Electrophysiology

ENVIRONMENTAL ELECTROLYTIC INFLUENCE IN FARADIC CAPACITY ELECTRODES WITH P-NAPHTOQUINONE.
# KINETIC STUDY OF THE REDOX REACTION

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SUMMARY: Our aim in this presentation is to study the paranaphtoquinone electrode with the smoke black as electronic conductor. We have studied the influence of the acidity of the electrolytical environment on the Faradic capacity of paranaphtoquinone by chronocoulometry. In the other part, the coefficient of the electronic electrode transfer have been determined using the Tafel's laws.

Key Words: Paranaphtoquinone, faradic capacity, transfer coefficient.

INTRODUCTION

It appeared from recent studies that the reactions raised by quinone compounds, require three contacts: active matter (Q)-electronic conductor (e⁻)-proton (H⁺) (1):

$$Q + 2H^+ + 2e^{--} \rightarrow QH_2\downarrow$$
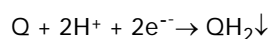
The purpose of this work is to determine the influence of electrolytical environment upon the faradic capacity of the carbon past electrode with paranaphtoquinone in intentiostatic regime and the coefficients of the electronic transfer by the same method.

MATERIALS AND METHODS

The working electrode has been prepared by mixing the active matter (paranaphtoquinone), electronic conductor (smoke black) and a small amount of Teflon as

Figure 1: Working electrode.

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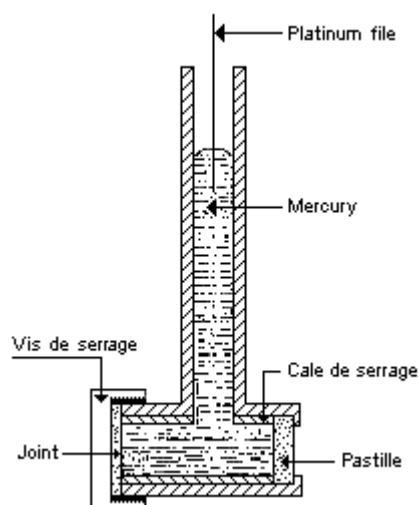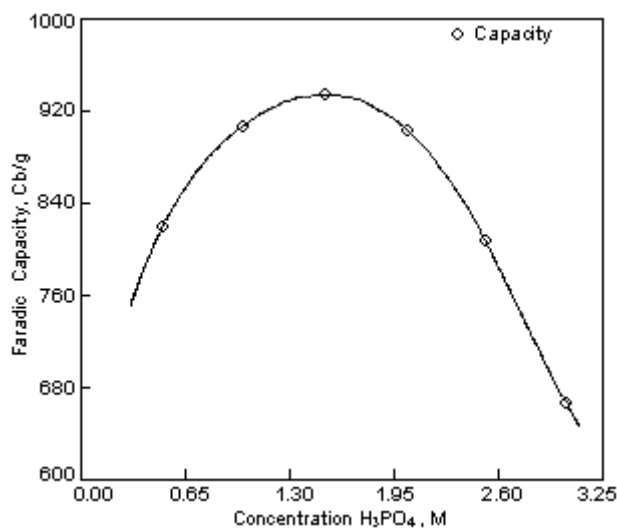** From Laboratoire de Microbiologie de Bel-Air, Orstom de Dakar, Senegal.

Figure 2: Faradic capacity in function acidity. Effect of H_3PO_4 concentration on the faradic capacity.

binder. The mixture was homogenized in a mortar, then compacted after being pressed into a Beckman mould during 10 minutes under the pressure of the 5 t/cm^2. So we obtained a pallet 13 mm of diameter and about 1 mm thick.

The electrode is composed of the T-tube in which the pellet is introduced (Figure 1).

The transport of the electrons is ensured by the mercury introduced into the tube and by a platinum wire connected to the exterior circuit (2-8).

The electrochemical cell of the measurement is composed of a glass vessel containing an electrolytic solution in which the working electrode is dipped and also the (reference electrode) and the platinum auxiliary electrodes.

The layout used for the chronocoulometric measurement is composed of a Tacussel potentiostat type PJT35-2. The curves were obtained on the L6512 Linseis scan table.

The measurements of faradic capacity were realized with the solutions of H_3PO_4 of concentration comprised between 0.5 and 3 M. The Tafel laws with the density of the imposed current which varies between 1 to 2.4 mA/cm^2 (the concentration of the H_3PO_4 being 1.5 M).

**Influence of acidity over the faradic capacity**

The phosphoric acid has been used because the paranaphtoquinone is soluble into the electrolytes so far used (H_2SO_4, HCl, HNO_3,...) as we have said earlier, the reaction required a protonic contribution. It is important to see the influence of the protonic concentration over the faradic capacity. Then we have followed the faradic capacity as a function of the concentration of the phosphoric acid.

One can realize that the faradic capacity increases with the concentration of the H_3PO_4 and passes by a maximum which is reached at a concentration of 1.5 M (Figure 2).

In order to explain this maximum of the capacity at 1.5 M, we have determined experimentally the activity coefficients of the phosphoric acid by measuring the pH of the H_3PO_4 solutions from 0.01 to 8 M and we have determined the acidity coefficients.

The study of the activity coefficients variation ($\pm$ H$^+$) in function H_3PO_4 concentration (Figure 3) shows a minimum which is reached at 1,5 M; *a maximum of faradic capacity corresponds to this minimum* (Figure 2). In the case the activity coefficient represents the correction to be made to the protons concentration, it seems logical that the mini-

Figure 3: Activity coefficient in function acidity concentration.
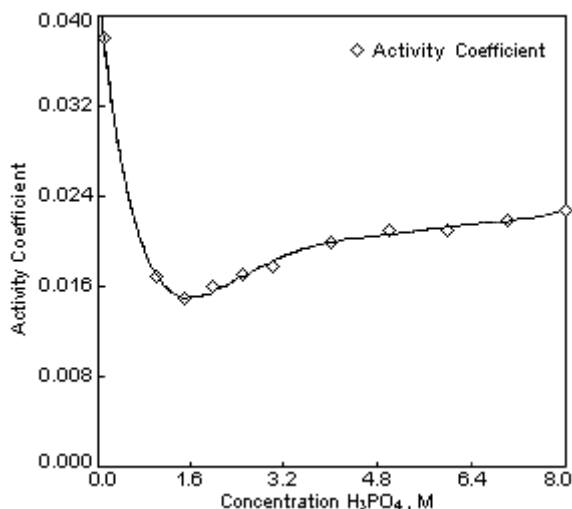
mum of the correction (minimum of interaction between these different ions) implies a maximum of degree of liberty to participating in a more quantitative way to the reaction. This more quantitative representativity involves a maximum of the faradic capacity.

Determination of the transfer coefficients

It has been determined that the redox reaction of the paranaphtoquinone implicated two electrons (5-8).

In order to check out this hypothesis, we have determined the transfer coefficients. These coefficients are obtained from the BUTTLER-VOLMER LAW (9 to 17).

i - Current density,

$$i = i_0 * \left[\exp\left(\frac{\alpha nF}{RT} \, \dot{}s \right) - \exp\left(\frac{\beta nF}{RT} \right) \dot{}s \right], \text{where}$$

i_0 - Exchange current density,

's - Over potential (difference between the potential taken by electrode crossed by the current i and that of the electrode with a nil intensity),

F - Faraday constant,

R - Constant of perfect gases,

α - Anodic transfer coefficient,

β - Cathodic transfer coefficient,

The density of pure transfer current (with diffusion) is in the case of the oxidation:

$$i^* = i_0 * \exp\left(\frac{\alpha nF}{RT} \, \dot{}s \right), \text{where}$$

$$\ln i = \ln i_0 + \frac{\alpha nF}{RT} \, \dot{}s$$

$$\frac{\alpha nF}{RT} \, \dot{}s = \ln i - \ln i_0$$

$$\dot{}s = \frac{-RT}{\alpha nF} \cdot \ln i_0 + \frac{RT}{\alpha nF} \cdot \ln i$$

$$\dot{}s = \frac{-RT}{\alpha nF} * \ln i_0 + \frac{RT}{\alpha nF} * \ln i^*, \text{with}$$

$$i^* = i^{ox} * \frac{i}{i^{ox} - i}, \text{where}$$

i_∞ - Current density limit of diffusion (is obtained from the chronocoulometry: It is the value of i from which we have no obtain plateau).

It is important to note that the obtained chronocoulometric curves present two plateau for paranaphtoquinone (Figure 4). We apply ourselves into determining the transfert coefficients corresponding to each plateau.

Figure 4: Chronocoulometry curves.
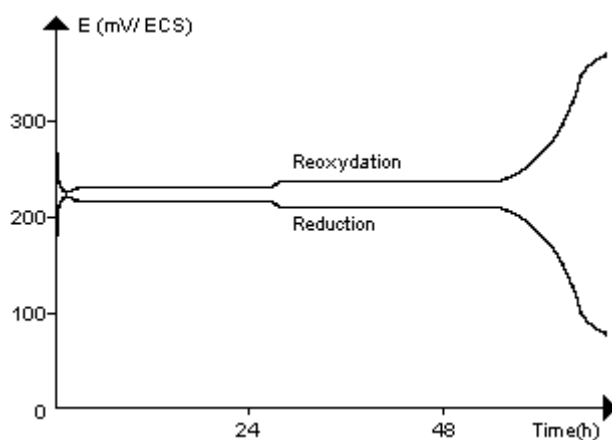
The method consists of measuring the values of the potential in different intensities and to determine the potentials in nil intensity.

This last measurement is obtained in open circuit curing a oxidation or reduction phase. We have noticed the potential at the different intensities (E, i) [then the points ('s, i) and calculated for each intensity i the pure transfert current density i (Table 1, Figure 5).

The linear regressions have allowed to obtained the slopes **a**, the y intercept **b**, the correlations coefficients **r** and the exchange current density **i0**.

First plateau

at oxidation : $a_1 = 45, 499$ mV; $b_1 = 4.188$ mV; r=0.992;

$i_0 = 0.912$ mA/cm^2

at reduction : $a_2 = 59.515$ mV; $b_2 = 4.925$ mV; r=0.998;

$i_0 = 0.912$ mA/cm^2

We have for this graduation :

$\alpha n + \beta n = (\alpha + \beta)n = 0.995 \# 1)$

The resultants are compatible with a mechanism reactional of an electron, with the transfert coefficients next to 0.5 ($\alpha = 0.564$ and $\beta = 0.431$).

Second plateau

at oxidation : $a_3 = 45.795$ mV; $b_3 = 1.679$ mV; r=0.989;

$i_1 = 0.964$ mA/cm^2

at reduction : $a_4 = 59.084$ mV; $b_4 = 6.302$ mV; r=0.998;

$i_1 = 0.899$ mA/cm^2

Table 1: Overtension in function of the intensity.

Oxydation				Reduction			
$s' = E - E_{io}$ mV	i, mA	i^*, mA	Lni^*	's$= E_{io} - E$ mV	$\lvert i \rvert$, mA	$\lvert i^* \rvert$, mA	$Ln.\lvert i^* \rvert$
14 (11) #	1,0	1,22	0,2	17 (18)	1,0	1,22	0,2
35 (34)	1,4	2,01	0,7	46 (48)	1,4	2,01	0,7
54 (51)	1,9	3,00	1,1	71 (71)	1,9	3,00	1,1
73 (71)	2,4	4,48	1,5	94 (95)	2,4	4,48	1,5

(#) Overtension for the second plateau.

Figure 5: Tafels line.
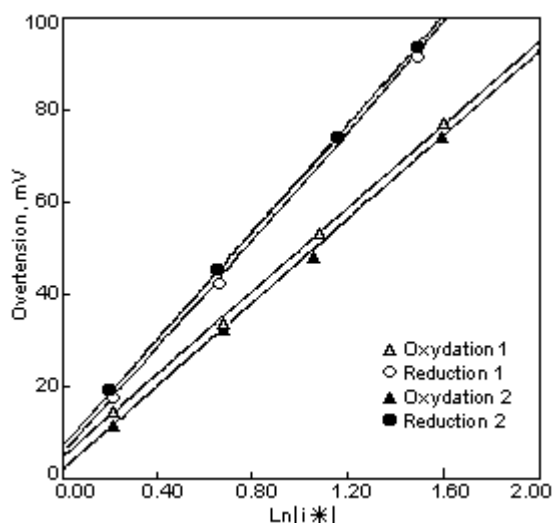
We'll obtain: $\alpha'n + \beta'n = (\alpha'+\beta')n = 0.996 \# 1$

These resultants are also compatible with a mechanism reactional of an electron, the transfer coefficients: $\alpha'=0.561$ and $\beta'=0.435$.

CONCLUSION

This study shows that for the electrode with paranaphtoquinone it is important to work in an electrolytical environment of phosphoric acid about 1.5 M in order to obtain maximum faradic capacity.

The resulting transfer coefficients values are quite equal 0.5 and their sum to unity. In each graduation, the number of exchanged electrons (n) equal to unity: the bi-electronic exchange, for the paranaphtoquinone electrodes, happens into two different stages.

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