

# *Evaluation of organic battery electrodes: voltammetric study of the redox behaviour of solid quinones*

H. ALT\*, H. BINDER, G. KLEMPERT, A. KÖHLING AND G. SANDSTEDT†

*Battelle-Institut e.V., Frankfurt (Main), Germany*

Received 3 January 1972

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The redox behaviour of solid quinones has been examined by potential sweep and cyclic voltammetry. A number of quinones are insoluble in aqueous electrolytes and can be completely discharged and recharged without appreciable polarization, as found, for example, with solid chloranil (tetrachloro-*p*-benzoquinone) and solid duroquinone (tetramethyl-*p*-benzoquinone). Hence quinones are reversible redox systems not only in solutions but also in the solid state. During discharge and recharge in dilute sulphuric acid only slight polarization occurs, which is attributed to a pure diffusion overvoltage. Polarization is not much greater in salt solutions. In this case, however, the peaks of the voltammetric curves are broader. In ammonium chloride solutions a double peak corresponding to the two electron transfers is obtained for chloranil both anodically and cathodically; this shows that the semiquinone is stable in ammonium chloride solution. Duroquinone also gives two peaks, but these are observed only in non-stationary measurements so that they do not correspond to the state of equilibrium. The pH dependence of the redox potential is 59 mV per pH unit. Only chloranil in ammonium chloride solution shows two redox potentials, depending on the discharge depth, which are both lower than the potential corresponding to the pH. The possible application of quinones in secondary battery cathodes is discussed.

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## 1. Introduction

Voltammetry with linear potential sweep has long been used in the investigation of electrode reactions of solutes [1]. By reversing the direction of the voltage change (triangular voltage), cyclic current-voltage curves are obtained and both the reduction and the oxidation behaviour of the solutes can be studied [1]. This method is also suitable, by varying the electrode material (catalyst), for determining the influence of the electrode material on the reaction process [2-6]. Furthermore it can be used as an analytical method in the anodic stripping of metal

\* Now at Farbwerke Hoechst AG, Frankfurt (Main)-Höchst.

† Paper presented by G. Sandstede at the meeting of the Battery Section of the Comité International de Thermodynamique et de Cinétique Electrochimiques (C.I.T.C.E.) at Strasbourg, April 1971.

deposits [7]. Also the theory of linear sweep voltammetry has been developed extensively for all these cases. It remains to be seen whether the same theoretical treatment can be applied to solid active substances (depolarizers). However, as regards battery research it is just this simple method which can supply valuable information on the electrode reactions. We therefore studied the potentiodynamic behaviour of a simple system—quinone/hydroquinone. Quinones can in principle be used also as cathode materials [8].

Solutions of quinone/hydroquinone systems have long been known to be reversible redox systems [9, 10]. The mechanism of the oxidation and reduction of dissolved quinones has also been studied repeatedly [11-14]. As regards solid insoluble quinones, electrochemical measurements were recently made by us [8, 15]. It was here found, among other results, that the

non-conductive quinones when mixed with graphite can be reduced completely. Chloranil (tetrachloro-*p*-benzoquinone) and duroquinone (tetramethyl-*p*-benzoquinone) were found to be insoluble in aqueous electrolytes and chemically completely stable over the potential range considered. The potention-dynamic investigations on these two quinones will be described in the following.

## 2. Method of measurement

In linear sweep voltammetry (non-stationary voltammetry, potention-dynamic voltammetry, chrono-voltammetry) the potential of the electrode is increased or decreased linearly with time. When the potential is increased, the (hydroquinone-containing) electrode generally responds with an anodic current (oxidation of the hydroquinone to quinone) while when the potential is decreased there generally flows a cathodic current (reduction of the quinone to hydroquinone). The potention-dynamic current-voltage curves thus reflect the oxidation or reduction behaviour. If the voltage decrease follows directly on the voltage increase after a given potential value is reached, cyclic current-voltage curves are obtained. If the curve is closed upon itself and the cyclic curves when passing periodically through the same potential region are congruent, this indicates that, on the one hand, the substance is recovered each time in oxidized and reduced form, i.e. that no further chemical change occurs within the time of measurement, and, on the other, the reactions that take place are in 'dynamic equilibrium'.

The quinone electrodes used, just like other battery electrodes, have a large internal surface area and therefore a correspondingly large double-layer capacity  $C_D$ . In order that the capacitive component of the current can be neglected, the selected voltage speed (sweep rate)  $dU/dt$  must be low. This follows from the fact that the total current is composed of the Faraday component  $i_F$  and the capacitive component in accordance with

$$i = i_F + C_D (dU/dt) \quad (1)$$

The sweep rate must be low also for the reason that, if the double-layer capacity is large, the

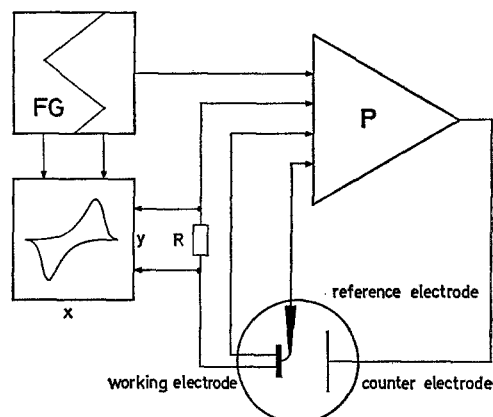


Fig. 1. Schematic diagram of the arrangement for single sweep and cyclic voltammetric measurements.

time constant  $RC_D$  is large and the current would not otherwise reach the value required by the potential.

The measuring arrangement (Fig. 1) therefore comprises a function generator FG, which supplies a voltage that changes very slowly with time [16]. The voltage is, in the usual manner, applied to a potentiostat which is connected to the test electrode and reference electrode of the half-cell. The potentiostat adjusts the current between test electrode and counter-electrode; the current is fed to one coordinate of an X-Y recorder, while the time-proportional voltage is applied to the other coordinate of the recorder.

Conducting electrodes were produced from the non-conductive quinones by mixing them thoroughly in a ball mill with powdered graphite in the proportion by weight of 1 : 1 and compacting the powder mixture between discs of graphite felt. A holding device (Fig. 2) incorporates a tantalum plate with current supply at the bottom of the electrode and above it a disc of conducting graphite; the active compound is placed on this and again covered with a disc of graphic felt. The layers are then pressed together using a tantalum mesh and a clamping nut. The original thickness of the graphite felt (1.5 cm) then is reduced to approximately 0.4 mm. Its resistance is *c.* 0.1 ohm. The electrolyte within the pore volume of the graphite felt has a resistance of <0.1 ohm. This means that the ohmic drop within the electrode will exceed a few millivolts only if the current is greater than 100 mA (which was not the case).

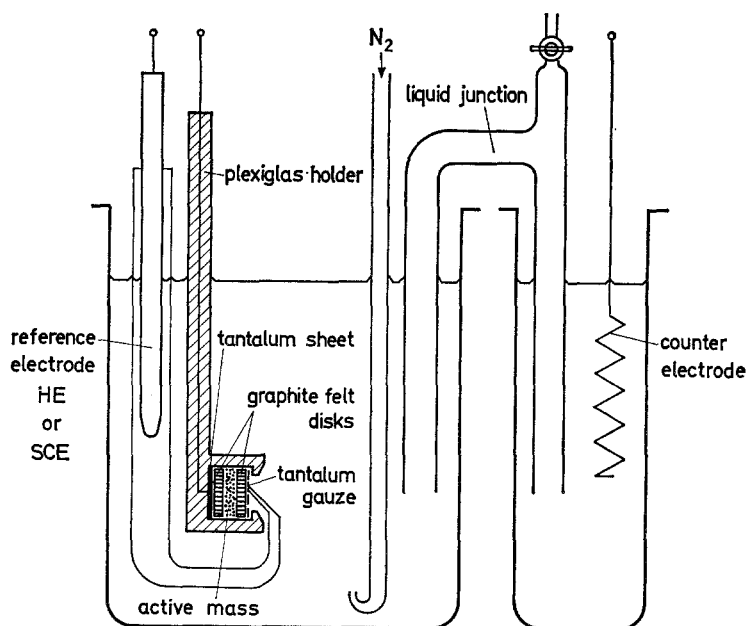


Fig. 2. Half cell arrangement with an unbonded powder electrode as working electrode.

Apart from the unbonded powder electrode, pressure-bonded electrodes were also produced. The powder mixture was compressed with gold powder and sodium sulphate. After the sodium sulphate had been dissolved, the quinone-graphite mixture was present in a porous gold skeleton.

An autogenous hydrogen electrode [17] was used as reference electrode in dilute sulphuric acid, and a saturated calomel electrode in the salt solutions; in this case the potential was converted to the normal hydrogen electrode. Any oxygen influence was eliminated by bubbling nitrogen through the electrolyte.

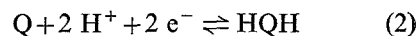
The porous gold electrodes were fixed to a simple grip made of gold sheet.

### 3. Results on duroquinone

#### 3.1. Results in acid

Fig. 3 gives the cyclic current-voltage curve obtained for duroquinone in 3 N H<sub>2</sub>SO<sub>4</sub> at 25°C. The curve portion in the anodic region represents the oxidation of the hydroquinone to the quinone, whilst the cathodic portion of the curve arises during the reduction of the quinone

to hydroquinone. The charge that has been converted is represented by the areas bounded by the respective curves and the abscissa. It corresponds 100% to the charge contained in the weighed quantity of substance used, on the assumption that the following gross equation holds:



The cyclic curve can be reproduced repeatedly, that is to say the curve is periodic and the total available charge is converted during each period. If, instead of a sweep rate of 40 mV/min (=  $0.67 \times 10^{-3}$  V/s), a value greater or smaller by a factor of 10 is selected, the current peaks are correspondingly greater for higher sweep rates and smaller for lower sweep rates, as the voltage axis is proportional to time. In every case the area corresponds to the converted charge present in the electrode.

Polarization is very low, both in the anodic oxidation and the cathodic reduction (Fig. 3). It can be assumed that only diffusion overvoltage due to pH shift is involved, considering that the hydrogen ions take part in the reaction, in accordance with equation (2). During the cathodic sweep, for example, hydrogen ions are

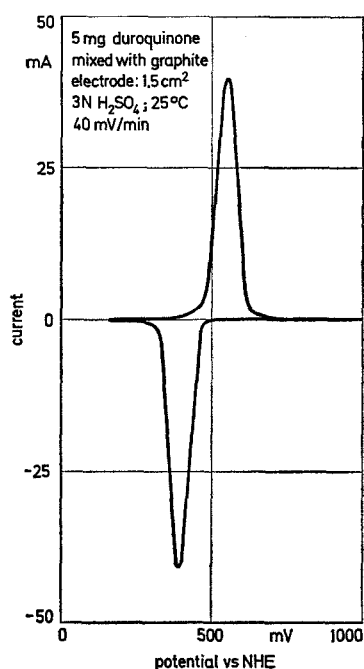


Fig. 3. Cyclic voltammogram of a duroquinone electrode in dilute sulphuric acid.

consumed. Hence, the hydrogen ion concentration in the immediate neighbourhood of the inner electrode surface is decreased. The deficit must be made up by diffusion which takes some time because the pores between the quinone-graphite particles are very narrow. According to

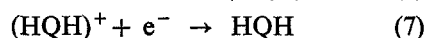
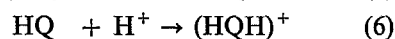
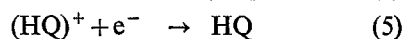
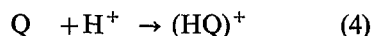
$$\varepsilon = \varepsilon_0 + \frac{RT}{nF} \ln[H^+] \quad (3)$$

the potential shift amounts to 59 mV for each decade of hydrogen ion concentration. In addition, as follows from galvanostatic discharge curves [8, 15], there may be a small crystallization overvoltage contribution.

A rest potential of 478 mV was measured. This value is in fairly good agreement with that given in the literature [12, 15] at 480 mV, which was measured for a solution of duroquinone in a mixture of 50% methanol and 50% 2 N HCl. This leads to the conclusion that it is the redox potential (the equilibrium potential) which is measured also on the electrodes containing the solid quinone. This conclusion is supported by the fact that the potential remains constant even if the ratio of quinone to hydroquinone is

changed, as long as at least some small amount of the second phase is present.

The mechanism of the reduction of the dissolved duroquinone has been elucidated by Dohrmann and Vetter [12]. In acid solutions the reaction sequence is as follows:



Dohrmann and Vetter found that, as is the case for p-benzoquinone, the two charge-transfer reactions take place at approximately the same rate. It must be assumed that this mechanism holds also for solid duroquinone, because only one current peak appears in the potentiodynamic current-voltage curve and the two charge-transfer reactions must therefore take place at roughly the same potential.

### 3.2. Results in ammonium chloride solution

In ammonium chloride solution at a very low

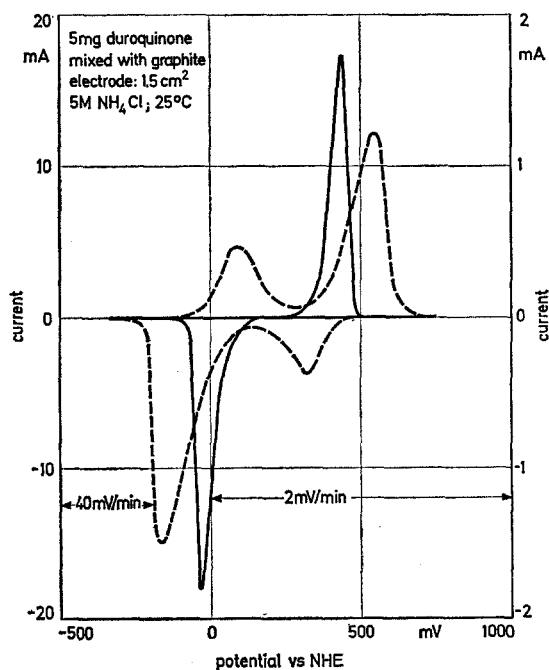


Fig. 4. Cyclic voltammograms of a duroquinone electrode in ammonium chloride solution at different sweep rates.

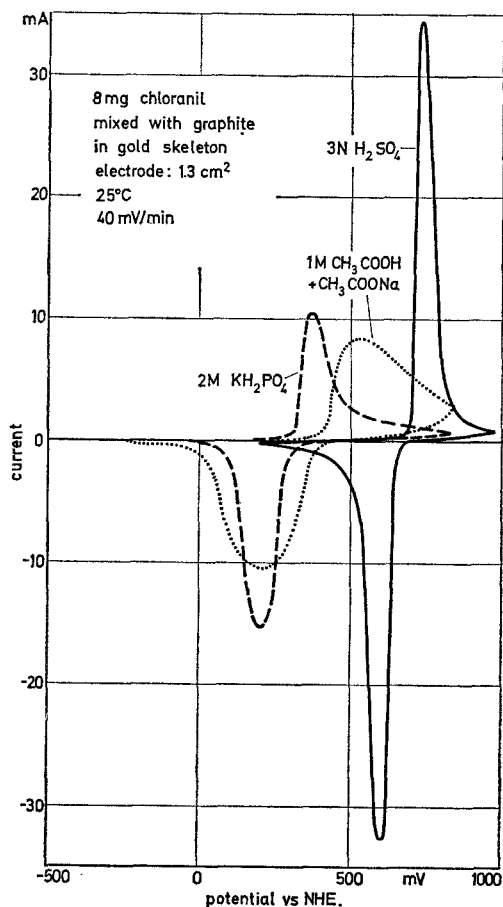


Fig. 5. Cyclic voltammetric curves of a chloranil electrode in various electrolytes.

sweep rate (2 mV/min) a cyclic current-voltage curve is obtained, which is fairly similar to that in dilute sulphuric acid. The two current maxima are, however, much further away from each other and thus polarization is considerably greater. Fig. 4 shows that the anodic and cathodic curves are nevertheless congruent.

The cyclic curve taken at a potential sweep of 40 mV/min shows two peaks in either branch (see also Fig. 4); one prepeak occurs both in the cathodic and in the anodic branch. This may be due to two different charge-transfer reactions involving the semiquinone or simply to a local pH-shift within the electrode because an unbuffered electrolyte is used. Further investigations must be carried out before more precise information on details of the mechanism involved can be given. In any case it can be stated that the diffusion of the hydrogen ions must

have a major influence, because the prepeak does not occur at very low sweep rates.

#### 4. Results on chloranil

##### 4.1. Results in acids

In dilute sulphuric acid basically the same results are obtained for chloranil as for duroquinone. Fig. 5 gives the cyclic current-voltage curve. Also this curve is reproducible by periodic reiteration. Compared with duroquinone the curve lies altogether in a region of higher potential; the rest potential measured was 668 mV. Here again the equilibrium redox potential is involved, which is independent of the composition of the electrode mass. This redox potential, obtained at pH 0, for the solid quinone/hydroquinone, is again in very good agreement with the known value for dissolved chloranil. In an acid aqueous-alcoholic solution saturated with both quinone and hydroquinone the value is here 663 mV [18].

It can be found from the area bounded by the curves that chloranil is also 100% reduced to the

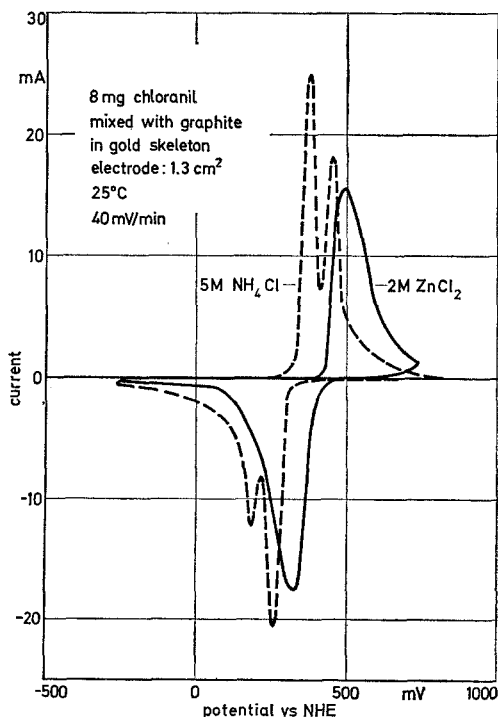


Fig. 6. Cyclic voltammetric curves of a chloranil electrode in ammonium chloride and zinc chloride solution.

corresponding hydroquinone; again the two charge-transfer reactions take place at about the same potential.

Just as for duroquinone, the polarization is very low in dilute sulphuric acid. This applies to both charging and discharging.

#### 4.2. Results in sodium acetate, potassium phosphate and zinc chloride

It is seen in Fig. 5 and 6 that basically similar cyclic current-voltage curves are obtained in these salt solutions as in dilute sulphuric acid. The curves are shifted relative to the latter in accordance with the difference in pH value (see below). When using sodium acetate buffer solution, the peaks are substantially flatter compared with the results in sulphuric acid, and the curves are accordingly considerably broader. The peak current is also much smaller in potassium phosphate solution and zinc chloride solution compared with sulphuric acid solution. The diffusion of the hydrogen ions, which take part in the reaction, is presumably responsible for this. The matter cannot at present be stated more precisely because the relationship between current density and diffusion in solid redox systems has not yet been determined quantitatively.

Fig. 7 shows the dependence of the rest potential of the electrodes on the pH value (measured with a glass electrode). The rest potential values, with the exception of those for ammonium chloride, lie approximately on the straight line obtained from the theoretical pH-dependence for the gross reaction (2). The

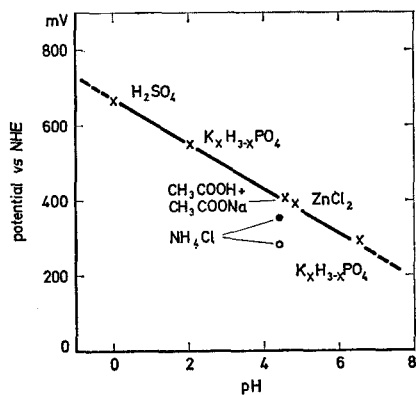


Fig. 7. Redox potentials of solid chloranil as a function of pH.

values are therefore those of the redox potentials for the appropriate pH values. It should be noted that chloranil is not stable in alkaline electrolytes. The different behaviour in ammonium chloride solution is discussed in the following section.

#### 4.3. Results in ammonium chloride solution

The cyclic current-voltage curve obtained in ammonium chloride is also included in Fig. 6. It will be noticed that instead of one current peak, each curve shows two. In order to determine whether this is a kinetic phenomenon, the sweep rate was increased. The result is shown in Fig. 8. Both current peaks are less pronounced at higher sweep rates, and at a sweep rate of 400 mV/min there is only one peak. However, as the curve concerned is a wide one, the details are blurred. The resolution is inadequate because the time constant for the charging of the double-layer capacitance already plays a part.

In Fig. 8 the ordinate does not give the current density but the pseudo-capacity, which is obtained if the current density is divided by the voltage speed. The unit As/V is equal to the farad, but it should be borne in mind that we are not dealing with a capacity but a quantity analogous to it, which was calculated from the (essentially)

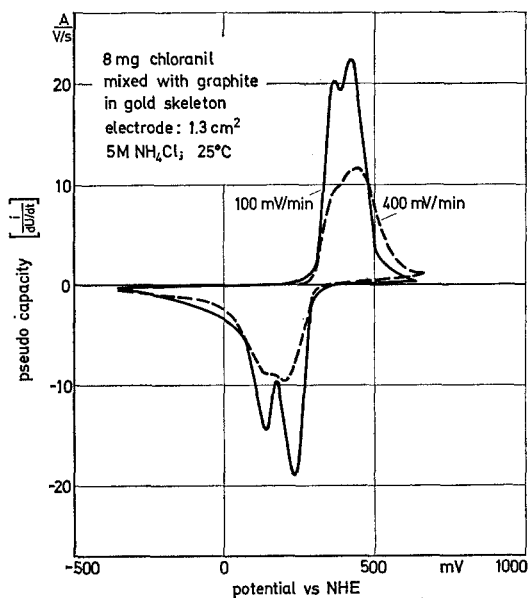


Fig. 8. Cyclic voltammograms of a chloranil electrode in ammonium chloride solution at different sweep rates.

Faradaic current. This representation offers advantages, because equal areas below the curves here correspond to equal amounts of charge. In addition, the branching of the curve, which increases as the sweep rate drops, is expressed more clearly in this way. It is not proposed to discuss here the plotting of  $i/\sqrt{(dU/dt)}$ , as is usual in the voltammetry of solutes, because such curves can be evaluated only after further experimental data are available. As can be seen from Fig. 8, the amount of sample reduced or oxidized is decreased as the sweep rate is increased. For the further study of the behaviour of chloranil in ammonium chloride solution the sweep rate was then reduced. The result is shown in Fig. 9 where, for the sake of clarity, only the respective cathodic branches are reproduced. The anodic curves are nearly mirror-symmetric and shifted in a manner that can be seen in Fig. 8. It should also be noted that the maxima of the pseudo-capacity decrease with higher sweep rates, while the current shows the opposite behaviour. The areas under the curves are equal, which indicates that the amount of substance reduced or oxidized

is no longer dependent on the sweep rate.

In Fig. 9 it is seen that the current maxima become increasingly more pronounced as the sweep rate drops. If the voltage is kept constant at a value corresponding to the current minimum, the current returns to zero. This indicates that a stable substance is present after half the charge is consumed. It should be noted that this charge is exactly equal to half the charge contained in the sample, calculated on the basis of a two-electron process. The two current maxima must therefore be assigned to two subsequent one-electron-transfer reactions which differ in potential.

Two different rest potentials can in fact be measured, depending on the composition of the electrode mixture. When the active component has been reduced or oxidized so that it apparently contains about 25% quinone and 75% hydroquinone, a value of 280 mV is measured for the rest potential, while for a composition corresponding to a reduction of the quinone to about 25%, the measured value is 350 mV. These values are constant with time. We assign them to the quinone-semiquinone transition and the semiquinone-hydroquinone transition and believe that they, too, are true redox potentials. The values are also entered in Fig. 7. It can be conjectured that the semiquinone anion, which normally is formed only in alkaline media, is also stable in an ammonium salt solution. In any case, the quinhydrone cannot be involved, because chloranil is incapable of forming this complex. Further investigations are in progress to elucidate the mechanism involved.

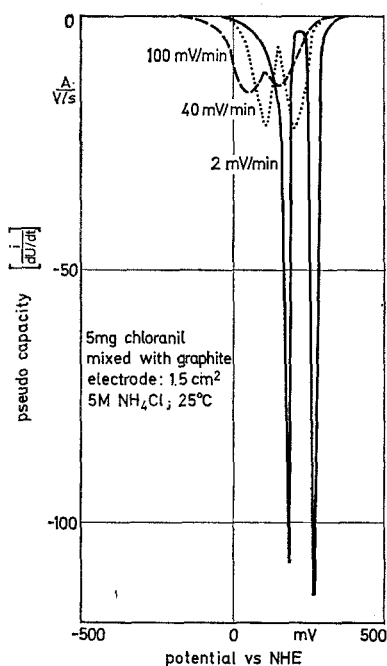


Fig. 9. Cyclic voltammetric curves of a chloranil electrode in ammonium chloride solution at different sweep rates (cathodic branch only).

## 5. Outlook for battery cathode applications

In an earlier publication [19] it was shown that the capacity (in Ah) is relatively favourable, compared with inorganic active compounds. Also the theoretical energy density of quinones in combination with zinc gives favourable values. It is true that the anodes would also have to be rechargeable in acid electrolytes. Duroquinone should also be suitable for use in alkaline electrolytes, although the equilibrium potential is here relatively low compared with, say, that of manganese dioxide. In aprotic solvents certain quinones are particularly suitable as rechargeable cathodes [8].

Another potential application is offered by the chemical regeneration of the hydroquinone with the aid of oxygen or hydrogen peroxide [20, 21]. The high loading power, the low temperature dependence of the discharge characteristic and the low polarization of quinone cathodes could be exploited in this way, provided that intermittent operation of the battery can be tolerated. The recharging with hydrogen peroxide is achieved very quickly, but regeneration with air takes time, of the order of some hours.

Further technological research is necessary before the industrial use of quinones as cathode materials can be assessed more accurately. In addition, it is attractive to study the precise reaction mechanism for solid electrode masses.

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