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Carbon air electrode with regenerative short time overload capacity. II. Effects of duroquinone and 2-amino-1.4 naphthoquinone

P. ŻÓLTOWSKI* D.M. DRAŽIĆ, L. VORKAPIĆ

Faculty of Technology and Metallurgy, University of Belgrade and Institute of Chemistry, Technology and Metallurgy, Belgrade, Yugoslavia

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The short time overload capacity of the carbon-air electrode in a strongly alkaline electrolyte can be increased by addition of organic redox substances such as duroquinone (DQ) or 2-amino-1·4-naphthoquinone (ANQ). DQ, however, slowly decomposes in alkalies, while ANQ is quite stable even in 9M KOH. Small amounts of both quinones have a catalytic effect on the oxygen reduction at the carbon-air electrode.

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1. Introduction

The essential idea of this work is to introduce into the normal carbon-air electrode a redox system with a reduction potential in the range of −400 mV which would take over the cathodic process during the short overload periods, and thus hinder a further increase of polarization. During the normal or off periods, the substance should be easily reoxidized by air.

In the previous paper [1] the results of an investigation of the effects of addition of manganese (IV) compounds on the transient and stationary characteristics of carbon-air electrodes in strongly alkaline solutions were reported. This paper presents the results of a similar investigation of the effects of additions of the two quinone compounds: duroquinone and 2-amino-1·4-naphthoquinone. Henceforth we shall refer to them as DQ and ANQ, respectively.

The quinones represent an interesting class of organic compounds for the cathode material because of the rather convenient values of their redox potentials, well-known reversibilities and reasonable electrochemical discharging capacity if used as cathodes. Many attempts have been made to use quinones as the primary cathode material, especially the simple [2] or substituted benzoquinones. Recently, a German group from the Battelle Institute presented the results [3, 4] of an investigation of two benzoquinones (chloranil and duroquinone) as the primary material in low or medium pH regions and demonstrated the recharging possibilities by anodic charging or air regeneration.

Our investigation was directed towards the cathodic reduction and anodic or air regeneration of quinones in concentrated alkaline solutions. Quinhydrone decomposes under the influence of oxygen at pH higher than 7 [5, 6] with the formation of polymeric 'humic acids'. Chlorine-substituted benzoquinone compounds are more stable in alkalis, but even tetrachloro-*p*-benzoquinone (called chloranil) reacts with alkalies with the substitution of two chlorines with hydroxyl groups [7].

The most stable benzoquinone seems to be tetramethylo-*p*-benzoquinone, called duroquinone, having a rather low solubility in alkalies. Several investigators have successfully carried out research with a DQ redox system up to pH values higher than 10 [8–11], but the authors indicated that at high pH DQ is not quite stable; the product of alkali attack seems to be unknown. However, according to Fieser [7], 2-amino-1·4-naphthoquinone is not soluble in strong alkalis and is stable.

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*Permanent address: Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw

The normal redox potential of DQ is 480 mV (NHE) [3, 4, 10–12] and for ANQ 238 mV (NHE) [13, 14]. The usual 59 mV/pH dependence of redox potential for quinones is not valid for high pH regions having a tendency to decrease or even become zero for very high pH [10, 15–18]. The redox potential of DQ is independent of pH above pH 13·5 [10, 11] and is equal to −280 mV (NHE), and the redox potential for ANQ is also independent of pH above pH 11·5 [18] and is equal to −330 mV (NHE).

Since the carbon-air electrode potential under the normal current load lies in the range of −150 to −200 mV (NHE), the redox potentials of DQ and ANQ seemed to meet the idea of this work; i.e. to have a substance which can be reduced at larger current loads (overload) when the polarization is more negative, and reoxidized by air when the current is lower or zero.

2. Experimental

The active carbon powder used in the experiments was GM Type (Miloje Zakić Factory, Kruševac, Yugoslavia), treated as described elsewhere [19,20] to obtain a surface area higher than 1500 m^2g^{-1}, without any supplementary catalyst impregnation.

Duroquinone (Purum) was supplied by Fluka AG, Buchs SA – Switzerland, and 2-amino-1·4-naphthoquinone (m.p. 202–205°C) was prepared following the method of Fieser and Hartwell [21].

In the experiments the active carbon was used in a mixture with P.T.F.E. emulsion (Du Pont, TEF30) in a proportion by weight of 4:1 if not stated otherwise. Prior to mixing with P.T.F.E., one of the quinones was added to the carbon. The quinones were mixed with the carbon as powders either by mechanical mixing only, or as solutions in a small quantity of pyridine. The quantity of pyridine used was such as to form a smooth homogenous paste with the carbon after mixing. After mixing with pyridine solution the samples were dried for two days at room temperature prior to mixing with P.T.F.E. emulsion, and thereupon the samples were dried for a further day.

The pressed samples were prepared as described in the previous paper [1]. All other experimental conditions were the same, too. All experiments were carried out in 9 N KOH electrolyte, at 30°C, and potentials referred to the Hg/HgO/9N KOH electrode.

3. Results and discussion

3.1. *Potentiodynamic measurements*

In order to investigate the reversibility of the electrochemical reduction and oxidation, and reoxidation by the air of the cathodically reduced material, the cyclic potentiodynamic current/potential characteristics were recorded for powder (unpressed) samples in air-free electrolyte in a similar manner to that described previously [1]. The chosen potential range was between 0 and −950 mV, and the sweep rate 20 mV min^{-1}.

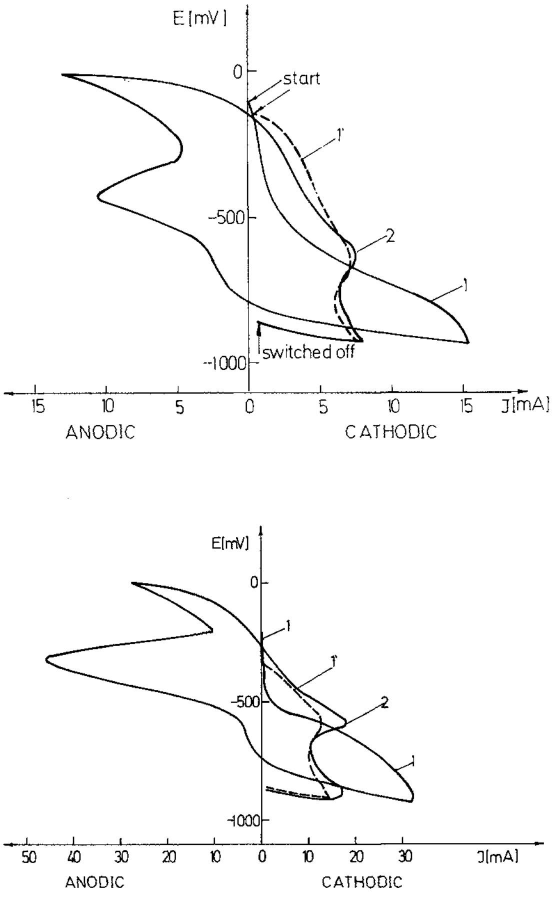

Fig. 1. (a) The cyclic potentiodynamic curves for a carbon electrode with 8% DQ. 1-first cycle; 2-second cycle; (a) after 1 h air regeneration. (b) The same as (a) but with 40% DQ.

In Figs. 1a and b the representative curves for small and large quantities of DQ, and in Figs. 2a

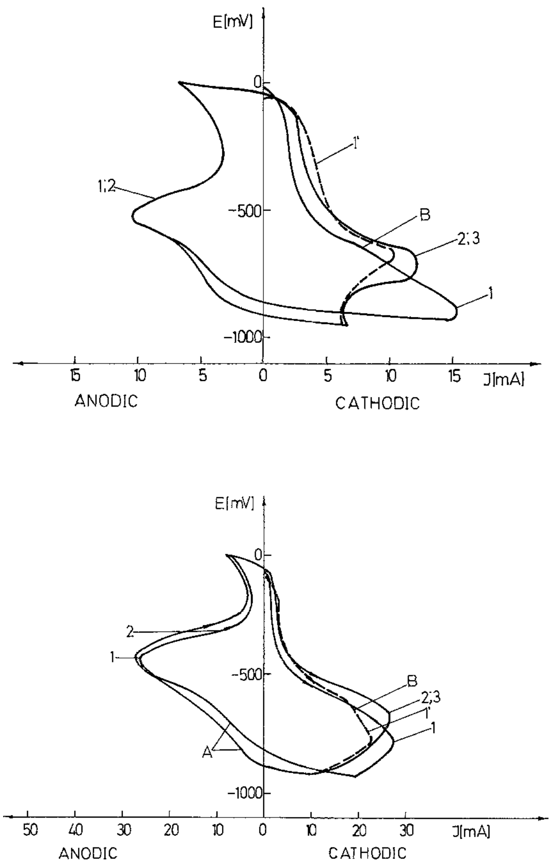

Fig. 2. (a) The cyclic potentiodynamic curves for a carbon electrode with 8% ANQ. 1-first cycle; 2-second cycle; 1'-after 1 h air-regeneration. (b) The same as (a) but with 40% ANQ.

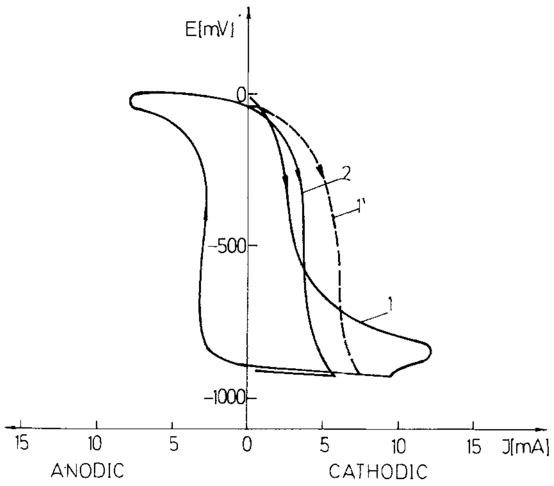

Fig. 3. The cyclic potentiodynamic curves for a carbon electrode without quinone additive (background). 1-first cycle; 2-second cycle; 1'-after air passing through, 3-third cycle.

and b those for the equivalent quantities of ANQ, are presented. The corresponding curves for a carbon sample without quinones added are presented for comparison in Fig. 3.

The method of introduction of both quinones into the carbon sample (by mechanical mixing or in pyridine solution) had no effect on the shape of the curves. One can observe for both quinones, but especially for DQ, that at the beginning of the first cathodic discharge curve the current at low polarizations is considerably lower than that for the pure carbon sample; it seems that the carbon capacity is decreased in the presence of quinone, probably because the carbon surface is screened. These two observations permit one to assume a slight solubility of both quinones in the electrolyte and some adsorption of quinones on the carbon. The assumed screening of the original carbon surface disappears very slowly during the rise of polarization and it is probably the reason why on all quinone diagrams the first peak appears at very high polarizations. The inflection point or semi-plateau (B) seen in Fig. 2a can be interpreted as the point from which the carbon surface began to be accessible to a larger extent for the electrochemical reduction process. A similar inflection point can be seen in Fig. 2b after the air recharge. The lowering of the assumed screening during the following cathodic discharges has no explanation.

For samples with small quantities of both quinones the first discharge capacity, calculated from the areas under the peaks, was 16·9 C for the DQ sample and 19·0 C for the ANQ sample. The theoretical capacities for the amounts of both quinones used were 6·1 C and 5·8 C respectively, while that for the pure carbon electrode capacity (background) was 11·8 C. Hence, the total capacities of the samples with small quinone additions were nearly equal to the algebraic sum of the quinone and carbon capacities in the chosen range of potentials. The first discharge capacity for samples with larger quinone contents was 38·3 C for the DQ sample and 33·9 C for the ANQ sample, in comparison to 30·8 C and 29·8 C for the theoretical capacities of the two quinones respectively. Hence the total capacities of the samples with large quinone additions were lower than the summed-up capacities of the quinone and the carbon. However, a careful examination of the figures shows that the whole amounts of quinones were not reduced during the cathodic sweep of the potential; at the beginning of the anodic sweep the current was still cathodic.

The next discharges, after anodic reoxidations, gave for both quantities of DQ successively lower capacities. At the same time the anodic recharge capacities, calculated from the areas below the peaks of the curves on the left side of the figures (the negative currents) were nearly two times higher than the respective following cathodic capacities. These two observations indicate a rather rapid decomposition of DQ with, probably, simultaneous hydrogen peroxide formation, which is a known process for the simple *p*-benzoquinone in high pH electrolytes [5, 6].

For both amounts of ANQ the following cathodic discharges, after the anodic reoxidation, gave quite well reproducible capacities: 16·5 C for small and 33·8 C for larger amounts of quinone (the carbon capacity is about 9·4 C in this case), i.e. nearly the same as during the first discharge. The anodic recharge capacities were nearly the same as the cathodic ones, too. This indicates a rather good stability of the ANQ and its reduction product under the conditions used. The air reoxidation for a half-hour gave for all the samples slightly lower capacities during the discharge than those following anodic recharging.

During all the measurements with both quinones no reduction by-product (quinhydrone or semiquinone) was observed.

3.2. *Galvanostatic measurements*

The galvanostatic discharge measurements were carried out for both quinones on pressed electrode samples, in the small cell, with 4 ml of electrolyte only, as described previously [1]. The IR drop was stable during all the quinone measurements. Usually the galvanostatic discharge curves were recorded for a freshly prepared electrode (curve 0), then after the first (1 h) air regeneration, after the second (1 h) regeneration, the third (1/2 h) regeneration and after the fourth (1/4 h) air regeneration (respectively curves I, II, III and IV). For several samples additional characteristics after the supplementary fifth (1 h) air regeneration were also recorded (curves V). The analogous characteristics were recorded for the carbon electrodes without any quinone addition at the same currents as for the samples with quinone. An example of such a typical characteristic for a pure carbon electrode is presented in Fig. 4 by dashed lines; for the sake of clarity only limiting curves are presented. The problem of the pure carbon electrode capacity has been discussed more fully elsewhere [1].

The typical discharge characteristics of the electrodes with 22% of DQ and ANQ are presented in Fig. 5 for 2C discharge rates [1]. The curves are corrected for IR drop and recalculated as percentages of the theoretical quinone capacity. Since the results of the potentiodynamic measurements show that no reasonable correction for the carbon background can be done, the pure carbon sample capacity is only indicated at one potential for comparison. The screening effect observed during the potentiodynamic measurements is well-seen also in this diagram. The comparison of Figs. 5a and b indicates that the ANQ discharge starts at more negative potentials than DQ. Hence ANQ seems to be less reactive than DQ. At the same time it can be seen that the air regeneration gives better results for ANQ than for DQ. After several rechargings, the ANQ sample characteristic is stabilized and reproducible, but the DQ sample capacity progressively decreases. The probable cause of the DQ sample capacity degradation is the decomposition of the DQ, as demonstrated by the potentiodynamic measurements.

The first galvanostatic discharge curves (curves 0) for the electrodes discharged at different rates are presented in Figs. 5a and b. The discharge potential for ANQ was also more negative than that for DQ. Another essential difference between the two quinones used was that the increase of the amount of DQ in the sample causes a considerable rise of the discharge polarization; this effect was not observed for the ANQ samples. In handling the electrodes we observed that the presence of DQ in the carbon sample increases the apparent hydrophobicity of the electrode, whereas the presence of ANQ reduces it. Therefore we tried to reduce the effective hydrophobicity of the DQ-containing electrodes by reducing the amount of P.T.F.E. emulsion introduced into the carbon, from the normally used 20% to 5%. Such an electrode was mechanically very weak, but as shown in Fig. 6a the reduction of the amount of P.T.F.E.

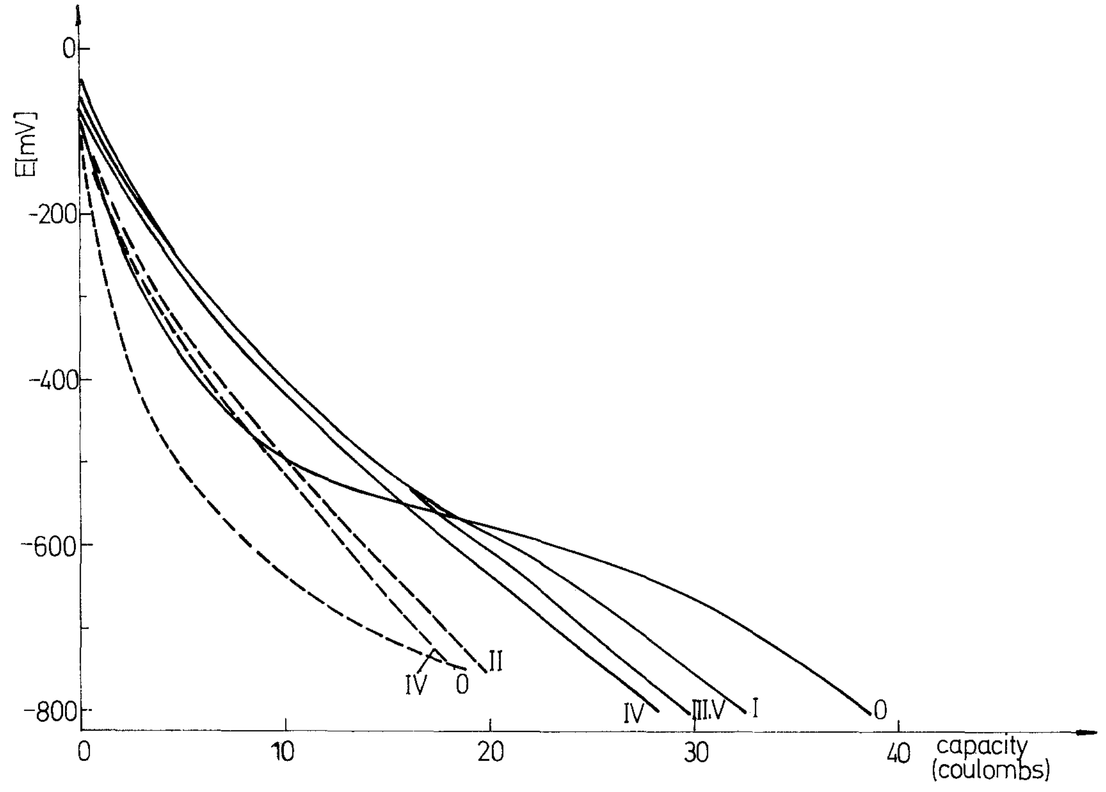

Fig. 4. The galvanostatic discharge curves for a pure carbon electrode (dashed lines) and with a small addition (8%) of ANQ, recorded at 21·6 mA. IR drops-corrected. The figures indicate the number of air regenerations.

had a considerable benficial effect on the discharge characteristics of the electrode with DQ addition.

The galvanostatic discharge curves for a sample with a low (8%) content of ANQ discharged at 21·6 mA (i.e. at a relatively very high discharge rate of 5·5 C for the theoretical capacity of 14·1 C of the quinone present) are shown in Fig. 4. When comparing this quinone sample discharge curve with the pure carbon sample curve presented in the same figure, a large, nearly 50%, increase of the capacity is seen. This additional capacity is quite quickly and reproducibly restored by the air regeneration.

During the experiments some additional observations concerning the solubilities of the species were done. DQ as well as ANQ have very low solubilities in the electrolyte used, but their reduction products (the respective hydroquinones) have considerable solubilities. After each measurement the porous glass disc and the electrolyte were distinctly coloured. In an experiment with ANQ and another with DQ an additional cellophane membrane was placed between the electrode and a fritted glass disc (a supplementary gas exit was made in the half-cell arrangement for this measurement) but it had no appreciable effect on the electrode characteristics and colouring. Hence, the cellophane membrane is not an effective barrier for the quinone reduction product transport. However, at the same time these experiments proved that the gas bubbling through the electrodes during all the previous galvanostatic measurements had no influence on the measured characteristics, i.e. the natural convection of air is sufficient to supply the reacting oxygen through the pores.

3.3. *Steady-state potential-current characteristics*

In a similar manner to that used in the previous investigation of the effect of MnO_2 [1], the steady-state potential-current characteristics of the electrodes in air were measured. The results obtained are presented in Fig. 7. They are quite similar to those obtained before with MnO_2 additions [1].

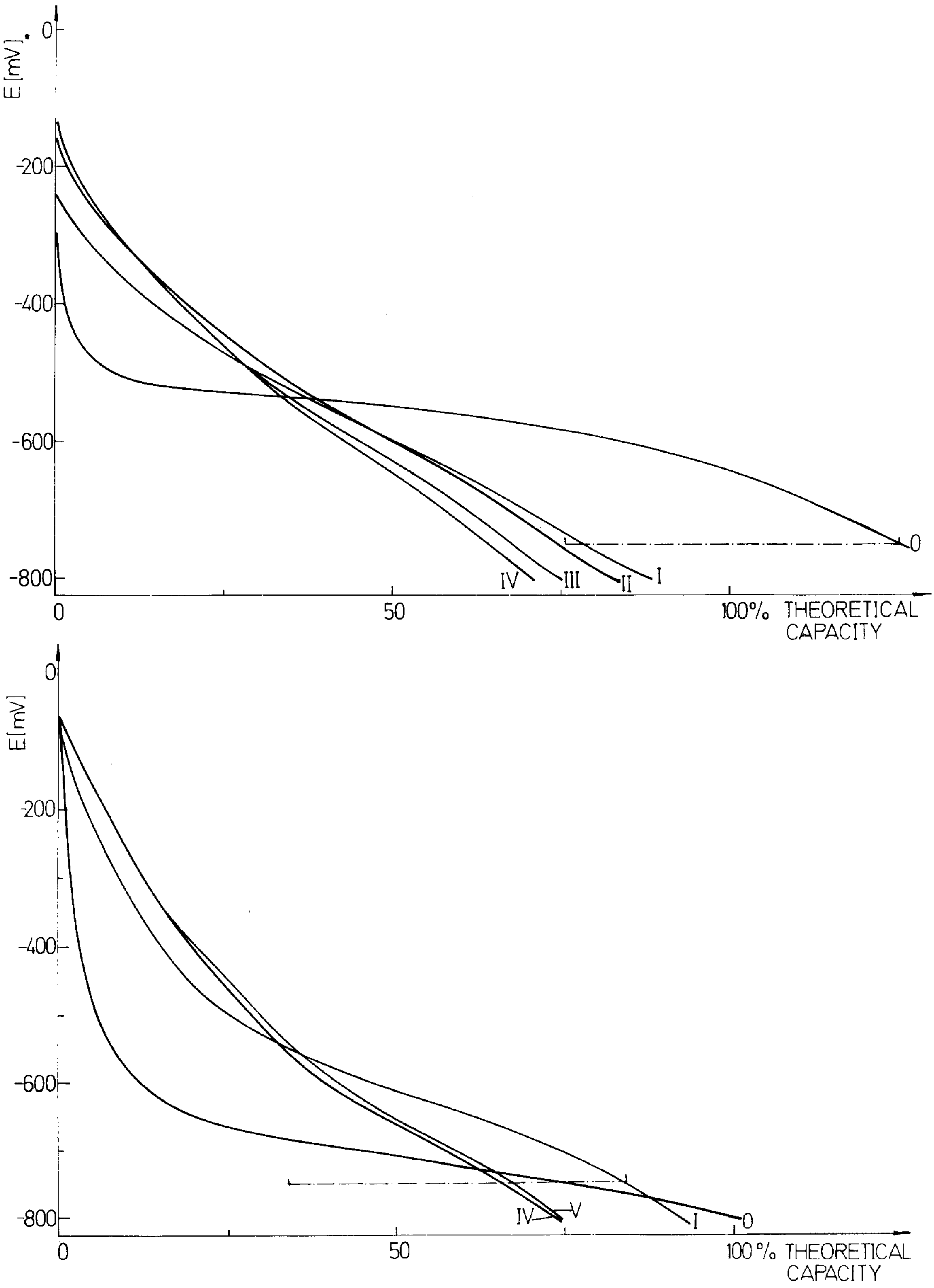

Fig. 5. The galvanostatic discharge curves for carbon electrodes with 22% of additive recorded at 2C discharge rate. The horizontal dashed lines indicate the pure carbon capacities (background) at the given potential (a) for DQ; (b) for ANQ.

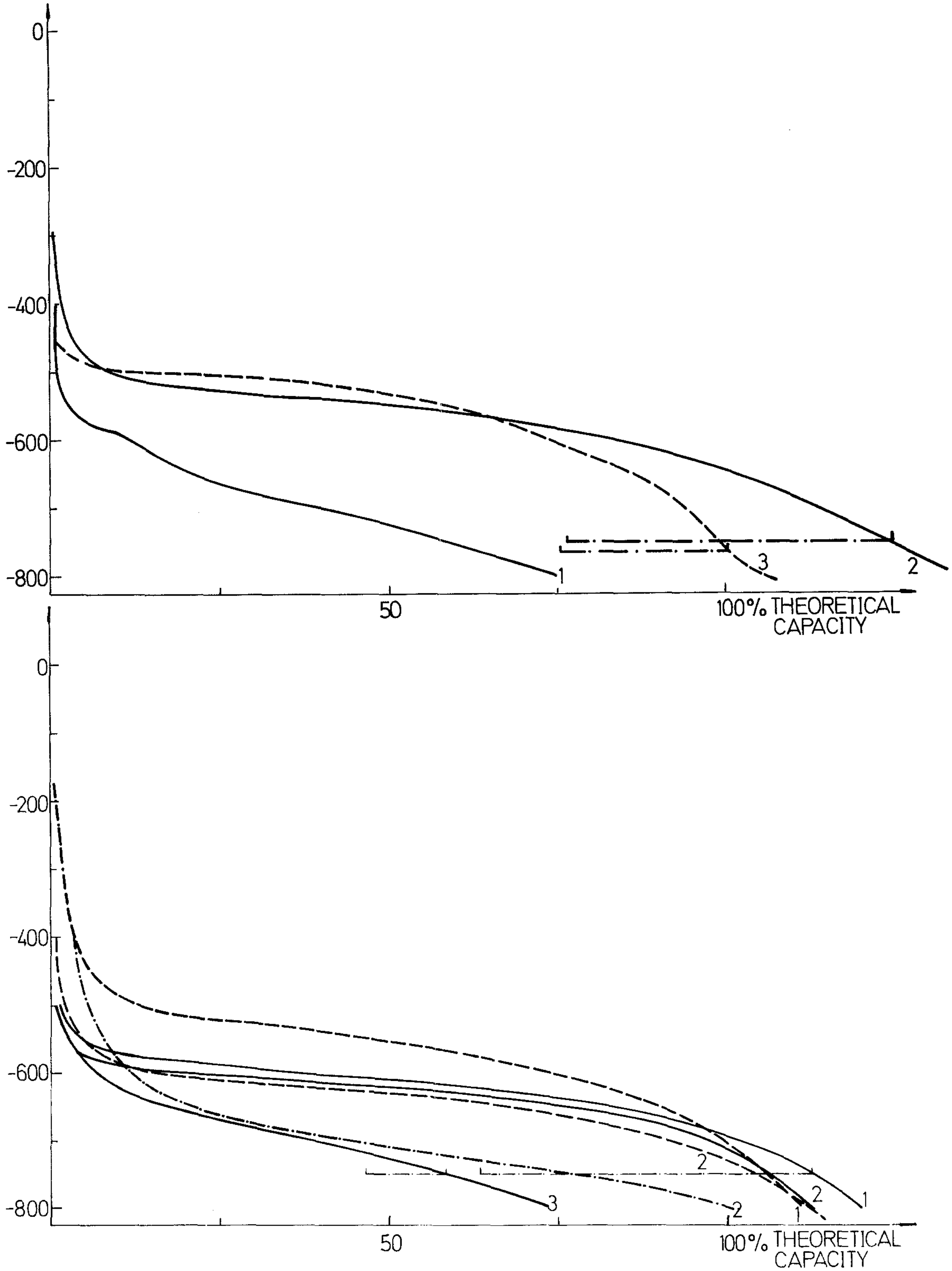

Fig. 6. The first galvanostatic discharge curves for the electrodes with different amounts of quinones: the horizontal dashed lines indicate the pure carbon capacities at the given potential. (a) for DQ discharged at 2C rate. 1–42% (66·5 mg) DQ in pyridine; 2–21% (33 mg) DQ mechanically mixed; 3–42% DQ in pyridine, P.T.F.E. emulsion reduced to 1/4 of the normal value. (b) for ANQ: dashed lines – 44% (70 mg) ANQ mechanically mixed; solid lines – 44% ANQ in pyridine; dotted lines – 22% (35 mg) ANQ in pyridine. Discharge rates: 1. – 1C; 2. – 2C; 3. – 4C. (For 44% quinone 1C is 21·3 mA, 2C is 42·6 mA etc).

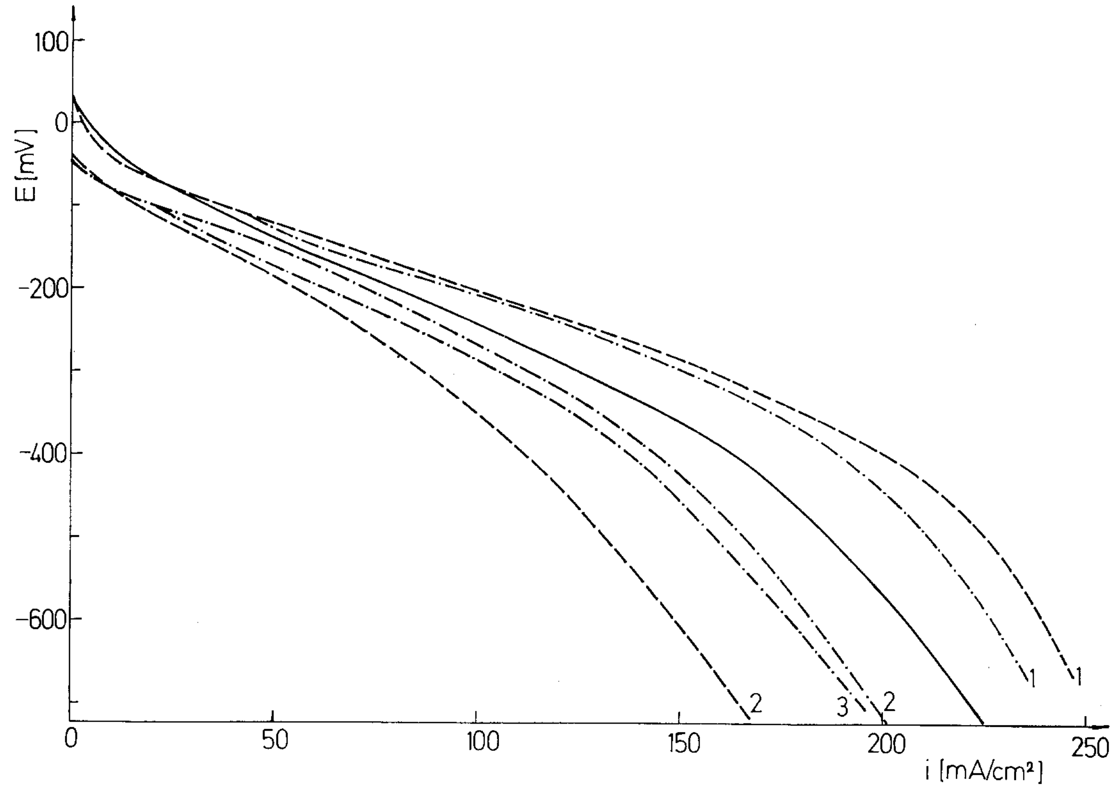

Fig. 7. The steady-state potential-current characteristics of the carbon-air electrodes; solid line – carbon without quinone added; dashed lines – ANQ added; dotted lines – DQ added. 1–7% of quinones mechanically mixed; 2–42% of DQ or 44% of ANQ in pyridine; 3–42% of DQ mechanically mixed.

The larger amounts of both quinones cause a drastic deterioration in the performance of the electrode but the small amounts proved to be beneficial i.e. the electrodes with the small amount of quinones had lower polarizations than those without quinone. For electrodes with the DQ this effect can be expected to be only temporary because of the instability of this quinone, but for the ANQ addition this beneficial effect should be a stable one. The mechanism of the effect of a small amount of quinone on the electrode performance in the air is not clear as yet. A possible explanation could be similar to that in the case of manganese dioxide: the catalytic decomposition of hydrogen peroxide formed during the oxygen reduction at the carbon air electrode.

4. Conclusions

Three essential conclusions can be drawn from the present investigation:

(1) The duroquinone/durohydroquinone couple is not stable in a concentrated alkaline electrolyte.

(2) The 2-amino-1·4-naphthoquinone/hydroquinone couple is fairly stable in 9N KOH electrolyte, but the solubility of the hydroquinone form is considerable. In the presence of active carbon, the hydroquinone form is easily oxidized by atmospheric oxygen. Hence, the presence of quinone in the carbon electrode increases considerably the electrochemical cathodic capacity of the electrode, improving its transient characteristics.

(3) The presence of a small quantity of quinone in the standard carbon air-electrode improves the steady-state performance of the electrode.

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