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**APPLICATION OF CARBON FIBER
MICROELECTRODES IN ELECTROCHEMICAL
INVESTIGATIONS¹**

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In this work, the electrocrystallization of nickel from Ni²⁺-acidic bath has been investigated using an assembly of carbon fiber microelectrodes, consisting of single and multi microdiscs ($\varnothing = 7 \mu\text{m}$) randomly distributed inside the matrix of a non-conducting polymer. The microdiscs were far enough apart that the crystals could not interact, thus limiting the total observed current density to a linear superposition of the current densities from each crystal considered independently. The current-time transient response was quantitatively evaluated using the Scharifker and Hills' nucleation model. The high rate of nucleation after a rapid increase in the overpotential was discussed in relation to the physical model for three-dimensional (3D) nucleation with diffusion-controlled growth. Excellent agreement between the experimental results and the theoretical curve for 3D progressive nucleation was obtained.

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Introduction

In electrochemistry, the performance of the electrode with respect to response time and spatial resolution is inversely proportional to the electrode radius. During the past few decades, intensive research has resulted in electrodes of radii down to 1 μm and 1 nm. With a decrease in radius, elemental detection levels have been brought down to parts per billion (ppb) levels. At the present time, the diameter of carbon nanotubes is about 100 nm. With these nanoelectrodes, the smallest of sensors can be made, for example, for *in situ* monitoring of chemical reactions inside tissue, as well as measurement of the potential on cell membranes.

The beneficial properties of microelectrodes include: a steady state for a Faradaic process is attained very rapidly, the ohmic IR potential drop is decreased, the charging current I_C is suppressed, the applied potential can be scanned very rapidly, the signal-to-noise ratio is greatly improved, etc. These effects make microelectrodes attractive in many areas of electrochemistry (various sensors), electroanalytical chemistry (reaction mechanisms and kinetics), *in vivo* measurements, scanning electrochemical microscopy etc.

Since the spacing between the microelectrodes used was large compared to the diffusion layer thickness, it was possible to avoid overlap of diffusion interaction of the growing nuclei. This is not possible on continuous macroelectrodes where interaction of diffusion zones regularly occurs [1].

Nucleation on a unipotent surface represents a limiting case when the electrode contains no defects, and may be described by the Jakob–Tompkinson equation [2]

$$N(t) = N_0\{1 - \exp(-At)\} \quad (1)$$

It should be stressed that the application of Eq. (1) assumes a perfect surface. Once stable nuclei have been created, they will grow readily unless the deposition conditions (for example the potential) are changed. The growth may be either, (a) two-dimensional, in which case only a monolayer can be deposited without additional nucleation, or (b) three-dimensional, in the shape of cones or hemispheres, when, at least in principle, thick layers can be formed simply by continual growth.

The most powerful electrochemical technique for investigation of the early deposition steps of a new phase on the electrode surface is a stepwise change in the potential of a clean, polished electrode from the potential value where no reaction takes place, up to the value at which nucleation of a new phase takes place (at this potential the nuclei grow undisturbed). Such a chronoamperometric experiment results in a growing $j - t$ transient. At the instant when the potential is applied, there are no nuclei at the surface, and the current of the deposition

reaction has to be zero. With time, the current increases, because (a) the number of nuclei increases (if the nucleation is progressive) and (b) the surface of each nucleus increases with time. Indeed, it is possible to derive an expression for the current-time dependence, while the details of the shape of the growing transient will depend on nucleation kinetics, two-dimensional or three-dimensional growth, as well as the slow step of the reaction.

The work presented herein deals with investigation of the mechanism and kinetics of nucleation and growth of Ni on the carbon fiber microelectrode in 0.14 mol l^{-1} solution of NiCl_2 . The electrode behaviour and kinetic parameters determined under potentiostatic conditions have been compared with Scharifker and Hills' model of nucleation and growth of nuclei.

Experimental

The carbon fibre microdisc electrode was used as an inert, conducting substrate for the study of nickel nucleation and growth. The microelectrode assembly was prepared from carbon fibre microdiscs (Goodfellow) and consisted of 36,000 carbon fibre microdiscs (each of $\sim 7 \text{ }\mu\text{m}$ diameter). The microelectrode assembly was embedded in a matrix of non-conducting epoxy resin. The electrical contact between the epoxy encapsulated carbon fibres and a copper wire was made using a thin copper foil and a thin layer of silver-conducting epoxy resin at the rear of the electrode.

The electrode surface was refreshed before each measurement by mechanical abrasion with emery paper (1200) and polishing with alumina powder of 1, 0.3 and $0.05 \text{ }\mu\text{m}$ average particle size. The final cleaning of the electrode was performed in redistilled water in an ultrasonic bath. All the measurements were carried out on freshly prepared working microelectrodes.

The electrochemical treatment of pre-polished electrodes was performed by anodic polarization in $0.5 \text{ M H}_2\text{SO}_4$ at 3.2 V versus an Ag/AgCl/3M KCl electrode for 25 s [3].

The electrochemical measurements were performed using an EG&G PAR potentiostat/galvanostat (Model 273 A, Princeton Applied Research, USA) controlled by a personal computer. All the experiments were carried out at room temperature (298 K) in a standard three-electrode cell. The counter electrode was a large-area platinum electrode and the reference electrode to which all potentials were referred was an Ag/AgCl/3M KCl electrode.

The reagents used were from Kemika (Zagreb, Croatia), of p.a. (pro analysi) purity. Solutions ($0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ and $0.14 \text{ mol l}^{-1} \text{ NiCl}_2 \cdot 6\text{H}_2\text{O}$) were prepared with redistilled water. The electrolytes were purged with purified nitrogen prior to each experiment.

Potentiostatic transient experiments were carried out according to the

following procedure. The first potential step of +3.2 V for 25 s was applied in order to form a reproducible and active electrode surface. After holding the potential at +3.2 V for 25 s, a potential step from open circuit potential E_{oc} to different transient potentials E_t was applied and the corresponding cathodic current transient was recorded.

Results and Discussion

Cyclic Voltammetry

The cyclic voltammogram presented in Fig. 1 was obtained on a freshly polished microelectrode, after anodic polarization at +3.2 V in $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$. The spectra obtained are very stable and reproducible with clearly defined anodic (A) and cathodic (C) current peaks.

From the cathodic range of the cyclic voltammogram (the inset in Fig. 1), the potential range for chronoamperometric measurements was determined.

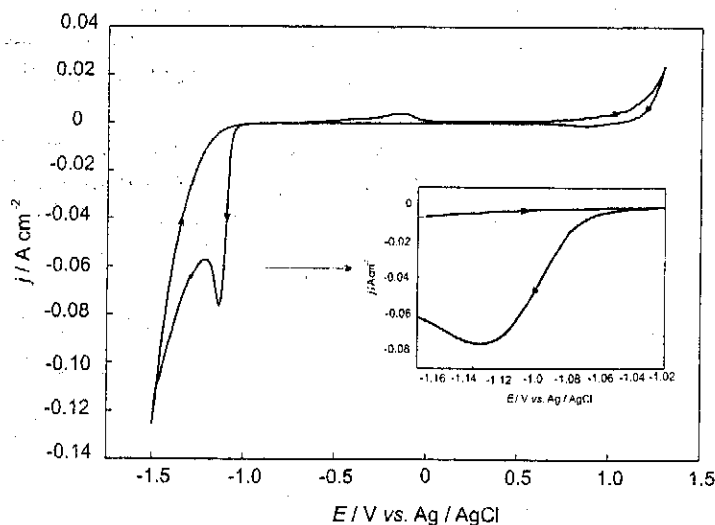


Fig. 1 A cyclic voltammogram for the carbon fiber microelectrode in $0.14 \text{ mol l}^{-1} \text{ NiCl}_2$, $\nu = 30 \text{ mV s}^{-1}$: The inset: a cathodic range of cyclic voltammogram which represents the nucleation of nickel

Potentiostatic Pulse Technique

Chronoamperometric transients were used to study the kinetics and mechanism of Ni nucleation and growth on the carbon fiber microelectrode. The measurements were performed in $0.14 \text{ mol l}^{-1} \text{ NiCl}_2$, in the potential range between -1.10 V and -1.25 V .

A family of typical current-time transients obtained for Ni nucleation is shown in Fig. 2. The transients show an abrupt increase in current, a maximum of the current density (j_m) in time (t_m), followed by a current drop. Such a transient shape is characteristic for cathodic nucleation and growth of nuclei on a conducting surface under diffusion control [4–6]. The current density maximum (j_m) shifted to shorter times when the applied potential was made more negative, as can be observed in Fig. 2.

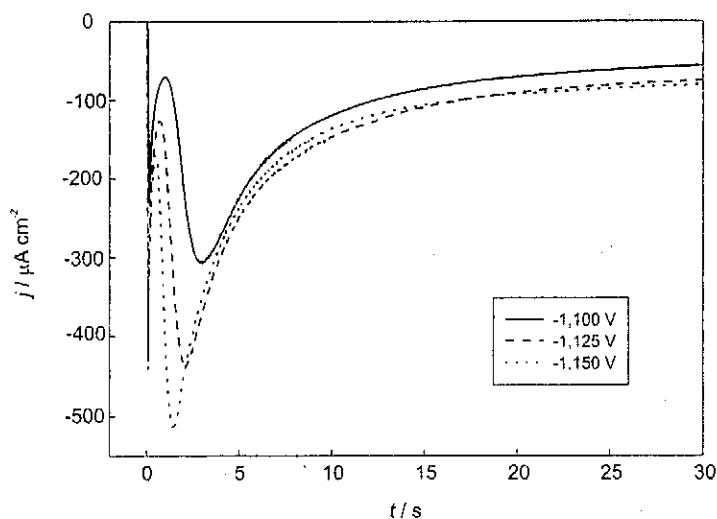


Fig. 2 Current-time transients resulting from chronoamperometry experiments recorded on the carbon fiber microelectrode in $0.14 \text{ mol l}^{-1} \text{ NiCl}_2$. The potential was stepped from open circuit potential, $E_{oc} \approx +0.40 \text{ V}$, to the transient potential values, E_t .

At the instant when the potential is applied, there are no nuclei at the surface, the double layer charging current is present and drops during nucleation and growth. The double layer charging current is followed by a current increase caused by the expansion of the electroactive surface due to isolated nucleus growth. This increase, limited by spherical diffusion around each nucleus, is due to an increase in the nucleus size and in the number of nuclei. The spherical diffusion zones then overlap and the mass transfer becomes linear to an effectively

smooth surface. The current decreases and the shape of the transient corresponds to linear diffusion toward the electrode surface.

In order to determine the mechanism of nucleation and growth of Ni on the carbon fiber microelectrode, the transients obtained were normalized according to the coordinates of their maxima, (j_m) and (t_m) , and then graphically compared with the theoretical expressions for 3D nucleation [7–9]. In multiple nucleation, two limiting cases have been considered: *instantaneous nucleation* — all nuclei are immediately created and *progressive nucleation* — nuclei are continuously formed during the whole deposition process.

The best fit of experimental results for the investigated potential range was obtained with a 3D progressive nucleation theoretical curve, under diffusion control (Fig. 3). The theoretical expressions for 3D nucleation under diffusion control are given by the following equations

$$\left(\frac{j}{j_m}\right)^2 = \frac{1.9542}{t/t_m} \{1 - \exp[-1.2564(t/t_m)]\}^2 \quad (2)$$

for instantaneous nucleation

$$\left(\frac{j}{j_m}\right)^2 = \frac{1.2254}{t/t_m} \{1 - \exp[-2.3367(t/t_m)]\}^2 \quad (3)$$

for progressive nucleation.

The dashed lines in Fig. 3 correspond to 3D instantaneous and 3D progressive nucleation. For the investigated potential range, the experimental curves practically overlap with the theoretical curve for 3D progressive nucleation.

The relations below give the dependences between the electrochemical values and the kinetic nucleation parameters 3D progressive nucleation [7–9]

$$j_m^2 t_m = 0.2598 (nFc)^2 D \quad (4)$$

$$j_m = 0.4615 nFD^{3/4} c (k' AN_\infty)^{1/4} \quad (5)$$

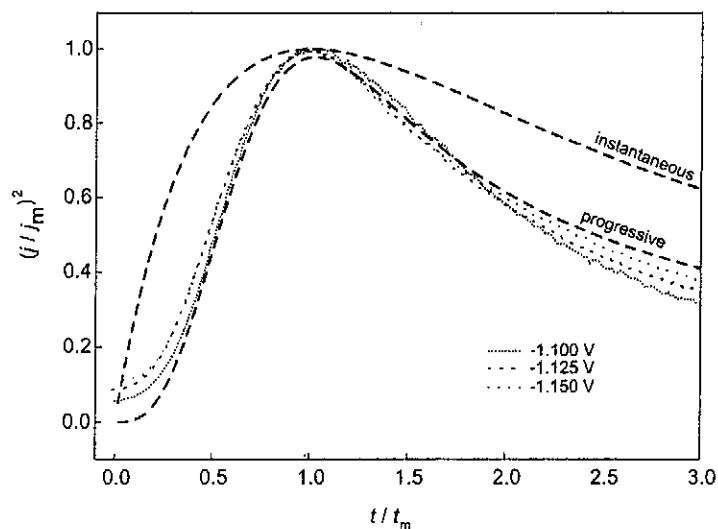


Fig. 3 A comparison of the experimental non-dimensional plot of $(j/j_m)^2$ against t/t_m for the three-dimensional growth with theoretical models. The dashed lines represent the theoretical models

$$N_s = \left(\frac{AN_\infty}{2k'D} \right)^{0.5} \quad (6)$$

The basic requirement (in the analysis of transients according to the relations) for 3D nucleation is that the product $j_m^2 t_m$ remains constant, or does not significantly change, with a change in the overpotential. Applying the mean value of $j_m^2 t_m$ and Eq. (4) enabled the determination of the diffusion coefficient (D) shown in Table I.

The diffusion coefficient values determined from the previous equation show good agreement with the values obtained from the Cottrell equation, which applies to the falling portion of the transient. In an unstirred electrolyte, diffusion will take place in a linear diffusion field, so that the Cottrell equation may be applied at a constant potential

$$|j| = \frac{nFD^{1/2}c_0}{\pi^{1/2}t^{1/2}} \quad (7)$$

The values obtained for the diffusion coefficients ($D \approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) are

characteristic of diffusion in solutions of the corresponding ionic species. It may be concluded then that electrolyte diffusion determines the rate of the nucleation process.

Table I The values of the diffusion coefficient, D .

E vs. Ag/AgCl V	Scharifker–Hills $D \times 10^5$ $\text{cm}^2 \text{s}^{-1}$	Cottrell $D \times 10^5$ $\text{cm}^2 \text{s}^{-1}$
-1.100	0.81	2.72
-1.125	1.16	2.63
-1.150	1.16	2.17

The product AN_∞ is calculated from Eq. (5) where the parameter A is the rate constant of nucleation at steady state, and N_∞ is the density of active sites. The material constant k' for Ni is

$$k' = \frac{4}{3} \left(\frac{8\pi cM}{\rho} \right)^{1/2} \quad (8)$$

where c is the concentration of diffusing species in electrolyte bulk, D is the diffusion coefficient, M is the molar mass and ρ is the density of deposited substance.

The density of nuclei upon completion of the nucleation process may be approximated from Eq. (6). The calculated values of the nucleation rate (AN_∞) and the density of nuclei upon surface coverage by nucleation regions (N_s) are shown in Table II.

Table II The values of the nucleation rate (AN_∞) and the density of nuclei upon surface coverage by nucleation regions (N_s) for the carbon fiber microelectrode in 0.14 mol l⁻¹ NiCl₂

E vs. Ag/AgCl V	$AN_\infty \times 10^{-5}$ $\text{s}^{-1} \text{cm}^{-2}$	N_s cm^{-2}
-1.100	1.10	584
-1.125	2.95	570
-1.150	0.89	799

Conclusion

The electrodeposition of nickel on carbon fiber microelectrodes was studied in 0.14 mol l⁻¹ NiCl₂ solution using cyclic voltammetry and chronoamperometry.

The electro-deposition current-time transients were quantitatively evaluated with Scharifker and Hills' nucleation model. Fitting the experimental results to theoretical curves for instantaneous or progressive nucleation indicated that nucleation of Ni on carbon fiber microelectrodes takes place *via* a 3D mechanism of progressive nucleation and growth under diffusion control. Through the application of relations for 3D progressive nucleation, the following parameters were determined: the rate of nucleation (AN_{∞}), the density of growing sites (N_s), and the diffusion coefficient (D).

Symbols

A	nucleation rate per active site, s^{-1}
AN_{∞}	nucleation rate, $s^{-1} \text{ cm}^{-2}$
c	concentration, mol cm^{-3}
D	diffusion coefficient, $\text{cm}^2 \text{ s}^{-1}$
E	potential, V
E_{oc}	open circuit potential, V
E_t	transient potential, V
F	Faraday constant, 96485 C mol^{-1}
I	current, A
j	current density, A cm^{-2}
k'	dimensionless constant affecting the growth rate of diffusion zones
M	molar mass, g mol^{-1}
N_{∞}	number density of active sites, cm^{-2}
N_s	nuclei number density at long times, cm^{-2}
n	number of electrons
P	area, cm^2
t	time, s
ρ	density, g cm^{-3}
v	scan rate, V s^{-1}

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