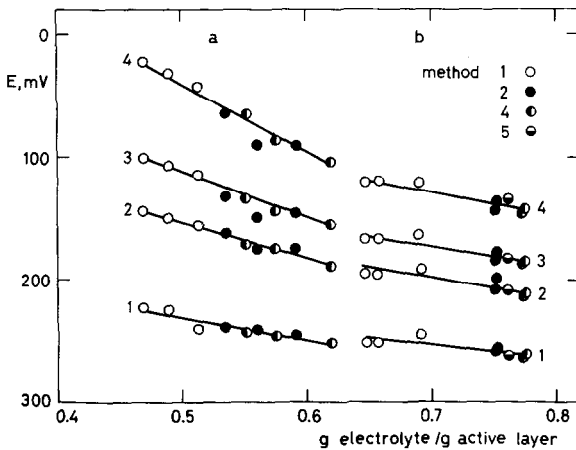

Fig. 7. Electrode potential as a function of the amount of electrolyte (g) soaked in the active layer (g) at different current densities: 1, 5; 2, 20; 3, 40; 4, 100 mA/cm^2. (a) Method (1), (2) and (4), without carbon black; (b) method (1), (2), (4) and (5), with carbon black.

TABLE 1

Influence of Pt-promotion on the electrochemical performance

Type of electrode	i (mA/cm^2)	Electrode potential (mV)		Potential difference (mV)
		Pure active carbon	Active carbon + Pt	
Without carbon black	5	− 40	+250	290
	20	−215	+180	395
	40	−320	+150	470
With carbon black	5	+ 20	+260	240
	20	−100	+200	300
	40	−170	+180	350
	100	−300	+135	435

and for electrodes without or with addition of carbon black (0.6 or 0.75 g electrolyte/g electrode mass in the active layer), was made and the corresponding data are listed in Table 1.

In spite of the relatively narrow range of electrolyte content with the different methods of Teflon deposition, in the case of active carbon promoted with platinum a less uniform Teflon deposit [modes (3), (2)] is also more suitable for the oxygen electrode, this can be attributed, as in the case of electrodes with pure active carbon, to the relatively higher electrolyte content in the electrodes (see Figs. 6 and 7a). The positive influence of the presence of carbon black is also noticeable (Figs. 6 and 7b) but is less pronounced than in the case of unpromoted active carbon. The oxygen electrodes with carbon black and Teflon deposited by method (2) show the best electrochemical performance and the slope of the linear part of their current–voltage characteristic is already comparable with the corresponding slope of the same type of electrodes in alkaline solutions.

Figure 8 shows the $\Delta E(i)$ curves for single-layer electrodes without (Fig. 8a) and with (Fig. 8b) addition of carbon black. Contrary to the electrode with pure active carbon (Fig. 3), in the presence of platinum no steep rise of $\Delta E(i)$ values at current densities up to 10 mA/cm^2 was observed and a plateau-like region up to 15 - 20 mA/cm^2 with $\Delta E(i)$ values in the range of 35 - 40 mV, corresponding to the reversible mechanism of oxygen reduction as in alkaline solutions, is visible.

The presence of carbon black does not change the shape and position of the $\Delta E(i)$ curve at low current densities and the same low $\Delta E(i)$ values were obtained (Fig. 8b). At high current densities the presence of carbon black negatively influences the rate of gas transport as in the case of electrodes with pure active carbon (Figs. 3 and 4). This is caused again by the higher electrolyte content due to the addition of carbon black (from 0.47 - 0.62 to 0.65 - 0.8 g electrolyte/g electrode mass in the active layer) and therefore increasing gas transport hindrances are to be expected.
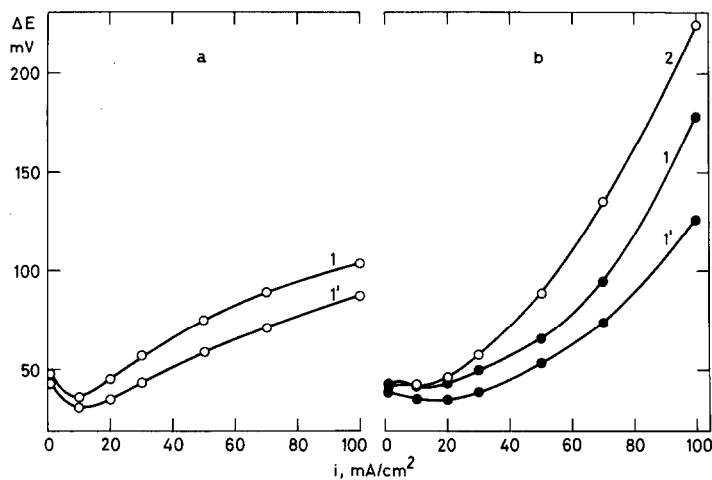
Fig. 8. $\Delta E(i)$ curves calculated from current–voltage characteristics of oxygen (Fig. 6) and air electrodes. (a) 1-1', range of $\Delta E(i)$ curves of electrodes method (1), (2) and (4), without carbon black. (b) 1-1', range of $\Delta E(i)$ curves of electrodes method (1), (2) and (4), with carbon black; 2, $\Delta E(i)$ curve of electrode method (5).

In Fig. 5 the ionic conductivities of single-layer electrodes with active carbon promoted with platinum are plotted as a function of electrolyte content in the electrode. A linear plot is observed to be shifted, in comparison with pure active carbon, towards lower electrolyte contents. Because of the presence of platinum a lower volume of pores (by $\sim 13\%$) and reduced hydrophobicity is to be expected and these two facts are most probably responsible for this shift.

Conclusions

(1) Teflon deposited onto the carbon surface from diluted water solutions leads to hydrophobic mixes.

(2) Teflon deposited onto the carbon surface in the presence of ethanol produces more hydrophilic electrodes.

(3) Carbon black reduces porosity and repellency.

(4) Active carbon with Teflon binder produces very porous and hydrophobic active layers.

(5) The presence of platinum partly destroys hydrophobicity but reduces electrode polarization due to its superior catalytic activity for peroxide decomposition.

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