REFERENCES

1) H.T. Ikeda and H. Tamura, Manganese dioxide Symposium, Vol.1, Cleveland,(1975) p.384

2) A.N. Dey, Extended Abstrats, Vol73-2, Oct. (1973) Abstract No.54, p.132

3) K.V. Prasad, P.N.N. Namboodiri and R. Gangadharan, Proc. Symp. Advances in Electrochemical Energy Storage and Conversion, CECRI, Karaikudi, India., Jan.(1983)

4) M. Beltowska, E. Dutkiewicz and J. Stuczynska, J. Electroanal. Chem., Vol.135,(1982) p.103

5) Dao-zhi Bi, Ji-qiang Wang, Dang-Jun, Proc. Power Sources for Biomedical implantable applications and ambient temperature lithium batteries eds B.B. Owen and N. Margalit, The Electrochemical Society, Inc., Princeton, (1980)p.283

6) K.I. Tikhonov, S.L. Tsapakh and K.A. Mikhailova, Soviet Electrochemistry, Vol.16 (1980) p.123

(Received, 22 October 1992
Revised form, 17 May 1993)

A Voltammetric Study of Silver Electrodeposition Coupled with Hydrogen Peroxide Oxidation and Reduction on Carbon Microelectrodes

J.P. SOUSA
Departamento de Engenharia Química
Faculdade de Engenharia da Universidade do Porto
Rua dos Bragas
4099 Porto Codex
PORTUGAL

ABSTRACT

Measurements are reported of the linear sweep voltammograms of silver on the presence of mixed catalytic oxidation/reduction of hydrogen peroxide on to vitreous carbon microdisk electrode. The catalytic rate constants were determined by performing theoretical simulations of the expected responses of the current-potential profiles and good agreement was found between these calculated profiles and the experimental responses in the cathodic branch for $k_2^o = 2.5 \cdot 10^{-6}\ mol\ cm^{-2} s^{-1}$. The occurrence of a nonelectrochemical pathway reaction associated to the catalytic behaviour of hydrogen peroxide at silver substrates was observed experimentally and the density flux rate constant of this reaction was found to be $3.2 \cdot 10^{-6}\ mol\ cm^{-2} s^{-1}$.

INTRODUCTION

The coupled reduction and oxidation of hydrogen peroxide has been repeatedly investigated following the initial work towards the end of the last century [1]. The interest in this reaction has stemmed both from the view that it should be one of the simplest examples of catalytic processes (a view hardly born out by the results obtained experimentally) and, latterly, because of the participation of hydrogen peroxide as an intermediate in the technologically important

Portugaliæ Electrochimica Acta, 11 (1993) 199-210

electrochemical reduction of oxygen such as in oxygen cathodes in batteries and fuel cells (see review [2]).

The initial interest in the reaction was in the catalytic oxygen evolution on metal catalyst surfaces in the absence of any imposed cathodic or anodic currents, i.e., under open circuit conditions, generally at platinum surfaces [1]. The decomposition of the hydrogen peroxide was assumed to be due to the irreversible formation and decomposition of surface oxides such as

$$Pt + H_2O_2 \longmapsto PtO + H_2O \tag{1}$$

$$PtO + H_2O_2 \longmapsto Pt + O_2 + H_2O \tag{2}$$

giving the overall reaction

$$2\,H_2O_2 \longmapsto 2\,H_2O + O_2 \tag{3}$$

A number of more recent studies of hydrogen peroxide decomposition at catalytically active metal surfaces under open circuit conditions have continued to be interpreted in terms of modified forms of this mechanism [3-5] such as in the intervention of adsorbed HO_2^- species in alkaline solutions at silver surfaces [4].

The alternative view that the overall reaction (3) at open circuit conditions is due to the balance of two separate cathodic and anodic reactions was originally put forward by Weiss [6]:

$$H_2O_2 + 2e \longmapsto 2\,OH^- \tag{4}$$

$$H_2O_2 \rightleftharpoons O_2 + 2H^+ + 2e \tag{5}$$

the overall reaction being again (3). It is important to note that reaction (4) is totally irreversible; reaction (5) is to some extent reversible so that hydrogen peroxide is formed as an intermediate in oxygen reduction process.

The deposition of silver catalytic centres on carbon substrates affords significant new opportunities for the study of the electrocatalytic oxidation/reduction of hydrogen peroxide. These

reactions are very slow at carbon substrates but are extremely fast at silver surfaces [6-7]. The *in situ* deposition of silver centres should therefore permit the investigation of the kinetics associated to the oxidation/reduction of hydrogen peroxide.

Considering the particular properties of microelectrodes [8-10], one can consider that the most plausible conditions for silver deposition coupled with catalytic reaction of H_2O_2 is a combination of diffusion controlled crystal growth and mixed diffusion control of the mixed catalytic reactions for the cathodic branch. As deposition and crystal growth starts at very negative potentials, one can assume that the deposition of silver is diffusion controlled with

$$C^{\sigma}_{Ag^+} = C^{\infty}_{Ag^+}\,[1 - \exp(\frac{F\eta}{RT})] \tag{6}$$

The current due to the silver deposition coupled with the mixed catalytic reaction is [11]:

$$I = \frac{2\pi F D_{H_2O_2} C^{\infty}_{H_2O_2} \left(\frac{2MD_{Ag^+}C^{\infty}_{Ag^+}}{\rho}\right)^{1/2} (t-t_0)^{1/2} \left\{ z_{c,H_2O_2} k_{c,H_2O_2} \exp\left(\frac{-\alpha_{c,H_2O_2} z_{c,H_2O_2} F(\nu t-\eta_{o.c.})}{RT}\right) - z_{a,H_2O_2} k_{a,H_2O_2} \exp\left(\frac{\beta_{a,H_2O_2} z_{a,H_2O_2} F(\nu t-\eta_{o.c.})}{RT}\right) \right\}}{\left\{ \frac{D_{H_2O_2} C^{\infty}_{H_2O_2}}{\left[\frac{2MD_{Ag^+}C^{\infty}_{Ag^+}}{\rho}\right]^{1/2} (t-t_0)^{1/2}} + k_{c,H_2O_2} \exp\left(\frac{-\alpha_{c,H_2O_2} z_{c,H_2O_2} F(\nu t-\eta_{o.c.})}{RT}\right) + k_{a,H_2O_2} \exp\left(\frac{\beta_{a,H_2O_2} z_{a,H_2O_2} F(\nu t-\eta_{o.c.})}{RT}\right) \right\}} \tag{7}$$

where t is the time (*s*), D_i is the diffusion coefficient of peroxy and silver species ($cm^2 s^{-1}$), C_i is the bulk concentrations ($mol\ cm^{-3}$), α_i and β_i is the transfer coefficients, k_i are the flux density rate constants ($mol\ cm^{-2} s^{-1}$) for the cathodic and anodic regions respectively, M is the silver molecular weight ($g\ mol^{-1}$), z_i is the charges, $\eta_{o.c.}$ is the open circuit overpotencial (mV) and v is the scan rate ($mV\ s^{-1}$).

Several research workers since Haber and Grinshberg [1] have studied the catalytic oxidation/reduction of hydrogen peroxide on silver surfaces and they have postulated that a nonelectrochemical decomposition pathway occurs according to the following reaction

$$Ag + 2H_2O_2 \xrightarrow{k_3} Ag + 2H_2O + O_2 \tag{8}$$

where k_3 is the flux density rate constant of the chemical reaction. Also several other research groups who have investigated this system [2, 12-13] have obtained quite good evidence about the occurrence of the above reaction. For the cases where reaction (8) occurs the equation for the linear sweep voltammetry presented above, equation (7), will now be affected by the term k_3 in the denominator.

For the case of reaction (8) coupled with silver deposition, considering that the growth of silver is diffusion controlled, the current-potential transient for the overall reaction within the cathodic region is given by the following equation:

$$I = \frac{4\pi z_2 k_2^0 F D_2 C_2^\infty \frac{M D_1 C_1^\infty t}{\rho} \left[\exp\left(\frac{-\alpha_2 z_2 F \eta_2}{RT}\right) - \exp\left(\frac{\beta_2 z_2 F \eta_2}{RT}\right)\right]}{D_2 C_2^\infty + k_3 \left(\frac{M D_1 C_1^\infty t}{\rho}\right)^{\frac{1}{2}} + k_2^0 \left(\frac{M D_1 C_1^\infty t}{\rho}\right)^{\frac{1}{2}} \left[\exp\left(\frac{-\alpha_2 z_2 F \eta_2}{RT}\right) + \exp\left(\frac{\beta_2 z_2 F \eta_2}{RT}\right)\right]} \qquad (9)$$

where the parameters have the same meaning and units as described for equation (7) and $\eta_2 = \nu t_2$. The important point of this current-potential transient is the new term $k_3 \left(\frac{2 M D_1 C_1^\infty t}{\rho}\right)^{1/2}$ which illustrates that there is a rapid transition from the initial kinetic control of the peroxide oxidation/reduction to diffusion controlled behaviour with increasing time.

In the present study, the theoretical models developed elsewhere [11] are applied to the experimental voltammograms in order to obtain the kinetic parameters that characterises the system herein investigated. The occurrence of the nonelectrochemical pathway reaction is also illustrated from the comparison between the theoretical and experimental plots.

EXPERIMENTAL

The experiments were carried out using a two-compartment cell shown in Fig.1. The anodic compartment was filled with a solution of composition 5.0 mM $AgNO_3$ + 0.1 M KNO_3 while the cathodic compartment contain a solution of composition 5.0 mM $AgNO_3$ + 0.1 M

KNO_3 + 45.0 mM H_2O_2. The concentration of the peroxy species was established after carrying out several experiments at different concentrations of H_2O_2 but beyond a certain value, passivation of the substrate takes place which inhibits both the silver deposition process and the catalytic reaction. This is the main reason why there was no H_2O_2 in the anodic compartment because a silver foil was used as the anode which could promote the autocatalytic decomposition. All solutions were prepared using reactants as purchased from J.T. Baker Co. and triply distilled water. These solutions were deareated for 20 minutes before starting the experimental measurements.

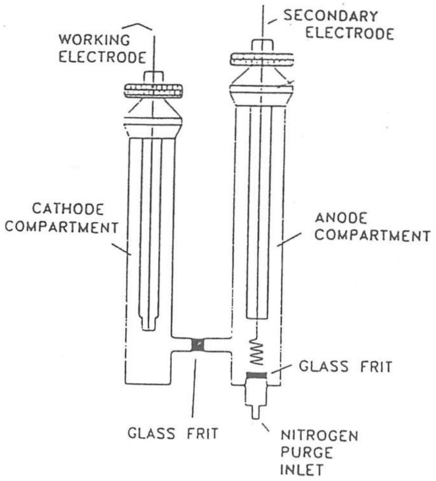

Figure 1 Side view of the two-compartment electrochemical cell used.

A two-electrode system was used throughout the experiments. The working electrode was a vitreous carbon microdisk electrode of 5.o µm diameter and as the secondary electrode was used a silver foil of large dimensions. Before each measurement the working electrode was mechanically polished with successively fine grade alumina powder (0.05 - 1.0 µm).

The equipment used herein was a waveform generator, Hi-Tek PPR1, to switch the potential between the chosen limits. A programmable electrometer, Keithley Model 617, was used to measure the currents and the current-potentials responses were recorded on a

Houston Instruments Model 200 X-Y recorder. The electrochemical system was maintained inside a Faraday cage, made of thick walled aluminium sheet, in order to avoid external interferences and low noise coaxial cables were used for the electrical connections.

All measurements were carried out at laboratory pressure and temperature.

RESULTS AND DISCUSSION

As a starting point for the interpretation of the experimental data obtained for the present system, a voltammogram is presented in Fig.2, which shows that the silver deposition occurs at cathodic overpotentials close to -200 mV. It was observed experimentally that the shapes of the linear sweep voltammograms are highly irreproducible which is due to the fact that each one represents the deposition/dissolution of a single crystallite. In addition, one would anticipate an irreproducibility due to the catalytic reactions since those will be sensitive to the surface conditions and therefore each voltammogram has to be interpreted separately, i.e., there is no general "working voltammetric response".

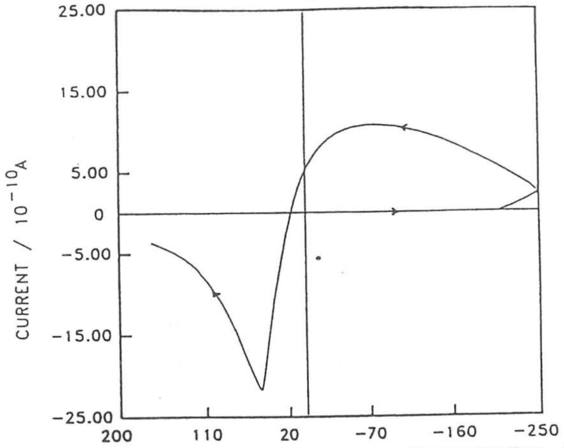

Figure 2 Linear sweep voltammogram for the deposition of silver onto vitreous carbon microdisk electrode from 5.0 mM $AgNO_3$ + 45.0 mM H_2O_2 in aqueous KNO_3; v = 100 mV/s.

The experimental measurements shows that the simplest conditions for the voltammograms will be found for silver deposition at very negative overpotentials. The deposition of the first centre will then lead to immediate crystal growth and this crystal growth process will rapidly become close to diffusion control. Moreover the diffusion controlled growth will reduce the concentration over the whole of the microelectrode surface (time scale 1.0 - 5.0 . 10^{-3} *s*) due to the spread of the diffusion layer so that crystal growth remains restricted to a single crystallite. This pattern of behaviour has been already observed for the case of silver deposition/dissolution alone [11, 14].

An example of a linear sweep voltammogram following such a course is the one presented in Fig.2 and the shape of this voltammogram is compared in Fig.3 with that predicted for diffusion controlled growth/dissolution of silver and oxidation/reduction of hydrogen peroxide (equation (9)) in the presence of a nonelectrochemical pathway reaction for the hydrogen peroxide.

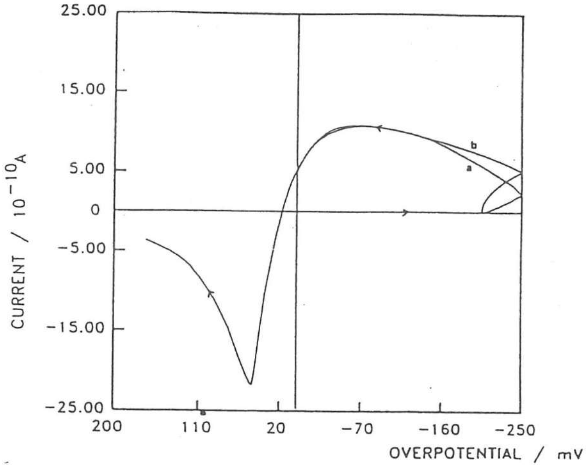

Figure 3 Plot of linear sweep voltammograms. a) Experimental (Fig.2) *versus* simulated (b) using $z_2 = 2.0$, $\alpha_2 = \beta_2 = 0.5$ and $k_2^o = 2.5 . 10^{-6}$ and $k_3 = 3.2 . 10^{-6}$ *mol* $cm^{-2}s^{-1}$ $\nu = 150$ mV/s, $\rho = 10.50$ g/cm^3, $D_1 = 0.75 . 10^{-5}$ cm^2 s^{-1}, M = 107.86 g/mol, $C_1 = 5.0$ mM, D2 = 1.0 . 10^{-5} cm^2 s^{-1} and $C_2 = 45.0$ mM (equation (9)).

It can be seen that there is, indeed, good agreement between the experimental and calculated responses in the cathodic region; however one needs to assume a rather high value of the rate constant for the oxidation/reduction process ($k_2{}^o = 2.5 \cdot 10^{-6}$ and $k_3 = 3.2 \cdot 10^{-6}$ $mol\ cm^{-2}s^{-1}$) and, moreover, that $\alpha_2 z_2$ and $\beta_2 z_2$ are large (namely $\alpha_2 = \beta_2 = 0.5$ and $z_2 = 2.0$).

It is of interest to point out that none of the models [11] can account for the observed shapes of the voltammograms at high overpotentials. The deviations must be due to kinetic complications in the catalytic reactions which have not been accounted for in the theoretical models or else to progressive modifications of the catalytic activity of silver centres.

In Figs. 4 and 5, a range of values for $k_2{}^o$ and k_3 have been investigated in attempts to deriving a more complete description of the observed experimental responses. However, while it is possible to obtain reasonable close form descriptions of the cathodic branch, the experimental response in the anodic region is far from any of the possible simulated shapes [11]. This kind of behaviour is not surprising as similar effects have been observed for the linear sweep voltammetry of silver alone [15]. In the case of voltammetry of systems containing hydrogen peroxide, it is entirely reasonable that the formation of sparingly soluble peroxy species should influence the shapes of the voltammograms in the anodic branch.

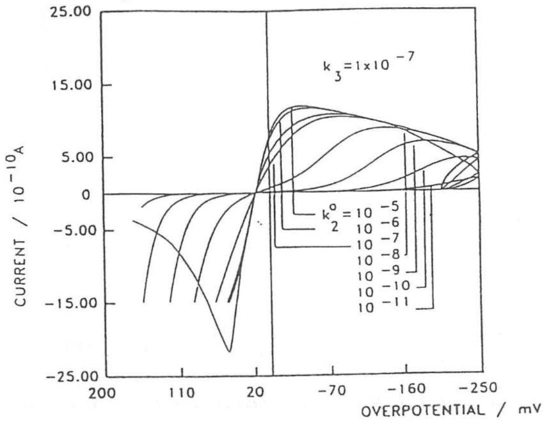

Figure 4 Plot of linear sweep voltammograms. Experimental (Fig.2) *versus* simulated (equation (9)) using a fixed value for k_3 and assuming different values for $k_2{}^o$.

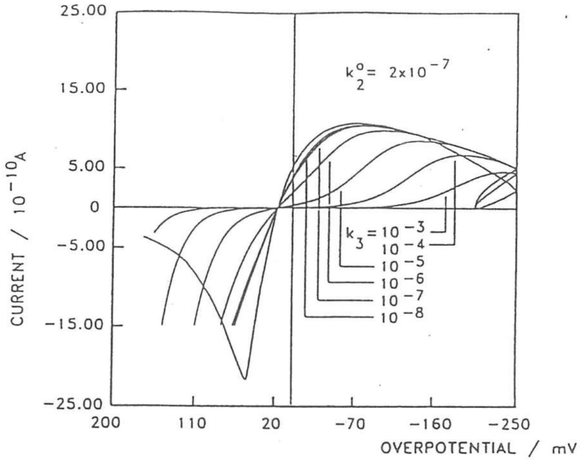

Figure 5 Plot of linear sweep voltammograms. Experimental (Fig.2) *versus* simulated (equation (9)) using a fixed value for $k_2{}^o$ and assuming different values for k_3.

From the data attained experimentally, one can observe that if the metallic deposition occurs at a lower cathodic potential than that leading to catalyst growth, then the formation of the critical nucleus will be delayed until a more cathodic potential is reached at which the nucleus will grow spontaneously. Under these circumstances, one will then observe the reduction of hydrogen peroxide on the first atom of the catalyst centre and that reduction will be diffusion controlled.

CONCLUSION

It has been shown that the theoretical model of diffusion controlled deposition/dissolution of silver coupled with mixed catalytic oxidation/reduction of hydrogen peroxide describes quite accurately the experimental responses within the cathodic region. Furthermore, it was possible to observe that for the system investigated herein, the occurrence of a nonelectrochemical pathway reaction markedly influence the expected behaviour of the voltammograms, i.e., reaction (11) indeed takes place.

In some experimental measurements, it has been possible to observe the electrocatalytic reaction on a single centre of the new metallic phase. These measurements have so far been restricted to a rather limited range of conditions mainly because of the restrictions imposed by the mathematical analysis. However, the extension of the analysis should lead to studies of kinetics on catalyst centres of almost molecular dimensions.

REFERENCES

1. F. Haber and S. Grinshberg, *Z. anorg. Chem.*, **18** (1898) 37.
2. M.R. Tarasevich, A. Sadkowski and E. Yeager, in *Comprehensive Treatise of Electrochemistry*, (Eds.) B.E. Conway, J.O'M. Bockris, E. Yeager, S.U.M. Khan and R.E. White, Plenum Press, New York, Volume 7, Chapter 6, 1983.
3. K. Gossner, H. Heidrich and D. Kosner, *Z. fur Physik. Chem. N. F.*, **67** (1969) 220.
4. K. Gossner and H. Bischof, *Z. fur Physik. Chem. N. F.*, **78** (1972) 277.
5. G. Bianchi, F. Mozza and T. Mussini, *Electrochim. Acta*, **7** (1962) 457.
6. W. Berl, *Trans. Electrochem. Soc.*, **83** (1943) 253.
7. E. Yeager, P. Krause and K.V. Rao, *Electrochim. Acta*, **9** (1964) 1057.
8. *Microelectrodes: Theory and Applications*, (Eds.) M.I.Montenegro, M.A. Queirós and J.L. Daschbach, NATO/ASI, Kluwer Academic Publishers, Netherlands, 1991.
9. S. Pons and M. Fleischmann, *Anal. Chem.*, **59** (1987) 1391A.
10. R.M. Wightman, *Anal. Chem.*, **53, 9** (1981) 1125A.
11. J.P. Sousa, Ph.D. Thesis, University of Utah, 1991.
12. V.S. Bagotsky, M.R. Tarasevich and V. Yu Filinovsky, *Elektrokhimiya*, **8** (1972) 84.
13. N.D. Wroblowa, Yen-chi Pan and G. Razumney, *J. Electroanal. Chem.*, **69** (1976) 195.

14. J.P. Sousa, S. Pons and M. Fleischmann, submitted to J. Electroanal. Chem, 1993.
15. J.P. Sousa, *VI Enc. Nac. da S.P.E.*, Vila Real, Outubro, 1992.

(Received, 25 March 1993
Revised form 29 Juni 1993)