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A potential-pulse interference method for studies of the nucleation of a single silver centre on carbon microelectrodes

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A potential-pulse interference method has been developed for detailed studies of the nucleation at a single nucleus. Following a potential step from a positive overpotential to a sufficiently negative overpotential at which nucleation takes place, a single reverse pulse or repetitive potential-pulse train is then applied at certain stage before a critical nucleus is formed to interfere with the nucleation process. Nucleation is then allowed to continue at a stable overpotential until a critical nucleus is formed. By comparing the arrival-time distributions of the critical nuclei with and without the pulse interference, information about the mechanism of the nucleation can be obtained. In particular, it is found that a termination process is involved in the formation of a single silver nucleus at medium and low potentials, and that the structures of the critical nuclei may be different at different overpotentials.

Nucleation in electrocrystallization has been studied extensively in terms of probability distributions in energy, space and time, in particular substrate activity distributions, spatial distributions of nuclei and arrival-time distributions of nucleation events.[1–12] In the past 15 years, investigations utilizing microelectrodes have stimulated this area and have resulted in a better understanding of the nucleation process and allowed the exploration of the possibility of utilizing a single nucleus as a catalytic centre for certain reactions. The advantages of microelectrodes for fundamental studies are that the number of nuclei can be restricted and the stochastic character of the nucleation process can be emphasized. On this basis, the probabilistic analysis of the nucleation process also becomes possible. However, studies are limited by the adequacy of theoretical models. It is generally accepted that clustering of atoms or molecules is responsible for the formation of nuclei,[7,11,13–15] but there are few papers describing the removal of atoms and molecules from existing clusters (a terminating process) before they become stable.

The 'arrival time' is a parameter of great importance for fundamental studies of nucleation processes using microelectrodes. By 'arrival time', we mean the time required to form a critical nucleus, which is indicated by the rapid, spontaneous growth of a nucleus causing an onset of current. A statistical treatment of the distribution of the arrival time was obtained by Fleischmann and co-workers[11,16] by assuming that at a sufficiently high overpotential the nucleation was a pure starting process. However, the relative rates of the starting and terminating processes are open questions and it is by no means clear that the terminating process can be neglected for more generalized situations. To gain further insight into this question, we propose overpotential modulation as a method of verifying that terminating processes are involved.

In this paper, we develop a potential-pulse method for modulating the nucleation process and give evidence that terminating processes are involved in the formation of silver single nuclei on carbon microelectrodes.

Principle of the method

The generalized form of clustering process during the formation of a critical nucleus at a medium overpotential can be described as follows:

$$n-1 \rightleftarrows n \rightleftarrows n+1 \rightleftarrows \cdots \rightarrow n' \quad (1)$$

$$n' \rightarrow n'+1 \rightarrow \cdots \rightarrow n^* \quad (2)$$

where n and n' refer to atom numbers of a subcritical nucleus and n^* refers to atom numbers of a critical nucleus. At medium overpotentials, it is reasonable to consider nucleation to be an initiation and termination process (1) in the initial stages and a pure initiation process (2) later on when the cluster is near its critical size.

Modulation is applied in the following way. After a potential step from a positive overpotential to a sufficiently negative overpotential of η_1 for a period of $t_{1,0}$, the electrode is then pulsed repetitively to a less negative overpotential of η_2 of pulse width t_2 to interfere with the nucleation process, Fig. 1. The pulse train lasts to the point t_p and the electrodeposition continues at a stable overpotential of η_1. The values of η_2, duty ratio (t_1/t_2) and duration time (t_p) of the pulse train are the parameters that can be varied for each experiment. The time duration of $t_{1,0}$ at the overpotential η_1 before the first

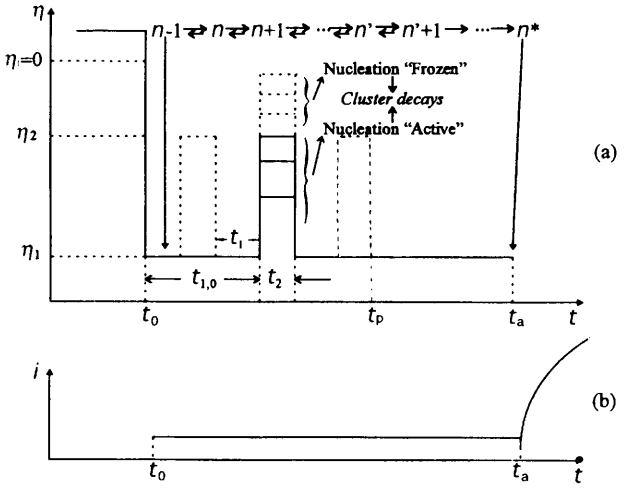

Fig. 1 Schematic of the potential-pulse interference method for detailed studies of nucleation of a single nucleus (a) and schematic of i–t behaviour of single nucleus formation and growth (b) (see text)

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pulse starts can also be chosen at different stages of the subcritical nucleus. A proper choice of variables is naturally very important in determining how much information about the kinetics of nuclei formation can be obtained.

In the simplest experiment, the first potential pulse is adequate to disturb the nucleus formation and thereby gain some kinetic information about the nucleation process. For example, the pulse can be applied at different times and thus disturb the process at different stages. Alternatively, by applying potential pulses of different amplitudes one can slow the nucleation process by different amounts. In the latter case, two different situations could arise, where either nucleation is 'frozen' at the least negative η_2 or nucleation is still 'active' at medium η_2, although slower. In either case the cluster will tend to decay if the terminating process is present. It is obvious, therefore that the arrival-time distribution with the pulse interference will be on a longer timescale if atoms or molecules leave the subcritical nucleus during t_2.

Results and Discussion

Arrival-time distribution

A detailed description of the arrival time measurements is given elsewhere.[17] Briefly, the automatic and repetitive *i–t* measurements of the nucleation and subsequent growth behaviours of Ag from the solution of 1 mmol dm^{-3} $AgNO_3$ + 0.1 mol dm^{-3} KNO_3 on 5 μm carbon microdisk electrodes were carried out *via* a microcomputer with 12 bit A/D and D/A boards as well as a homemade potentiostat and a commercial current amplifier (Keithley 428). Because of the marked effect of the electrodeposition history of the carbon microelectrode on the subsequent nucleation process, a 'cut-off' point was introduced, *i.e.* the growth of the nucleus was terminated soon after the first nucleus was observed on detection of a current bigger than a preset value and the nucleus just formed was anodically dissolved. The *i–t* curve remained typical of the growth behaviour of a single nucleus after several hundreds of runs. The complete *i–t* data of each run were recorded and retrieved for later analysis. The cumulative arrival-time distributions of single Ag nuclei at several overpotentials were formed with at least 200 data points by analysing each *i–t* curve, Fig. 2(A). This procedure can be completed automatically by the computer if all data are valid.

The theoretical prediction of the probability of finding clusters of size greater than n^* (n^* being the size of the critical nucleus) for the pure initiation process of nucleation at a sufficiently high overpotential was put forward by Fleischmann *et al.*[12] as follows:

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

where λ is the nucleation rate. The experimental cumulative arrival-time distribution for a pure initiation process should fit the theoretical plots for reasonable values of λ and n^*.

Within the timescale of measurement (60 s) in our work, single nuclei of silver were observed at −40 to −90 mV and multiple nuclei could be seen at overpotentials above −100 mV.[17] The arrival-time measurements were made at medium overpotentials of −50 to −70 mV by the single potential-step technique prior to the pulse interference measurements. It can be seen that the empirical arrival-time distribution of single Ag nuclei is rather broad. Indeed, the plots of the distribution at −70 mV *vs.* T with various λ and n^* values do not fit the theoretical prediction for the pure initiation process unless a meaningless value of cluster number ($n^* = 0$) is used, Fig. 2(B).

Arrival-time distribution with pulse interference

The observed arrival-time distribution indicates that nucleation at −70 mV is not a pure initiation process. To verify

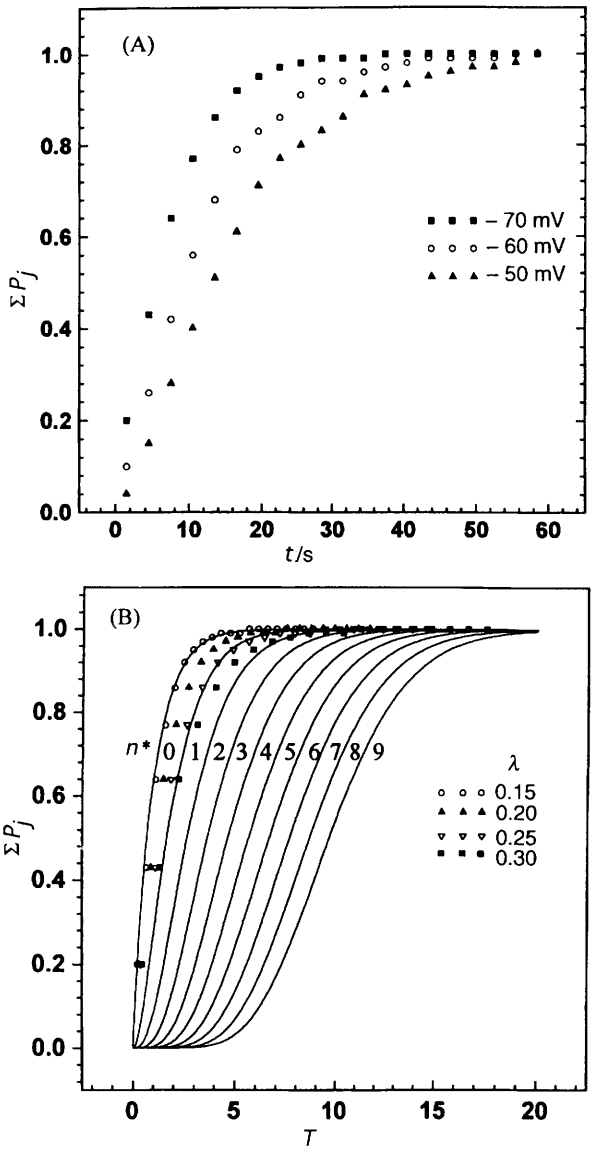


Fig. 2 Accumulative arrival-time distributions of the first single Ag nucleus at several overpotentials on a 5 μm carbon microelectrode in a solution of 1 mmol dm^{-3} $AgNO_3$ + 0.1 mol dm^{-3} KNO_3 (A) and comparisons of $\sum P_j \sim T$ ($T = t\lambda$) plots at −70 mV with the theoretical prediction (B)

that a terminating process is involved, a subcritical nucleus was allowed to form at −70 V for 500 ms, and then a pulse of lower overpotential was applied (see Fig. 1). During the pulse interference, atoms were allowed to leave so that the subcritical nucleus might become smaller, and the subcritical nucleus was allowed to undergo structural changes at this lower overpotential. After the pulse interference, growth was allowed to continue at −70 mV until the nucleus became critical. Data were rejected in cases where a nucleus was formed before or during the application of the pulse. At least 200 valid data points for each pulse amplitude and each pulse width were used to form the arrival-time distribution.

The measured cumulative arrival-time distributions, including the effects of the potential pulses at −50 mV for 1, 2 and 3 s are shown in Fig. 3. Note that the distributions were calculated and formed after subtraction of the pulse widths t_2 from each measured arrival time. It can be seen clearly that the pulses broadened the arrival time but this distribution was still able to approach unity on the same timescale. To test whether applying even lower overpotentials (*e.g.* $\eta_2 = -10$, −30 mV where nucleation does not take place) before making the arrival-time measurements would effect the results, experi-

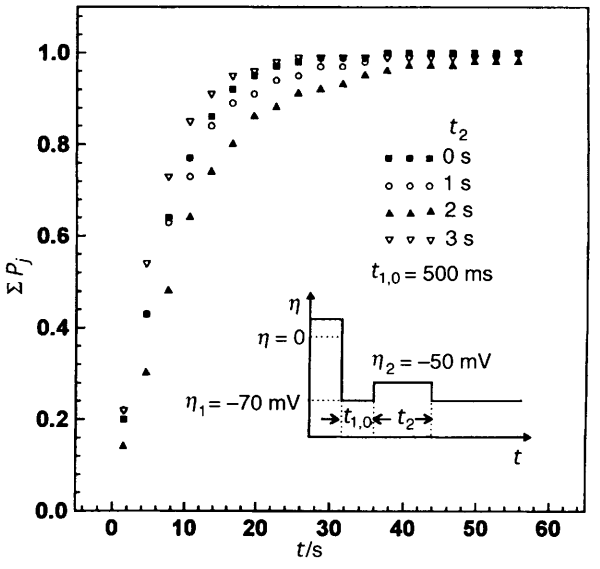
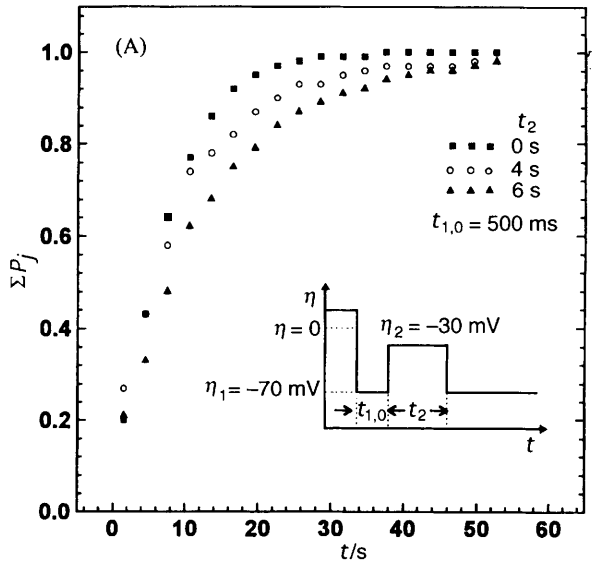


Fig. 3 Accumulative arrival-time distribution at $\eta_1 = -70$ mV with pulse interference at $\eta_2 = -50$ mV



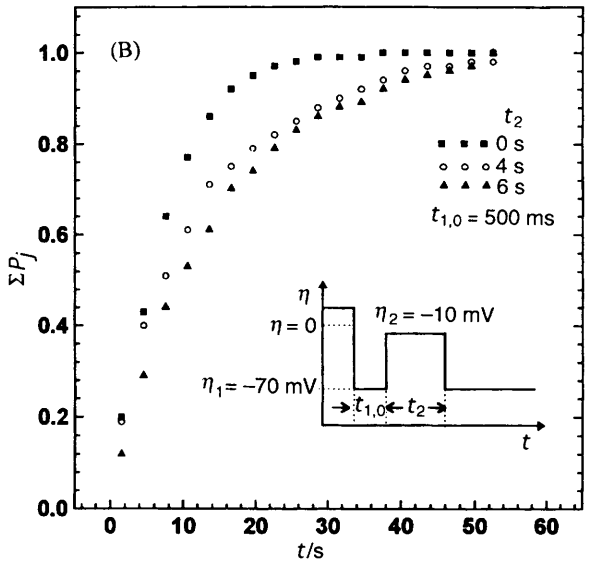


Fig. 4 Accumulative arrival-time distribution at $\eta_1 = -70$ mV with pulse interference at $\eta_2 = -30$ mV (A) and −10 mV (B)

ments were carried out as follows: after pulses from an initial positive potential to the specified low overpotentials for 1 or 2 s, nucleation was allowed to take place at −70 mV without further interference. This procedure gave almost identical arrival-time distributions to the normal one (not shown). This indicates that applying a low overpotential does not change the surface activity of the electrode for nucleation at high overpotential.

Returning to Fig. 3, we note that since nucleation is still active at −50 mV, although at a lower rate, the deviation of the distribution from normal may be related to a structural change in the subcritical nucleus. At any rate, further growth of this subcritical nucleus at −70 mV somehow becomes more difficult. However, as the pulse interference time is increased to 3 s, it is interesting to see that the cumulative arrival-time distribution becomes narrower than normal. This is presumably because, after completion of the 3 s pulse interference at −50 mV, the cluster was near the size of a critical nucleus and the pure initiation process had become dominant. In other words, nucleation at −50 mV proceeds *via* initiation and termination processes for the initial stage, followed by an initiation-only process after the cluster reaches a certain size.

The cumulative arrival-time distributions with the interference of pulses at −30 and −10 mV are shown in Fig. 4. Nucleation is not expected or can be considered 'frozen' at these overpotentials within the timescale of the measurements, and is by no means an initiation process at these overpotentials. As expected, the cumulative arrival-time distributions at −70 mV are much broader than normal. On the other hand, if the nucleation involves only the simple termination process at the pulsed overpotential, then the only effect of such a potential pulse should be the displacement of the arrival-time distribution by a time interval t_2, during which the subcritical nucleus decays. Keeping in mind that such a time interval has already been subtracted from each measured arrival time, the displacement should not be observed. However, this is not the case. Again, some structural change of the subcritical nucleus may be responsible, although direct confirmation is not possible because of the difficulties of controlling the size of the growing nucleus.

Concluding remarks

We have demonstrated a potential-pulse interference method for detailed studies of single nuclei. Nucleation of a critical nucleus can be slowed down or frozen for a certain time by the application of a reverse pulse. This allows a more detailed investigation of the nucleation than was possible previously. Using the new method, it has been shown that a termination process is involved in the formation of a single silver nucleus at medium and low potentials, and that the structure of the critical nucleus may be different at different overpotentials. In future, further kinetic information may be obtainable by performing more systematic experiments with different parameters of the pulse train.

The financial support of this project by the National Science Foundation of China is gratefully acknowledged.

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Paper 5/07857A; *Received* 4*th December*, 1995