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An Electrochemical Study of Silver Electrodeposition Coupled with Hydrogen Peroxide on Carbon Microelectrodes

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Abstract

Distributions of the induction times of silver potentiostatic electrodeposition coupled with hydrogen peroxide oxidation/reduction onto carbon microelectrodes have been obtained. The nucleation process has been shown to be affected by kinetic complexities due to the disproportionation of hydrogen peroxide and therefore neither the pure birth model nor the birth and death electronucleation model have shown to be applicable to this system. The double potential step and linear sweep voltammetry measurements point to the formation of silver peroxy species during the electrodeposition process.

Introduction

The early stages of the electrochemical deposition of silver centres i. e., the nucleation process on metallic surfaces has been repeatedly investigated either using carbon macroelectrodes and microelectrodes [1-6]. It has been observed that the centres are

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randomly distributed at the electrode surface and that the random birth of nuclei within a given time interval is assumed to follow a simple Poisson distribution law [7]. This statistical treatment of the number of nuclei yields useful information concerning the kinetics of the nucleation process.

As a consequence of the properties that characterise a microelectrode it is possible to observe experimentally the formation of a single silver centre or, at most, few centres [8]. Theoretically the process of forming a single nucleus can be described by the Chapman-Kolmogorov relations. The mathematical treatment as well as the algebraic solutions of those relations were obtained making several assumptions which have been reported elsewhere [4]. The mathematical distributions arrived at have been shown to apply to the nucleation of α -PbO₂, Pb and Ag systems applying high overpotentials on highly inert substrates such as carbon microelectrodes [4,8-12].

For simple systems such as those mentioned above, the applicability of such a simple model to describe the nucleation process can be accurate. Nevertheless for more complex systems it seems that the birth and death model developed by Fleichmann *et al.* [9-10] will not be suitable to interpret the results achieved experimentally.

The diffusion of H_2O_2 to the silver growth centres will influence the induction times. The overpotentials required to initiate the silver nucleation are so high that the most likely conditions are diffusion controlled crystal growth coupled to diffusion controlled mixed catalytic reactions [4]. In practice, the current-time transients will be dominated by the contributions of the catalytic reactions. Several research workers since Haber [13] have studied the catalytic oxidation/reduction of hydrogen peroxide on silver surfaces as well as its influence on the silver growth process. The use of ringdisk electrodes in which the oxygen and hydrogen peroxide intermediates generated at the disk are monitored on a ring electrode surrounding the disk has been especially important in these studies. A surprising conclusion of these studies has been that the disproportionation step is very fast, in fact close to diffusion control. However, the formation of silver peroxy species in solution has been detected in the catalytic decomposition of hydrogen peroxide by silver [14] and much of the work on silver electrodes is open to doubt because of the neglect of those species. The importance of the reduction of silver in the overall kinetics is hard to assess.

A further factor that is evidently important in the nucleation studies of silver is that the kinetics of the hydrogen peroxide oxidation and reduction depend markedly on the electrode prehistory. The effects of abrasion alone or abrasion followed by cathodic polarisation have frequently been noted but there has been little systematic work on this particular aspect.

The deposition of silver on carbon microelectrode substrates affords significant new opportunities for the study of the electrocatalytic oxidation/reduction of hydrogen peroxide. These reactions are very slow at carbon substrates [15-16] (so much so that high concentrations of hydrogen peroxide can be built up in solution via the reduction of the oxygen) whereas the reactions are extremely fast at silver sites so that it is not easy to explore the kinetics using normal electrochemical methods. The *in situ* deposition of single small

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catalyst centres should therefore permit the investigation of these kinetics at much higher rates of mass-transfer. It should also allow the exploration of the effects of the size of the catalyst particles and, in the limit, of the investigation of the reactions at subcritical nuclei of silver.

In this work we have obtained the experimental current-time transients distributions of silver nuclei in the presence of mixed catalytic reactions of hydrogen peroxide. Comparison of these distributions with those theoretically predicted for the deposition of silver alone are discussed, being the aim to show that the pure birth model is not applicable to complex systems.

Experimental

Experimental data were obtained using a two-compartment cell shown elsewhere [17]. The anodic compartment was filled with a solution of composition 5.0 mM AgNO₃ + 0.1 M KNO₃ where no H_2O_2 was present to avoid its disproportionation at the secondary electrode surface. The cathodic compartment was filled with a solution of composition 5.0 mM AgNO₃ + 0.1 M KNO₃ + 45.0 mM H_2O_2 (pH=4.8). All solutions were prepared in triply distilled water.

A carbon fibre microelectrode of 5 μ m diameter was used as the working substrate whereas the secondary electrode was a silver wire (99.99% purity) with an immersed area in the cm² range. The potentiostatic and voltammetric measurements were made using a waveform generator, Hi-Tek PPR1, to apply the chosen overpotential and potential sweeps to the working electrode. All currents were measured using a Keithley Model 617 programmable electrometer and either the current-time and current-potential transients were recorded on a Houston Instruments Model 200 X-Y.

Solutions were deaerated by bubbling dry nitrogen though both compartments during 20 minutes before each experiment. All experiments were carried out at laboratory temperature and pressure.

Results and Discussion

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Figure 1 shows a family of current-time transients obtained under constant potential conditions, using an overpotential of -190 mV. It can be seen that accurate values of the time needed to form the first nucleus can be readily obtained and is given by the time required to observe the rising current section. The figure illustrates clearly that the formation of the first nucleus at the carbon substrate is a random process either in time and shape.



Figure 1 Current-time transients for the growth of Ag on a 5 μ m diameter carbon fibre microelectrode from a solution of composition 5.0 mM AgNO₃ + 0.1 M KNO₃ + 45.0 mM H₂O₂ at $\eta = -190$ mV.

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Several overpotentials were investigated (-210, -200, -190, -180 and -170 mV) and at least 200 transients were measured for each overpotential in order to obtain a fair distribution of the induction times. However, for the lower overpotentials, -180 and -170 mV respectively, it was required to carry out more measurements (approximately 400) in order to observe the Poisson distribution of the induction times. This is in itself evidence that the H_2O_2 disproportionation influences the kinetics of the silver deposition.

The data obtained for the probabilities and induction times at each overpotential are listed in Table 1 where the probability values, $\Sigma^{\infty}_{K+1} P_j(t)$, were given directly from the ratio N_t/N_{total} . Here N_t represents the number of events observed within a certain time interval and N_{total} is the total number of events measured at each overpotential.

As a starting point for the interpretation of the experimental data obtained for the present system, the nucleation model proposed by Fleischmann *et al.* [9-10] was investigated. Accordingly to the authors model, the probability of forming a cluster of size greater than K, the size of the critical cluster being K, in a time interval 0 to t is then given by

$$\sum_{K+1}^{\infty} P_j(t) = 1 - \sum_{0}^{K} \frac{(\lambda t)^j}{j!} \exp(-\lambda t)$$
(1)

where λ is the birth rate. Defining a dimensionless variable T= λ t, equation (1) reduces to a more simplified form

$$\sum_{k+1}^{\infty} P_j(T) = 1 - \sum_{0}^{K} \frac{(T)}{j!}^{j} \exp(-T)$$
(2)

The theoretical plot of equation (2) for K=1 to 10 are represented by the solid lines illustrated in Fig.2.

Table 1 Experimental induction times and probabilities.

-210mV		-200mV		-190mV		-180mV		-170mV	
ln t	Ln P(t)								
1.609	-1.708	1.609	-2.396	1.609	-3.411	1.609	-6.907	2.995	-3.912
2.302	-0.310	2.302	-1.044	2.302	-1.877	2.302	-3.506	3.401	-2.103
2.708	-0.121	2.708	-0.482	2.708	-1.044	2.708	-2.813	3.688	-1.016
2.995	-0.069	2.995	-0.260	2.995	-0.536	2.995	-1.660	3.916	-0.569
3.218	-0 034	3.218	-0.132	3.218	-0.299	3.401	-0.787	4.094	-0.350
3.401	-0.014	3.401	-0.112	3.401	-0.185	3.688	-0.307	4.248	-0.128
3.555	0.000	3.555	-0.071	3.688	-0.065	3.912	-0.216	4.382	-0.097
		3.688	-0.047	3.912	-0.025	4.094	-0.099	4.499	-0.057
		3.800	-0.037	4.094	-0.020	4.248	-0.030	4.605	0.000
		3.912	-0.010	4.248	0.000	4.382	0.000		
		4.007	0.000						



Figure 2 Fit of experimental data obtained at $\eta = -210, -200, -190, -180$ and -170 mV to $\Sigma^{\infty}_{K+1} P_j(T)$ plots (solid lines) calculated for the pure birth model (equation (2)).

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As shown in Fig.2 the experimental data fit the model within the range of small induction times and very negative overpotentials. However, for higher induction times and less negative overpotentials the experimental data deviate markedly from their model. A "force fit" of the experimental data to the model allows to determine the rates of birth and critical cluster sizes which are listed in Table 2. It can be seen that the rates of birth and cluster sizes of silver in the presence of hydrogen peroxide are markedly reduced as is their potential dependence when compared to the values observed for the silver nucleation alone [4,8,11] under identical experimental conditions.

Table 2 Experimental values of λ and K for Ag nucleation in the presence of hydrogen peroxide using the pure birth model.

	OVERPOTENTIAL / mV								
	-210	-200	-190	-180	-170				
Rate of birth / s ⁻¹	0.255	0.200	0.187	0.173	0.164				
Critical cluster size K	1	2.	3	5	7				

This reduction in the rates of nucleation (or birth) suggests that the nucleation process is now affected by low rates of death, i. e., the deposition of silver in the presence of H_2O_2 is a birth and death process. Therefore, the experimental data presented in Table 1 needs to be fitted to the theoretical plots calculated for the birth and death model. As illustrated elsewhere [4,11] the influence of low rates of death in a general birth and death process is represented by

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Closed form solutions of equation (3), can only be derived provided K \leq 3. However, assuming that for a certain cluster size the rate birth (λ) is constant as well as the death rate (μ) and applying Laplace transforms to equation (3) a general expression has been achieved and is given by

$$\sum_{K+1}^{\infty} P_j(t) = 1 - \sum_{j=0}^{\infty} \frac{(\lambda t)^j}{j!} \exp(-\lambda t) + \frac{K(\lambda^{(K+1)}\mu t^{(K+2)})}{(K+2)!} \exp(-\lambda t)$$
(4)

Defining a new variable which gives the ratio between death and birth rates $(\beta = \mu/\lambda)$ it is possible to construct several theoretical plots for this model. In Fig.3 the solid lines illustrated this plots for K=1 to 10 and β =0.1.

The experimental data were fitted to the theoretical plots predicted by equation (4) which is illustrated in Fig.3. The comparison shows that the experimental data cannot be fitted to the calculated plots for the proposed model. Several other values of β were used namely from 0.1 to 1.0 and in none of the cases the experimental data give a close fit to the theoretical plots.

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Figure 3 Fit of experimental data obtained at $\eta = -210, -200, -190, -180$ and -170 mV to $\Sigma^{\infty}_{K+1} P_j(T)$ plots (solid lines) calculated for the birth and death model (equation (4)).

In a more general way we can see that in the presence of hydrogen peroxide a chemical reaction step between the peroxide and the silver cluster must lead to the removal of atoms from this cluster or else to a deactivation of the cluster for further reaction steps so that the formation of the critical nuclei must take place from species which involve hydrogen peroxide. This interpretation is consistent with what has been reported in the literature for the interaction of hydrogen peroxide with macroscopic silver surfaces [18-20]. It has been noted that the contact time between substrate surface and solution markedly influences the catalytic reaction which has been attributed to a progressive deactivation of the surfaces.

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For this particular system, it has been also observed that for the rising parts of the current-time transients I is not proportional to $t^{1/2}$ nor to $t^{3/2}$. Even though one observes a "quasi-linear" behaviour in $t^{1/2}$, the slope of the plots increases rather than decrease with decreasing overpotentials as observed for the growth of silver alone [5].

In search for more evidence about the kinetics of this system, double potential step measurements were performed. The double potential step current-time transient illustrated in Fig.4 show clear evidence of the occurrence of some sort of passivation phenomena at the substrate surface due to the participation and/or incorporation of some sort of peroxy species on the growing metallic centre. After the application of the second potential step some oscillations are observed which can be due to the formation and removal of such peroxy species or else to the evaluation of O_2 bubbles. However, if both redox systems took place under diffusion control, the pattern behaviour observed should be a continuous increase of the current-time transient. Hurlen et al. [21] have stated that the mixed potential of the silver in the presence of hydrogen peroxide is very close to the oxygen reduction potential and that the decomposition of H2O2 at silver centres occurs under diffusion-limited rate at low peroxide concentrations but above a low limit of peroxide concentration there was formation of silver peroxy species which affects the kinetics of silver electronucleation.

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Figure 4 Current-time transient for the growth of Ag using double potential step at $\eta_1 = -200 \text{ mV}$ and $\eta_2 = -100 \text{ mV}$ on a 5 μ m diameter carbon microelectrode and a solution composition 5.0 mM AgNO₃ + 0.1 M KNO₃ + 45.0 mM H₂O₂

It has been pointed out that it is possible to obtain closed form analytical descriptions of the linear sweep voltammetric experiments for a number of simple limiting conditions such as of pure diffusion controlled growth/dissolution of the catalyst centre or of pure kinetic control of such growth and dissolution; there are no restrictions on the degree of complexity with which one can describe the catalytic reactions [22-23]. However the shapes of the linear sweep voltammograms for this system are highly irreproducible. This is to be expected due to the catalytic reactions and disproportionation of the hydrogen peroxide which will be very sensitive to the substrate surface conditions. From the data on nucleation studies and of the growth of crystallites at constant potential, it is evident that the simplest conditions for the voltammograms will be found for nucleation at very negative overpotentials. The deposition of the first centre will then lead to immediate decomposition of the H_2O_2 which spreads the diffusion wave so that crystal growth remains restricted to a single crystallite for a certain period of time (time scale 1-5.10⁻³ s) after which a new crystallite is formed. This kind of behaviour will lead to the experimental observation of successive "kicks" within the forward sweep until the cathodic potential is reached.

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An example of a linear sweep voltammogram following such a course is the one given in Fig.5 and the shape of this voltammogram interpreted in terms of diffusion controlled growth/dissolution of silver and oxidation/reduction of hydrogen peroxide. In the case of voltammetry measurements of systems containing hydrogen peroxide, it is entirely reasonable that the formation of sparingly soluble peroxy species should influence the shapes of the voltammograms either in the cathodic and anodic branch.



Figure 5 Linear sweep voltammogram for the deposition of Ag from a solution 5.0 mM AgNO₃ + 0.1 M KNO₃ + 45.0 mM H₂O₂ onto a carbon 5 μ m diameter microelectrode. E_c = -250 mV; E_a = +250 mV and V = 150 mV/s.

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Furthermore, a comparison of the voltammograms for the silver alone and silver in the presence of hydrogen peroxide, shows that the cross over region differs in the second case for each voltammogram. This is due to fact that for a mixed catalytic reaction the zero current condition is quite variable and that the mixture potential is farther from the reversible Ag/Ag^+ potential. The experimental evidence shows that the present system is an irreversible one.

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The shape of the voltammogram in the anodic branch points to kinetic complications in the catalytic reactions which so far have not been considered in the mathematical models proposed. The observed oscillations must be due to progressive modifications of the catalytic activity of the silver centres followed by the formation of peroxy species at the substrate surface.

Conclusion

The analysis of the statistical distribution of the induction times associated with the formation of the first nucleus at constant overpotentials yields valuable information concerning the kinetics of nucleation. It has not proved possible so far to find a self consistent explanation of the arrival time distributions for this system and, moreover, to make this explanations consistent with those predicted by the pure birth model or to the birth and death model. It is evident that it is necessary to adjust the nucleation models to more complex systems. In effect, this requires a reinvestigation of several other system which was not feasible at the present time.

Attempts to interpret the experimental evidence however point to kinetic complexities in the silver electrocrystallization process coupled with the disproportionation of the hydrogen peroxide. Further research in this area, it is hoped, will explain the progressive decrease in the rates of electrocrystallization as well as complexities observed during the dissolution process.

We also reach a further general conclusion: the use of microelectrodes allows the study of the statistics of formation of single clusters using simple, straight forward, instrumentation. In some experimental measurements, it has been possible to observe the electrocatalytic reaction in a single silver centre. These measurements have so far been restricted to a rather narrow range of conditions mainly because of the restrictions posed by the mathematical analysis.

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IONIC ASSOCIATION:

ION PAIRS

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Abstract

The concept of *ion pair* and the way it has been presented in the literature is critically discussed.

Key words: ion pairs, complexes, electrolytes

The concept of ion pair

The presence of ion pairs is frequently invoked not only by those primarily interested in the behaviour of electrolyte solutions, but also by those concerned with the rates and mechanisms of both inorganic and organic reactions. However, it has been referred in the literature in different ways not equally clear.

This concept was introduced by Bjerrum in 1926 [1] to account for the behavior of ionophores in solvents of low dielectric constant and in his 1930 book Newman [2] says:

"(...) Bjerrum has come to the conclusion that certain electrolytes, among them potassium nitrate and the iodates of potassium and sodium, cannot be completely dissociated. His argument is that a certain proportion of the ions will form pairs which will act osmotically as single molecules if one, or both, of the ions has a radius smaller than a critical value. Under these conditions the ions will approach so near to each other that the attraction of a positive ion for a negative ion will be, for short periods, greater than the combined attractions of all the surrounding positive ions on the negative ion. (\ldots) ".

An identical idea is presented by Robinson and Stokes [3]: