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Nucleation mechanism of Fe nanoclusters inside of membranes nanopores

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Nucleation and growth of iron clusters inside of nanosized pores of porous polyethylene membrane was investigated. Iron clusters was electrodeposited from 0.1 M $FeCl_2$ at pH=2.0, constant temperature and constant applied potential. Variations of current density *vs* time durring deposition were recorded. Using Scharifker and Hills theory and normalized equation, experimental data were compared with theoretical curves. Progressive-type nucleation mechanism was found for deposition of iron in domain 850-990 mV of applied potential. A possible alteration of nucleation mechanism was detected at low applied potentials. Control of nucleation mechanism can be used in order to obtain desired nanostructures.

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1. Introduction

As a cornerstone of materials technology, electrodeposition - an old and well-established technique - remain an interest point for scientific research. This increased interest in the age of new materials, including here nanomaterials, have as reason various possibilities to study new phases via supersaturation potential control, and, in the new wave of technologies named nanotechnologies, possibilities to predict and control obtaining of nanoobjects: nanodots, nanorods, nanobelts and others. Initial stages of the formation and growth of metallic crystalline phases is also an particular interest for processes involving conventional electrodeposition for industrial use [1].

Considerable attention has been given to the theory of electrochemical nucleation and growth in initial stages of electrodeposition [16]. Number of published papers and reviews on this topics is also considerable. An excellent review of studied materials can be found here [2]. Well-established overpotential for optimum nucleation, nucleation and growth mechanism and types of substrates, permit an optimization and control of obtained nanostructures according of targeted application.

The thermodynamics of small clusters deviate significantly from bulk phases due to the large fraction of surface atoms. The first papers related to nucleation thermodynamics of electrodeposited materials was write in 1926 by Volmer and Weber [3]. Authors consider the energy of one cluster as a sum of its bulk and surface energies. While the bulk energy lowers the free energy, the surface energy increase it.

Modern theories was introduced by Sharifker et al. [4–6] using the concept of planar diffusion zones. This theory estimate the effect of diffusion fields on the observed current density to a planar electrode and is easy to verify using experimental current intensity *vs* time data. The hemispherical diffusion zone surrounding an individual nucleus is considered as a hypothetical planar zone of circular shape, to which only linear diffusion perpendicular to the electrode surface is permitted. The size of the diffusion zone is solved by equating the fluxes for the hemispherical and planar diffusion fields. The first hypothesis for this model consider a distribution of nuclei with interacting diffusion fields. In this case, the solution of the real diffusion problem can be approximated by the flux to the area fraction covered by diffusion zones. The obtained current transient for this distribution of nuclei is result as multiplication of the covered area fraction with the Cottrell equation initiated at the beginning of the potential application. The second hypothesis of the model is: the area fraction covered with randomly distributed circles is calculated using the Avrami theorem [7].

Model was improved over the time by several attempts. Sluyters-Rehbach et al. [8] consider that hypothetical planar flux should not relate only to nuclei age but also to their time of formation, in order to preserve a uniform thickness of the diffusion layer, closed to planar diffusion. In the other model, Mirkin and Nilov [9], consider as incorrect multiplication of Cottrell equation for the planar diffusion zones in progressive nucleation having different times of formation, and is necessary to initiate the Cottrell equation at different times for each zone. Heerman et al. [10–12] have later presented the same theory as Mirkin and Nilov, and discussed the resulting transients in detail. More authors report good result in using basic model of Scharifker and Hills or improved models on various types of materials [13-15]. The opportunities offered now by supercomputers permit Monte-Carlo-type simulation of nucleation and growth processes more closed to reality.

In this paper, we are focused on nucleation and growth of iron inside of nanosized pores of porous polyethylene membrane. Embedding of ferromagnetic elements and alloys inside of polymers is an alternative technology for obtaining nanocomposite, polymer-based nanomaterials. Iron was chose due of various application, such as magnetic devices (memory devices, sensors, micro- and nanoactuators) or catalytic application (after transformation in appropriate oxidizing state). These application can be integrated as micro- or nanodevices together with signal amplifiers and data conversion circuits in novel one-chip structures. These aims were realized using recorded potentiostatic transients (dependence of current intensity *vs* time at constant applied potential, also namely transients, recorded in chronoamperometric mode) during electrodeposition experiments. To generate theoretical curves, Scharifker-Hills equations and Scharifker-Hills reduced equations for instantaneous and progressive nucleation mechanism were used. Information about nucleation type in imposed condition of electrocrystallization are obtained from comparison of experimental data with the theoretical curves.

2. Theory

In order to compare experimental current transients with theoretical predicted ones, Scharifker and Hills equations were used.

Progressive nucleation start with a small number of growth nuclei but the nuclei are continuously formed during the electrodeposited structure growth. Corresponding equation is:

$$i(t) = \frac{zFD^{1/2}c}{\pi^{1/2}t^{1/2}}\left[1 - \exp\left(-AN_0\pi.k'D\frac{t^2}{2}\right)\right] \tag{1}$$

with:

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

For instantaneous nucleation, in which all nuclei are formed at beginning of the applied potential, we have the equation:

$$i(t) = \frac{zFD^{1/2}c}{\pi^{1/2}t^{1/2}}\left[1 - \exp(-N\pi.kDt)\right] \tag{3}$$

with k – dimensionless constant:

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

where, in Eq. (1)-(4):

A - nucleation rate per active site (s^{-1});
c - bulk concentration ($mol \cdot cm^{-3}$);
D - diffusion coefficient ($cm^2 \cdot s^{-1}$);
zF - the molar charge of electrodepositing species;
F - the Faraday constant ($C \cdot mol^{-1}$);
i - current density ($A \cdot cm^{-2}$);
M - molar mass of the deposit ($g \cdot mol^{-1}$);
N - number density of growing centers (cm^{-2});
N_0 - number density of active site (cm^{-2});
ρ – density of the deposit ($g \cdot cm^{-3}$).

Most useful are normalized equation. For progressive nucleation, we have:

$$\frac{i^2}{i_m^2} = \frac{1,2254}{t/t_m}\left\{1 - \exp\left[-2,3367(t/t_m)^2\right]\right\}^2 \tag{5}$$

with:

$$t_m = \left(\frac{4,6733}{AN_0\pi.k'D}\right)^{1/2} \tag{6}$$

$$i_m = 0,4615 \cdot zFD^{3/4}c(k'AN_0)^{1/4} \tag{7}$$

For instantaneous nucleation:

$$\frac{i^2}{i_m^2} = \frac{1,9542}{t/t_m}\left\{1 - \exp\left[-1,2564(t/t_m)\right]\right\}^2 \tag{8}$$

with:

$$t_m = \frac{1,2564}{N\pi \cdot kD} \tag{9}$$

$$i_m = 0,6382 \cdot zFDc(kN)^{1/2} \tag{10}$$

In Eq. (5)-(10), i_m is the maximum of current density ($A \cdot cm^{-2}$) and t_m is the corresponding time, in seconds.

3. Experiment

In order to obtain iron electrodeposited structures, 100 μm-tick polyethylene porous membrane was used. Polyethylene membrane present non-geometric shape pores, with average diameter from nanoscale to mezoscale. Membrane samples was covered on the one face with an average tick of 0.1 μm thin film of pure gold using magnetron sputtering. This metallic film serve as working electrode in electrodeposition system. Conventional three-electrodes glass cell was used. Working electrode was porous polyethylene membrane with gold film carefully sealed in order to prevent unexpected deposition avoiding membrane pores. Surface of working electrode was 2.24 cm^2. Counter electrode was a carbon graphite plate with 2x2 cm^2 area. As reference electrode was used a saturated calomel electrode (SCE) from industrial manufacturer. Electrodeposition bath composition was 0.1 M $FeCl_2 \cdot 4H_2O$ and 1 M KCl in distilled water, thermostated at 30°C and pH adjusted to 2.0 using HCl. Prior to electrodeposition, porous polyethylene sample was introduced in bath and electrolytic cell was sonicated for pores de-aeration and filling with electrolyte.

Electrodeposition was performed in potentiostatic mode at 600, 850, 900 and 990 mV cathode potential, measured versus SCE. During deposition, the beginning of recording for current intensity was performed synchronous with applied potential for an interval of 20 s/8 ms step using Keythley 12-bit data acquisition card and appropriate software. After deposition, part of each polymer samples with electrodeposited clusters were dissolved and clusters were harvested using filtration technique. Image of clusters was obtained using transmission electron microscopy-TEM.

Theoretical curves were generated using mathematical dedicated software, starting from Eq. (1) and Eq. (3). After first comparation of experimental transients with theoretical ones, D and $A \cdot N_0$ parameters were calculated using Eq. (6) and (7), respectively Eq. (9) and (10). Values were introduced again in Eq. (1) or Eq. 3 (depend of nucleation type detected) and theoretical curves were re-ploted.

4. Results and discussion

Fig. 1 present a typical TEM image of clusters electrodeposited in pores, found after membrane dissolution. Structures is an aggregate of various sizes, chain-linked nanoclusters. We suppose that first cluster of chain (that is the biggest one) was formed at gold back-electrode surface using all Fe^{2+} ions offered by electrolyte contained in the membrane pore. After reducing all iron ions of this volume and forming the first cluster, the growth stop for a time. This time depend of diffusion coefficient of ions in specific electrolyte and is necessary for migration of new ions from bath inside of pore volume.

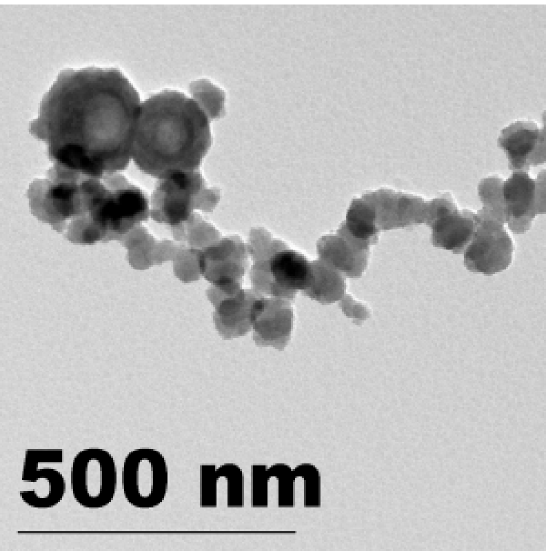

Fig. 1. TEM image of an representative aggregate of chain-linked nanoclusters of iron.

Exhausted electrolyte contribute to increasing of local electrical barrier. The process start again at a local overpotential with adequate value. The result is formation of a new cluster. The new cluster is linked to his predecessor, that serve as substrate. Due of this presented mechanism of nucleation and growth, we expect that nucleation is a progressive type at start of experiment, followed by a possible deviation to instantaneous nucleation after first seconds.

To establish type of nucleation inside of membrane nanopores, current intensity was recorded during deposition. Typical transients at different applied potential are depicted in Fig. 2. Values of current intensity was divided by working electrode surface in order to obtain current density. We observe an increase of current density at potential application, followed by a rapid initial decreasing. This variation is due of charging of double layer at the electrode surface. We observe also a rapidly increase of current after initial moments, denoting the growth of new phase – the first cluster. After reaching the maximum, current gradually decrease with time, denoting formation of small clusters of chain form Fig. 1. For values of potential lower than 600 mV, deposition not occur. For this value, form of transient is different from higher values denoting a possible other mechanism of nucleation, closed to instantaneous nucleation. In this case, formation of more nuclei and simultaneous growth of all is possible.

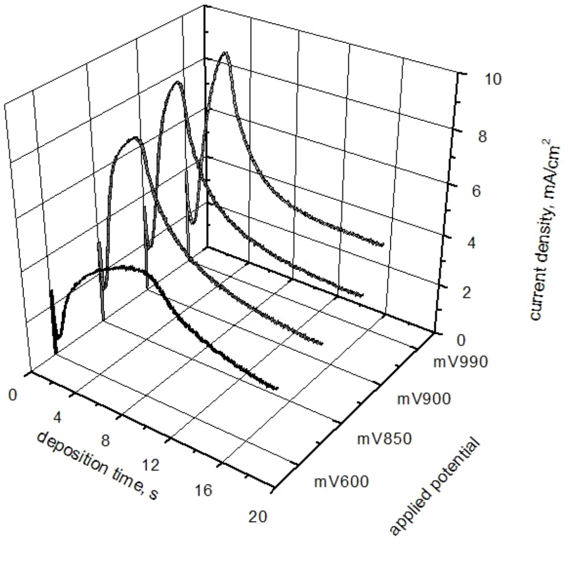

Fig.2. Potentiostatic transients at various applied potential.

Most reliable for determination of nucleation type are normalized transients, $(i/i_{max})^2$ versus (t/t_{max}). Normalized values were compared with those obtained from plotting theoretical curves given by eq. (5) and (8).

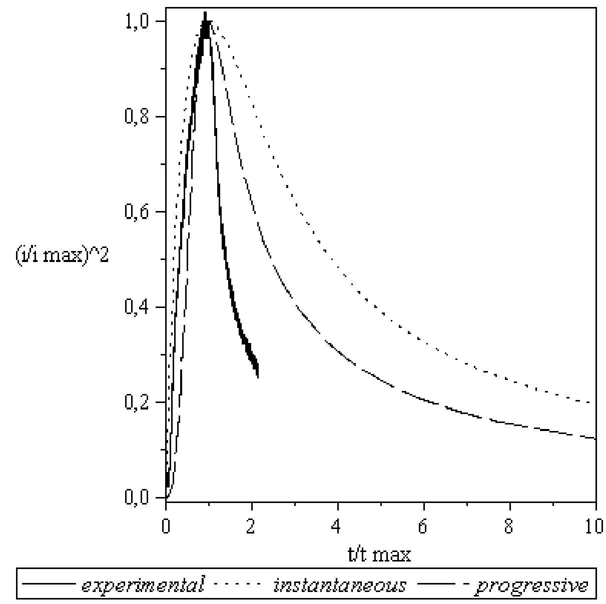

Fig. 3. Reduced experimental data (continuous curve) and theoretical curves (dash and doted) for 600 mV applied overpotential.

In Fig.3 and Fig.4 we can observe both reduced experimental curve and theoretical curves for two types of nucleation at 600 mV and 850 mV applied potential measured *vs* SCE. From Fig.3 is clearly that electrocrystallisation inside of membranes nanopores is an progressive-type nucleation mechanism before reaching the maximum of current density and a possible alterate nucleation type after the current density maximum.

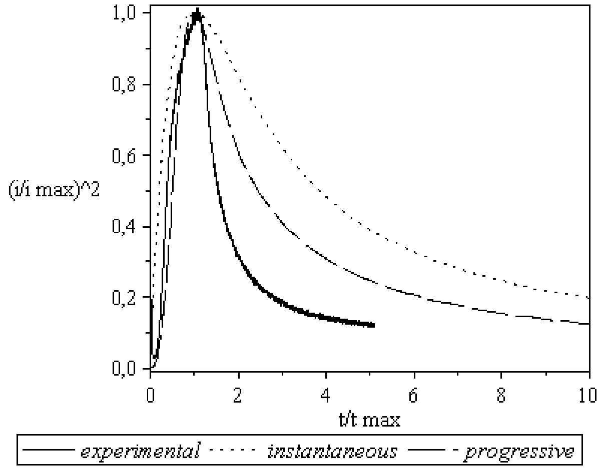

Fig. 4. Reduced experimental data (continuous curve) and theoretical curves (dash and doted) for 850 mV applied overpotential.

Alteration is more clear at low overpotential. For overpotential higher than 990 mV hydrogen reduction occur and current intensity is reduced to very low values. Hydrogen reduction a working electrode reduce possibilities of working electrolyte to fill membrane pores.

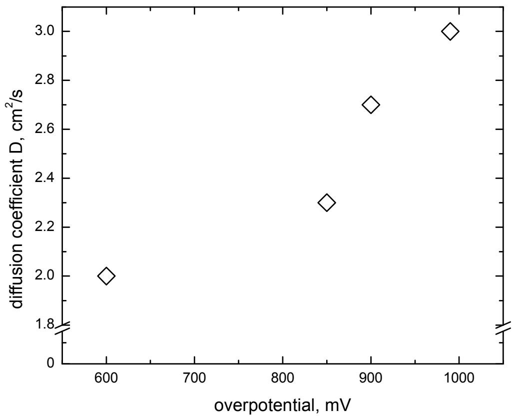

Fig. 5. Calculated diffusion coefficient, D, using Eq.(6) and (7) at different overpotential values.

Calculated value of diffusion coefficient from Eq. (6) and (7) gave us different values, depending of applied overpotential. These values increase with overpotential, as shown in Fig. 5. This increasing is probably due of drift imposed by electric field.

6. Conclusions

Nucleation mechanism is an important factor in nanostructures growth using electrodeposition. Mains nucleation mechanisms are progressive nucleation and instantaneous nucleation. Depend of targeted application for designed nanostructure or nanomaterials, one or other of nucleation type can be favorable. In case of electrodeposition of iron inside of nanosized irregular templates, due reducing of effective electrode surface nucleation inside of nanopore, progressive nucleation is main nucleation mechanism. In this case, only one single nucleus for a single nanopore is possibly created. Applied potential can change this mechanism. Also, temperature and pH can affect nucleation type. Desired crystalline structure of the nanoobject can be obtained controlling these parameters.

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