Kinetics of electrocrystallisation of PbO_2 on glassy carbon electrodes: influence of ultrasound

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Electrocrystallisation of lead dioxide on glassy carbon electrodes was studied in 1 M HNO_3 + 0.1 M $Pb(NO_3)_2$ in the presence of ultrasound using chronoamperometry and scanning electron microscopy. In order to compare these results with those obtained in the absence of ultrasound, numerical approximations of the current transients have been carried out. The results obtained can be explained assuming formation of a soluble intermediate.

Introduction

In the recent years, sonoelectroelectrochemistry has become an active research field.[1] Recent[2,3] and older reviews[4,5] have pointed out the benefits of an ultrasonic field on the electrode processes. The effects of ultrasound have been observed on mass transport to the electrode,[6–8] activation of the electrode surface,[9] on adsorption processes,[10] on the reaction path by generation of radicals,[11] *etc.* In this context, we can expect that the application of ultrasound will be useful in the development of new and/or improvement of actual methods.

Electrocrystallisation of lead dioxide was first investigated by Fleischmann and co-workers[12–15] who suggested the existence of insoluble intermediates adsorbed on the electrode. Further works have focused their attention on the nature of the intermediates,[16–19] and soluble intermediates have been detected. Recently, Velichenko and co-workers[20–22] have proposed a new mechanism involving soluble intermediates:

$$H_2O \rightarrow OH_{ads} + H^+ + e^- \quad (1)$$

$$Pb^{2+} + OH_{ads} \rightarrow Pb(OH)^{2+} \quad (2)$$

$$Pb(OH)^{2+} + H_2O \rightarrow PbO_2 + 3H^+ + e^- \quad (3)$$

Electrodeposition of lead dioxide on glassy carbon electrodes under ultrasound has been recently studied in our laboratory[23] and a strong influence of the ultrasonic field on the process was observed. The present paper studies the nucleation and growth of lead dioxide in the presence of ultrasound and is a continuation of our previous works where lead dioxide electrocrystallisation was studied in the absence of ultrasound[24] in a stagnant solution and in the presence of forced convection on a rotating disk electrode.[25] The classical models[26–28] have been used to obtain the kinetic parameters of the processes (N_0, A, k) and to quantify the influence of the ultrasonic field on the process mechanism.

Experimental

A standard two-compartment electrochemical cell with a volume of 50 mL was used in the experiments. The chemicals were Analar quality and were used as received. The cell was filled with an aqueous solutions of 0.1 M lead(II) nitrate + 1 M nitric acid, prepared using ultrapure water from a Millipore Milli-Q system. A platinum wire acted as the counter electrode. A SCE served as the reference electrode.

The working electrode was a glassy carbon rod (diam. 3 mm) CV25 from Sofacel (Le Carbone-Lorraine). Before each experiment, the glassy carbon electrode was polished first with fine emery paper, followed by polishing with decreasing size alumina particles in suspension, on a polishing cloth, until a mirror finish was obtained. After that, the electrode was thoroughly rinsed with water.

A Selecta commercial ultrasonic bath (30 kHz, 100 W) was employed in the sonoelectrochemical experiments. The system was maintained at a constant temperature of 25 °C using a thermostat Model Frigiterm-30 (Selecta). The electrochemical cell was positioned just over the transducer of the ultrasonic bath. The cell was immersed in such a way that the levels of both liquids (bath and electrolyte) were the same. The separation between the transducer and the electrode surface was 6 cm.[23]

Solutions were thoroughly purged of oxygen prior to running the experiment by bubbling with nitrogen N50 (Air Liquide) for 20 min. Nitrogen N50 (Air Liquide) was also used for saturation of the solutions before each experiment. During the measurements, a flow of gas was maintained over the solution surface. Lead dioxide deposits were removed from the surface with 1 : 1 H_2O_2–acetic acid mixture followed by rinsing with water.

All experiments were carried out using a Voltalab electrochemical system consisting of a DEA 332 potentiostat and an IMT 102 electrochemical interface. The system was connected to a personal computer for recording and treatment of curves.

A JSM-840 JEOL scanning electron microscope was employed to obtain topographical views of the electrodes surfaces.

Results

Fig. 1 shows the *j–t* transients for lead dioxide electrodeposition at a glassy carbon rod electrode under ultrasonic conditions. The curve shapes are different from those obtained with the same electrode in the absence of ultrasound (taken from ref. 24), several curves are compared in Fig. 2. A strong decrease in the induction time and a great enhancement of the

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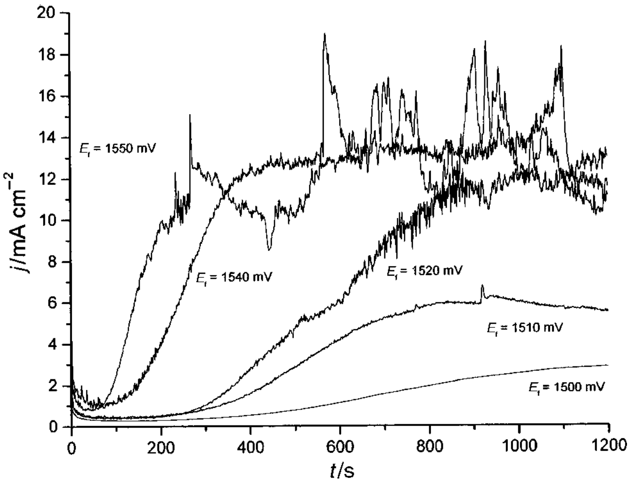

Fig. 1 Chronoamperometric curves for PbO_2 deposition in 0.1 M $Pb(NO_3)_2$ + 1 M HNO_3 at a glassy carbon electrode in ultrasonic conditions (potential steps in figure).

steady state current density is observed in the presence of ultrasound as compared to silent conditions. Therefore, ultrasound presents additional effects to those expected from pure convection,[18–25] because the experimental curves are absolutely different. Besides, the peak obtained in the absence of ultrasound on j–t transients disappeared under ultrasound (see the curves at E_f = 1540 mV *vs.* SCE).

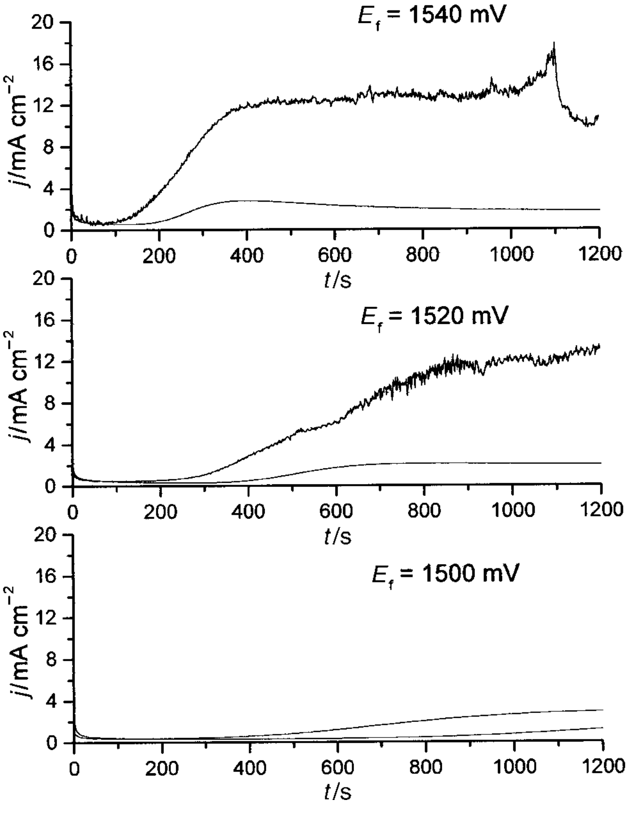

Fig. 2 Superposition of the chronoamperometric curves for PbO_2 deposition in 0.1 M $Pb(NO_3)_2$ + 1 M HNO_3 recorded under silent (taken from ref. 24) and ultrasonic conditions.

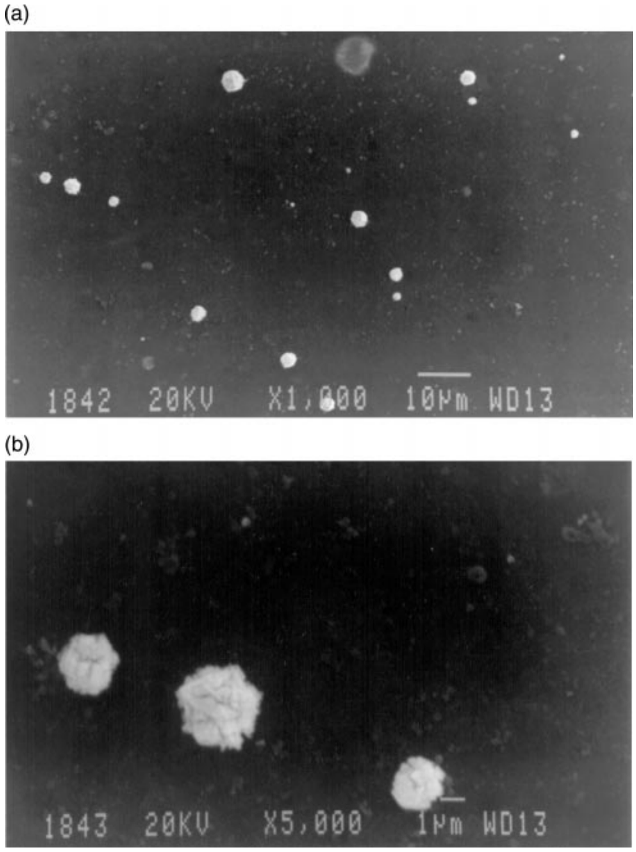

Fig. 3 Scanning electron micrographs of the glassy cabon electrode at the first stages of lead dioxide crystallization under ultrasound. Magnification: (a) ×1000; (b) ×5000.

Fig. 3 shows SEMs of the lead dioxide electrodeposition in the early stages of the electrocrystallisation.[29] In the SEM micrograph in Fig. 3(a), one can clearly see the different sizes of the nuclei, which suggests a progressive nucleation mechanism. Fig. 3(b) shows the morphology of the nuclei in detail. The topography of the single crystals is much more irregular than that for the crystals obtained in the absence of ultrasound[24] at the same substrate.

To explain the crystal growth, a model described by eqn. (4) was used. This equation corresponds to a simple progressive 3D nucleation and crystal growth model with the outward growth on a substrate base plane surface not covered by growing nuclei. This model was also used in the studies on the rotating disk electrode:[25]

$$j = j_0 \exp\left[-\frac{\pi M^2 k^2 N_0 A}{3\rho^2}(t - t_0)^3\right] + zFk\left[1 - \exp\left[-\frac{\pi M^2 k^2 N_0 A}{3\rho^2}(t - t_0)^3\right]\right] \quad (4)$$

This equation contains four parameters: t_0 (s), the induction time; j_0 (mA cm^{-2}), the current density in the induction time; k (mol cm^{-2} s^{-1}), the growth rate constant; and N_0A (nuclei cm^{-2} s^{-1}), the three-dimensional nucleation constant.

Table 1 Kinetic parameters of electronucleation and growth of lead dioxide electrodeposition

E_f/mV	j_0/mA cm^{-2}	t_0/s	k/mol cm^{-2} s^{-1}	N_0A/nuclei cm^{-2} s^{-1}	χ^2
1510	0.505 ± 0.008	103 ± 3	(3.163 ± 0.005) × 10^{-8}	(1.27 ± 0.03) × 10^4	0.01
1520	0.37 ± 0.03	64 ± 10	(6.39 ± 0.02) × 10^{-8}	(1.37 ± 0.07) × 10^3	0.1
1540	0.99 ± 0.04	29 ± 3	(6.785 ± 0.007) × 10^{-8}	(1.83 ± 0.07) × 10^4	0.09
1550	0.69 ± 0.09	16 ± 3	(6.60 ± 0.04) × 10^{-8}	(9.5 ± 0.9) × 10^4	0.1

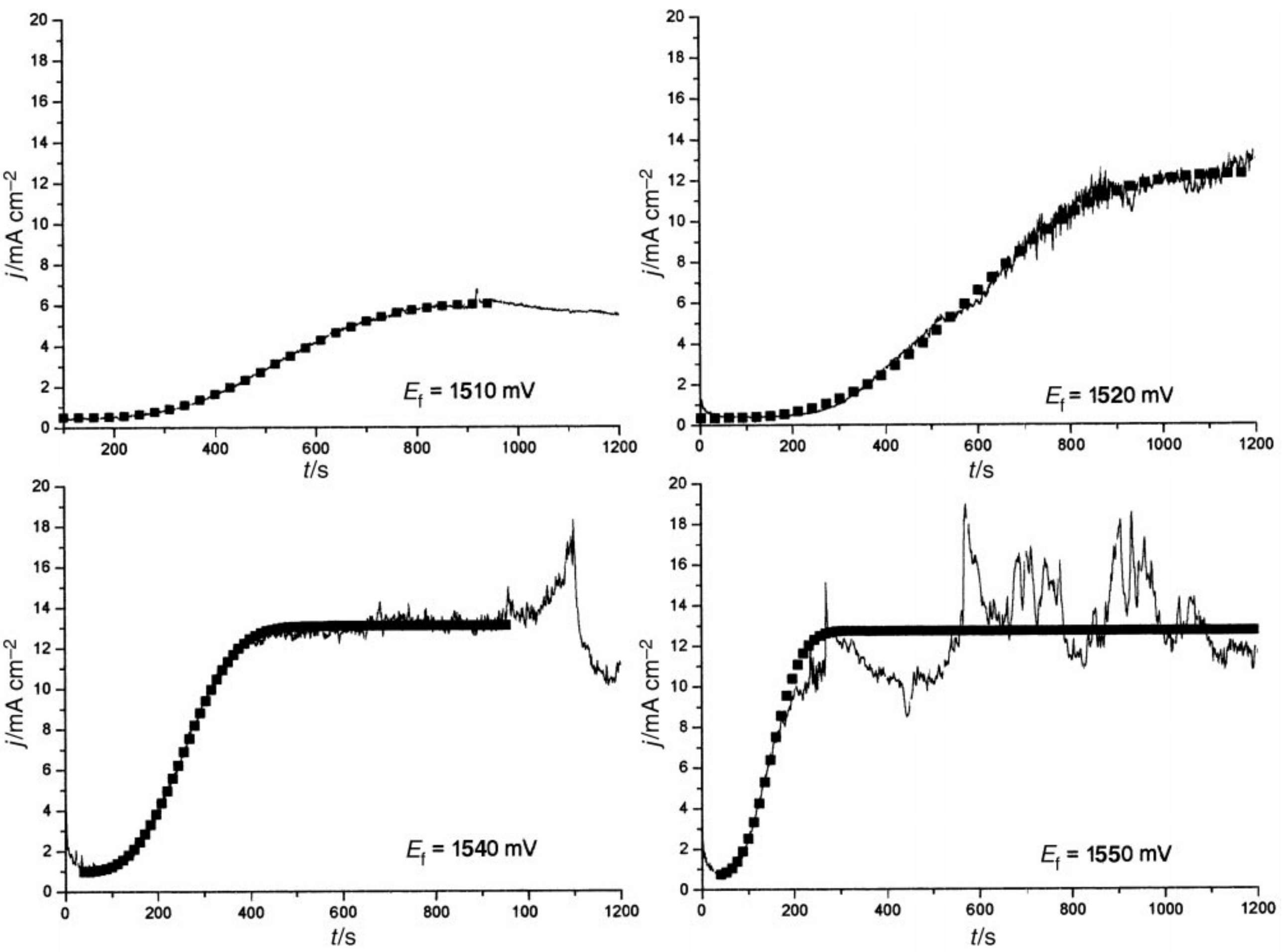

Fig. 4 Theoretical fit (■) of experimental curves (——) for lead dioxide electrodeposition under ultrasound.

However, j_0 is not very important in the whole approximation and the rate constant k is clearly determined when a well-defined current density plateau exists.[30] The results of the approximations are presented in Fig. 4 and in Table 1. With increasing applied potential, N_0A increases and induction time decreases, in agreement with the literature;[12,31] the growth constant seems to be constant, except at the most negative potential.

Discussion

Fig. 5 shows the influence of the potential step on the induction time, nucleation constant and growth constant in the presence and absence of ultrasound. There is a clear influence of the ultrasonic field on the process, which is stronger at lower potentials. The most marked effect is the decrease in the induction time. This phenomenon was already pointed out in our previous work[23] and can be associated with the surface fuctionalisation caused by the reaction of $OH^{\cdot}$ radicals (derived from aqueous sonolysis) with the carbon surface. This enhanced adsorption must increase the number of active sites on the surface (possible nucleation centres) and, therefore, decrease the time necessary for stabilisation of nuclei during the early stages of deposition, *i.e.* decrease the induction time. Another notable effect is the increase in the steady state current density, that is, the growth rate constant. The observed effect is fast growth of nucleation centres. Centres which are formed grow more quickly, although their number is lower than in the absence of ultrasound.

It is known that, under these experimental conditions [Pb(II) concentration and pH], the forced convection conditions using a rotating disk electrode do not enhance the electrocrystallisation of lead dioxide.[18,19,25] An ultrasonic field

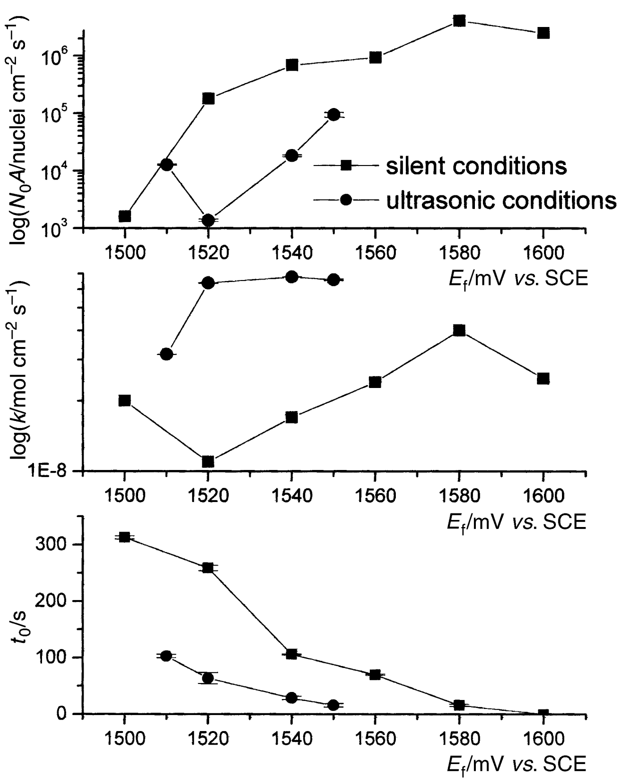

Fig. 5 Comparison of the dependence of t_0, log N_0A and log k on applied potential for lead dioxide electrodeposition in the absence (taken from ref. 24) and presence of ultrasound.

presents an inherent enhancement of the convection. Therefore, ultrasound presents a wide range of effects, both beneficial and disadvantageous, which balance the experimental results. Taking into a account the mechanism suggested by Velichenko and co-workers,[20–22] ultrasound seems to activate every step in the mechanism: it enhances the $OH^{\cdot}$ adsorption, *e.g.* a higher $[OH_{ads}]$ is obtained at shorter times. Higher $[OH_{ads}]$ concentration accelerates step (2). In this context, if the results obtained under ultrasonic conditions are opposite to the results in forced convection conditions, ultrasound must increase the rate of step (3) in order to reduce the half-life time of the soluble intermediate species, avoiding removal of the soluble intermediate from the electrode surface. However, confirmation of such an acceleration of step (3) needs further experimental work. Another possibility would be a new reaction mechanism in the presence of ultrasound, often observed in organic electrosynthesis.[32,33]

The lower nucleation rate constant observed in the presence of ultrasound can be related to the fact that the electrocrystallisation is easier on the same substrate (PbO_2) than on the other material (glassy carbon).[31,34] At higher potentials, the crystal growth can be inhibited[24] and one possible explanation could be the decomposition of OH_{ads} into O_{ads} and H^+ (in this potential range), as pointed out by other authors.[35] Further work with a commercial ultrasonic probe system is currently in progress in order to deliver ultrasound directly into the system, rather than rely on its transfer though the water of a tank and the voltammetric cell walls.

Conclusions

The application of an ultrasonic field on the electrocrystallisation of lead dioxide onto glassy carbon presents marked effects: (i) This process is a good example of the specific effects of ultrasound, different from enhancement of mass transport, through surface activation, radical formation, *etc.*, because the experimental results are very different from those obtained from RDE experiments. (ii) A comparison of the values of the kinetic parameters obtained in the presence and absence of ultrasound, suggests that after the nuclei become stable during the induction time, ultrasound enhances the growth of the already formed nuclei without acceleration of the nucleation rate N_0A. This observation is supported by the topology of the nuclei found by means of SEM.

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