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ELECTROCHEMICAL AND ENERGETIC CHARACTERISTICS OF A CARBON PASTE ELECTRODE WITH PARABENZOQUINONE AND PEAT

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ABSTRACT. The electrochemical and energetic characteristics of a carbon paste electrode prepared by mixing *p*-benzoquinone, peat, acetylene black and teflon was studied using chronocoulometry and cyclic voltammetry.

INTRODUCTION

The electrochemical properties of quinones make them a promising class of compounds to be utilized as active matter in secondary batteries. Quinones incorporated in carbon paste electrodes (CPE) have been frequently employed to investigate their electrochemical behavior [1,2,3]. The redox couple *p*-benzoquinone/hydroquinone was chosen for our studies because of its chemical stability, favorable equilibrium potential and electrochemical reversibility [1]. Furthermore, acetylene black has been substituted partially by peat, a carbon paste widely available in Senegalese quarries in order to investigate the possibility to use it in manufacturing batteries [4].

EXPERIMENTAL

The electrochemical cell employed has been described elsewhere [2,5,6]. The CPE used in the investigations was similar in construction to the electrode utilized by Yu *et al.* [7]. A saturated calomel electrode (SCE) and platinum wire served as reference electrode and as counter electrode, respectively. The measurements were carried out with a potentiostat/galvanostat (Model 273 EG & G Princeton Applied Research) and a chart recorder (JMI SE 120).

The carbon paste electrode was prepared by mixing 150 mg of *p*-benzoquinone, 67.5 mg of peat, 67.5 mg of acetylene black and 15 mg of teflon. All the electrochemical investigations were performed by chronocoulometry and cyclic voltammetry. The different curves were obtained after successive reduction and oxidation cycles. The scan rates were chosen in a range between 6 and 0.1 mV/s in order to minimize residual currents.

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RESULTS AND DISCUSSION

Figures 1 and 2 show the dependence of the peak current and the peak potential on scan rate. We observed that the values of $(E_p^{ox} + E_p^{red})/2$ are nearly constant and are assumed to be equal to the equilibrium potential (Tables 1 and 2).

The half peak and the peak potentials were not considered as representative of the system because they change with experimental conditions (scan rate, acidity). But it has already been shown [8] that the values of the equilibrium potential at open circuit are reproducible and can be considered as characteristic of the system.

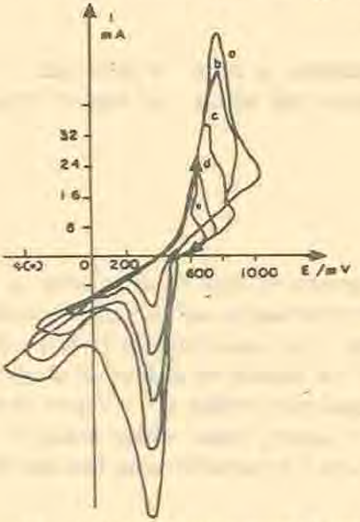

Figure 1. Variation of peak current with scan rate (2 N H_2SO_4). a) 6 mV/s; b) 4 mV/s; c) 2 mV/s; d) 1 mV/s; e) 0.5 mV/s

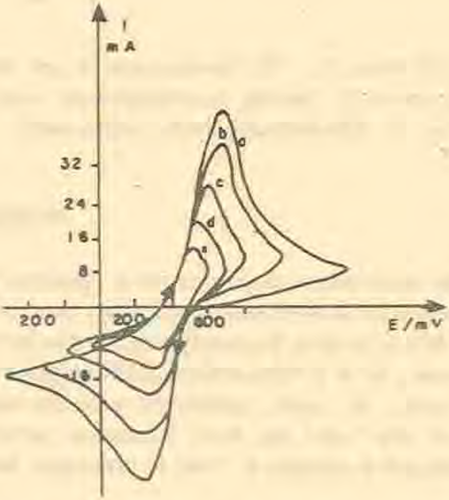

Figure 2. Variation of peak current with scan rates (1 N H_2SO_4). a) 6 mV/s; b) 4 mV/s; c) 2 mV/s; d) 1 mV/s; e) 0.5 mV/s.

Table 1. Variation of peak current and peak potential with scan rates (3 N H_2SO_4).

V (mV/s)	I_p (ox) (mA)	I_p (red) (mA)	E_p (ox) (mV)	E_p (red) (mV)	$(E_{ox} + E_{red})/2$ (mV)
0.5	16.0	-12.8	580	400	490
1	27.2	-26.4	540	400	420
2	38.4	-39.2	680	420	585
4	51.6	-51.6	740	420	590
6	60.0	-64.8	760	420	530

Table 2. Variation of peak current and peak potential with scan rates (5 N H_2SO_4).

V (mV/s)	I_p (ox) (mA)	I_p (red) (mA)	E_p (ox) (mV)	E_p (red) (mV)	$(E_{ox} + E_{red})/2$ (mV)
0.5	20.0	-12.0	480	400	440
1	45.6	-20.0	560	390	475
2	40.8	-32.8	600	390	495
4	53.6	-45.6	640	370	505
6	56.0	-60.0	700	360	530

Influence of temperature. Table 3 shows the influence of temperature upon the electrode capacity, determined by chronocoulometry (Figure 3) It appears that capacities increase considerably between 20 and 30° due to the faster diffusion of the proton. However between 35 and 50° the increase of diffusion is overcompensated by the increased solubility of p-benzoquinone. This fact explains the considerable decrease of the capacities at temperatures higher than 35°.

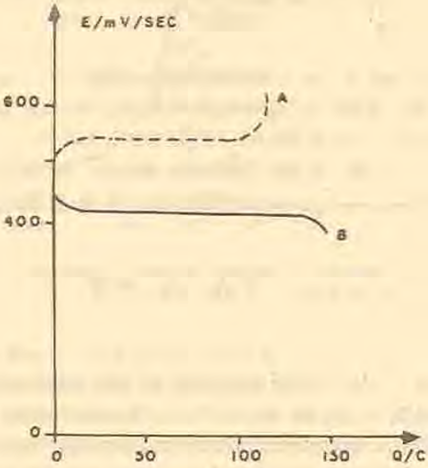

Figure 3. Variation of the capacities with the potentials (chronocoulometry) in 3 N H_2SO_4. A: Oxidation B: Reduction

Table 3. Variation of capacities with temperature.

Temperature (°C)	21	25	35	40	50
Capacity (C) reduction	86.4	115.2	108.4	104.8	86.5

Influence of the solution acidity. Figure 4 shows the dependence of the capacities on acid concentration. Our electrodes reach their best performances in a 1.5 M acid solution.

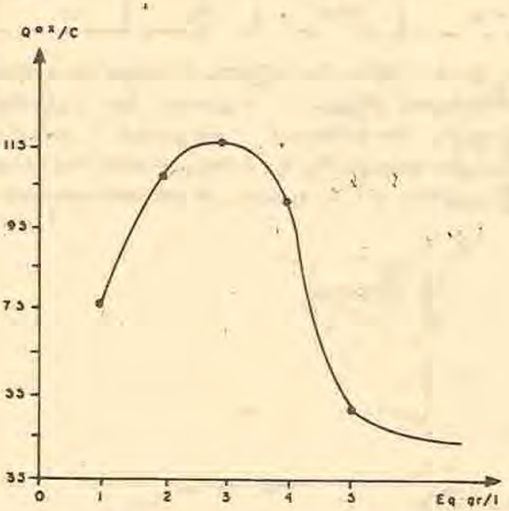

Figure 4. Variation of capacity (oxidation phase) with acid concentration.

Formal potential of the system. The formal potential of our electrode system was obtained by extrapolation of the curves $E^{red}_{i=0}$ = f(pH) and $E^{ox}_{i=0}$ = f(pH) (where $E^{red}_{i=0}$ and $E^{ox}_{i=0}$ are the equilibrium potentials in reduction and oxidation phases, respectively).

We have noted that our electrochemical system gives rise to a similar reaction like that proposed by Matricali [9] (Equation 1).

$$pB + 2H^+ + 2e^- \rightleftharpoons pBH_2 \qquad (1)$$

where pB and pBH_2 symbolize the oxidized and reduced forms of parabenzoquinone.

As pB and pBH_2 are in solid states, the potential of such an electrode is given by Nernst equation (Equation 2):

$$E_{i=0} = E_0 + RT/F \ln aH^+ \qquad (2)$$

where E_0 is the potential when H^+ activity is equal to unity.

Figure 5 gives the values of E_0:

$$E_0^{red} = 548.0 \text{ mV/SCE}; \; E_0^{ox} = 550.0 \text{ mV/SCE}.$$

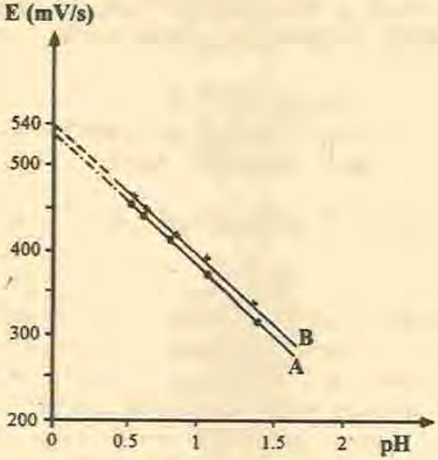

Figure 5. Determination of E_0^{red} and E_0^{ox} by extrapolation of the curves:
A. $E_{i=0}^{red} = f(pH)$, B. $E_{i=0}^{ox} = f(pH)$

These results allow us to place the equilibrium potential of the *p*-benzoquinone/hydroquinone couple at 549.0 mV/SCE; a potential comparable to that given Matricali *et al.* [9].

In conclusion the present work has allowed us to introduce partially scorched peat in a secondary generator electrode and to realize cathodic electrodes from *p*-benzoquinone, peat, acetylene black and a small amount of teflon as binder.

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