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INFLUENCE OF SUBSTITUTION ON THE ELECTROCHEMICAL PROPERTIES OF ANTHRAQUINONE IN THE SOLID STATE

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ABSTRACT. The electrochemical and energetic properties of a carbon paste electrode (CPE) containing lampblack, hydroxyanthraquinone and some teflon was studied and compared to that obtained with anthraquinone.

INTRODUCTION

Energy consumption and its impact on the natural environment is very well known. Presently, there is a great deal of effort spent on searches for renewable energy resources. Among such sources of energy are the secondary batteries which store energy in chemical form and which can be exploited by the conversion of chemical to electrical energy.

In most secondary batteries, metallic electrodes are used together with aqueous electrolytes. It is interesting to consider the possibilities offered by organic materials as source of active matter in order to improve the batteries' power. For this reason the theoretical and electrochemical properties of anthraquinone derivatives have previously been studied [1-5]. Most of them are well known to be reversible redox systems in aqueous electrolyte. They have been investigated for many years in search of anodic materials with favourable equilibrium potentials [6].

9,10-Anthraquinone is the most energy-rich anodic material known [1,2]. This compound, which is slightly soluble in acid media, can, without any transformation, constitute the anode in secondary batteries. Recently a great deal of attention has been given to the substitution effect on anthraquinone to improve its energetic possibilities. The idea is mainly based on increasing the molecular weight. This increase should cause a decrease in the equilibrium potential, due to the resonance effect or the electron releasing property of the substituent group. Matricali [2] and Kergreis *et al.* [7] have contributed particularly to the development of this concept.

EXPERIMENTAL

The pastille technique was used for the construction of the electrode [1,8,9]. The electrochemical cell employed was similar to that described by Yu *et al.* [10]. The best composition of our electrode was found to be 100 mg of hydroxyanthraquinone, 92 mg of lampblack and 8 mg of teflon.

The experiments were performed at room temperature using platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode. A potentiostat/galvanostat TACUSSEL P.J.T. 120-1 coupled to a TACUSSEL generator

G.S.T.P.4 and a SEFRAM chart recorder was used. All the experimental investigation were performed by chronocoulometry and cyclic voltammetry.

RESULTS AND DISCUSSION

Figures 1 and 2 show the dependence of the peak current and the peak potential on operating condition: scan rate, acidity of medium, nature of the electrode etc. They reveal that the values of $(E_p^{ox} + E_p^{red})/2$ are nearly constant; these are assumed to be equal to the equilibrium potential (Tables 1 and 2). On the other hand, in slightly concentrated solution (0.5 N H_2SO_4) the observed reduction peaks are flatter and the maximum currents are lower than in oxidation. This phenomenon can be explained by considering the mechanism of the quinone reduction. We present here a simplified reaction scheme similar to that proposed by Matricali [2].

$$hQ + 2H^+ + 2e^- \rightleftharpoons hQH_2$$

where hQ and hQH_2 are, respectively, the oxidized and reduced forms of hydroxy-anthraquinone and are in the solid state.

Table 1. Variation of peak potential with scan rates (2 N H_2SO_4).

V (mV/s)	E_p^{red} (mV)	E_p^{ox} (mV)	$(E_p^{ox} + E_p^{red})/2$ (mV)
0.5	-280	-20	-150
1	-360	+30	-160
2	-440	+120	-160

Table 2. Variation of peak potential with scan rates (4 N H_2SO_4).

V (mV/s)	E_p^{red} (mV)	E_p^{ox} (mV)	$(E_p^{ox} + E_p^{red})/2$ (mV)
0.5	-260	-20	-140
1	-280	+10	-145
2	-360	+60	-150

During reduction, when equilibrium is reached between the solution and the electrode (CPE), acidity of the environment imposes a proton concentration within the working electrode. At low proton concentration the proton supply in the solid phase cannot compensate for their consumption in the electrochemical reaction. This fact may also explain the appearance of a peak potential lower than in oxidation. Nevertheless, at high proton concentration (2 N) this restrictive process is only due to the contact between the different phases, and act in the same manner in oxidation and in reduction. The observed curves are symmetrical.

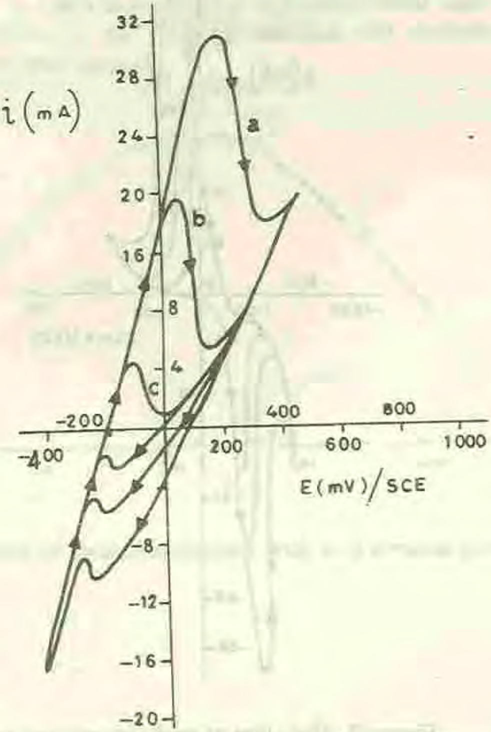

Figure 1. Variation of peak current and peak potential with scan rates (0.5 N H_2SO_4): (a) 2 mV/s, (b) 1 mV/s, (c) 0.5 mV/s.

Influence of the solution acidity. Figure 3 shows that the reduction capacity depends on the acid concentration. A maximum is revealed at about 3 eq/L, which corresponds to the best performance of our electrode. This value is lower than that obtained with anthraquinone (Table 3) and can be explained as a consequence of the substitution.

Table 3. Comparison of different values obtained with anthraquinone and hydroxyanthraquinone.

Compounds	E_0^{red} (mV)	E_0^{ox} (mV)	E_0 (mV)	Maximum capacity (cb/g)
Anthraquinone	-112	-108	-110	835.1
Hydroxyanthraquinone	-172.6	-171.4	-172	580

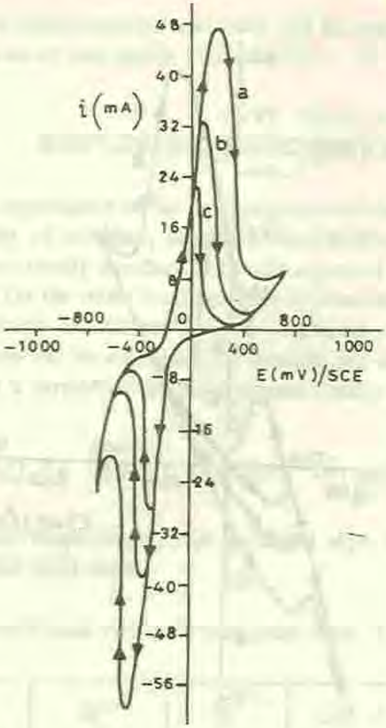

Figure 2. Variation of peak current and peak potential with scan rates (2 N H_2SO_4): (a) 2 mV/s, (b) 1 mV/s, (c) 0.5 mV/s.

Formal potential of the system. Several investigations [11-13] using quinones in carbon paste electrode have confirmed that the potential of such an electrode is given by the Nernst equation:

$$E_{i=0} = E_0 + RT/F \ . \ \ln a_{H^+}$$

E_0 is the potential when ln a_{H^+} is equal to zero, and was obtained by extrapolation of the curves $E_{i=0}^{red} = f(pH)$ and $E_{i=0}^{ox} = f(pH)$. The curves are shown in Figures 4 and 5 and the data are presented in Table 3.

CONCLUSION

In view of the result presented in Table 3, it appeared that hydroxyanthraquinone, also called quinizarin, has a lower potential owing to the resonance effect of the hydroxy group. The potential is 62 mV lower than that of anthraquinone, which is in agreement with the theoretical expectation. The experimental results obtained in this paper show that an increase of the molecular weight due to the substitution causes a decrease in the equilibrium potential.

Previous investigations [7] have shown that, to obtain a conservation of the capacity after substitution, it is necessary for the ratio of $\delta E/\delta M$ to be equal to 5.2. In this work we have obtained a ratio $\delta E/\delta M = 4$, which is comparable to the theoretical value. $\delta E = 62$ mV and $\delta M = 16$ mg are, respectively, the shifts in potential and molecular weight between anthraquinone and hydroxyanthraquinone.

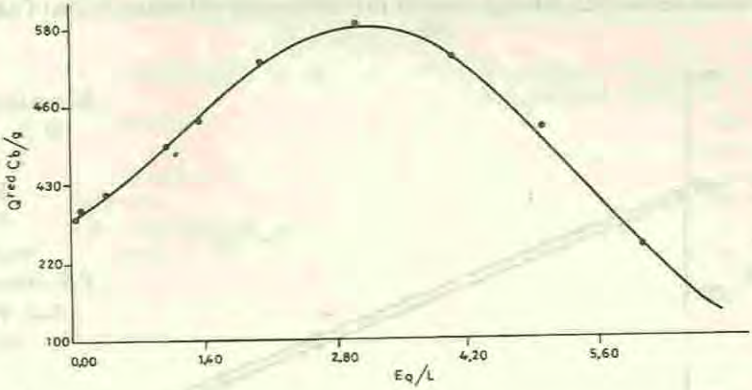

Figure 3. Variation of reduction capacity with acid concentration.

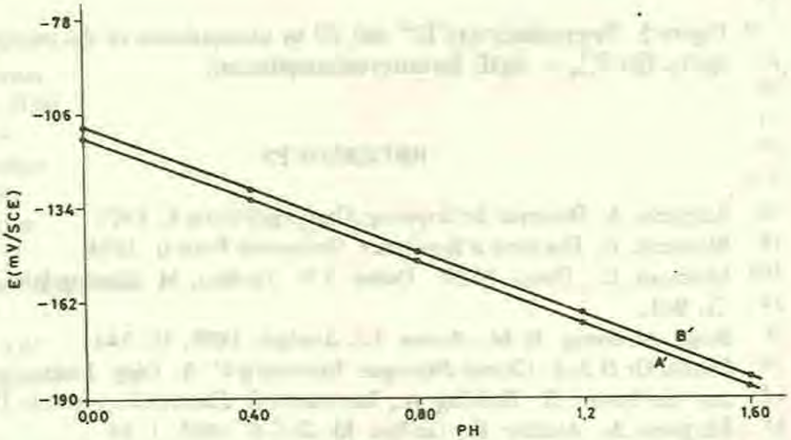

Figure 4. Determination of E_0^{red} and E_0^{ox} by extrapolation of the curves: (A') $E_{i=0}^{red}$ = f(pH); (B') $E_{i=0}^{ox}$ = f(pH) (anthraquinone).

On the other hand, as anthraquinone and related compounds are slightly soluble in aqueous electrolytes, there are few electrochemical data for the substitution effect on the electrochemical potential of anthraquinone. However, some measurements performed with hydroxyanthraquinone in organic solvents gave a decrease in potential of about 17 mV.

Investigations in progress give hope for improvement of the energetic properties of anthraquinone derivatives, through mastery in conditioning and construction of the electrodes.

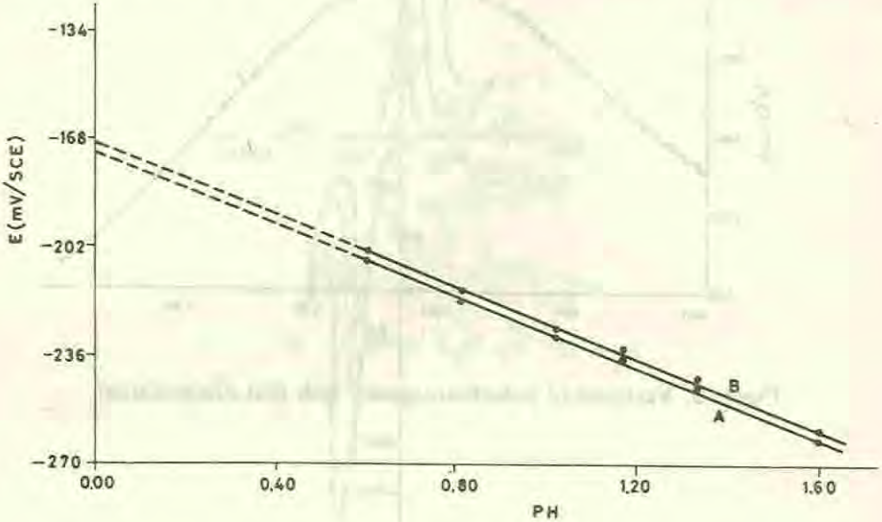

Figure 5. Determination of E_0^{red} and E_0^{ox} by extrapolation of the curves: (A) $E_{i=0}^{red}$ = f(pH); (B) $E_{i=0}^{ox}$ = f(pH) (hydroxyanthraquinone).

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