

Electrochemical Nucleation:

Comparison test of classical and atomistic nucleation models

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Abstract

Classical and atomistic nucleation models have been tested in several aqueous systems dealing with electrocrystallization. A lot of reported experimental nucleation data have been used, and in a wide range of overpotentials. The critical nucleus size has been calculated in those cases not reported in the original work, and the results obtained with the classical and atomistic models have been tabulated, compared and discussed. Small values for the critical nucleus size occur in most of the systems.

Keywords: electrochemical nucleation, classical model, atomistic model, critical nucleus size.

Introduction

Theories of nucleation have been developed along the last decades, from both thermodynamic and kinetic points of view [1-7], since nucleation is an important phenomenon which plays a fundamental role in crystal growth, precipitation and electrocrystallization. The phenomenon of electrocrystallization has been treated by several authors [8-14] and also reviewed recently [15-19]. Nucleation and its control are very important in the formation of nanoparticles and nanostructured materials [20-25], and has also been applied to monolayers of molecular materials [26].

Dependence in between the nucleation rate and the overpotential acting in the system is predicted in the nucleation models. To test the classical models as well the atomistic model of nucleation, several systems have been selected dealing with electrochemical nucleation. One point that deserves attention in the discussions of the different nucleation models is that about the critical nucleus size. In this work this point has been considered and, from the treatment of experimental data, the critical nucleus size has been calculated for different systems, and some discussions are presented.

At first, immediately afterwards, a brief revision of the nucleation models is shown.

Classical Models

In the case of 3D homogeneous or heterogeneous nucleation, the following expressions are obtained for the critical nucleus n^* , under the consideration that the surface of the nucleus is related to the power $2/3$ of the volume:

$$\Delta G(n^*) = \frac{b\omega^2\sigma^3}{(\Delta\mu)^2} F(\theta) = \frac{b\omega^2\sigma^3}{(kT \ln \beta)^2} F(\theta) \quad (1a)$$

$$n^* = \frac{2\Delta G(n^*)}{kT \ln \beta} F(\theta) \quad (1b)$$

where b : shape factor, ω : molecular volume and β : supersaturation ratio. The classical models use macroscopic magnitudes, as the interfacial tension σ , and the nucleus size is treated as a continuous value. The function $F(\theta)$ takes the value of 1 for homogeneous nucleation and depends on the contact angle, or the adhesion energy, between substrate and nucleation phase in the case of heterogeneous nucleation. This function is usually neglected in practise. A proposed solution [16] is to consider σ as an average specific interface energy that takes into account for the interface energy between nucleus and substrate. Under this assumption, the above expressions can be rewritten as:

$$\Delta G(n^*) = \frac{kT B_{3D}}{(\ln \beta)^2} \quad (2a)$$

$$n^* = \frac{2B_{3D}}{(\ln \beta)^3} \quad (2b)$$

$$B_{3D} = \frac{b\omega^2\sigma^3}{(kT)^3} \quad (2c)$$

The kinetic approach to the nucleation process considers that the nucleus formation proceeds in a reversible process by addition and aggregation of individual particles, where some aggregates growth while others redissolve, and some of them reach the critical size. The nucleation rate takes the form:

$$J = Zc^*b^* \quad (3a)$$

$$c^* = N_1 \exp\left(-\frac{\Delta G^*}{kT}\right) \quad (3b)$$

In eq. (3a) Z is the Zeldovich factor, b^* is the probability of a monomer to be incorporated in the critical nucleus, and c^* is the equilibrium concentration of the critical nuclei, expressed by eq. (3b) where N_1 is the monomer concentration. For most of the systems, the nucleation rate can be expressed by a general equation [5]:

$$J = J_o \exp\left(-\frac{\Delta G^*}{kT}\right) = J_o \exp\left(-\frac{B_{3D}}{(\ln \beta)^2}\right) \quad (4a)$$

In eq. (4a) J_o is a practically supersaturation independent term. Then

$$B_{3D} \approx -\frac{d \ln J}{d\left(\frac{1}{(\ln \beta)^2}\right)} \quad (4b)$$

Consequently, from eq. (4b) and (2b) the value of n^* can be calculated.

For ionic solutions, if $\beta=S^v$, where $v=v_++v_-$ and v_+ and v_- represents the number of cations and anions in the molecular formula, respectively, the previous equations can be rewritten as:

$$J = J_o \exp\left(-\frac{B'_{3D}}{(\ln S)^2}\right) \quad (5a)$$

$$B'_{3D} = \frac{B_{3D}}{v^2} \approx -\frac{d \ln J}{d\left(\frac{1}{(\ln S)^2}\right)} \quad (5b)$$

$$n^* = \frac{2B'_{3D}}{v(\ln S)^3} \quad (5c)$$

Atomistic Model

In the atomistic model the critical nucleus size has a discrete character and is not a continuous function of supersaturation. Then, there is a supersaturation interval where the size of the critical nucleus is the same. For the nucleation rate we have the following expressions:

$$J = J_o \exp\left(-\frac{\Phi(n^*) - n^* \Delta \mu}{kT}\right) \quad (6a)$$

$$\Phi(n^*) - n^* \Delta \mu = \Delta G(n^*) \quad (6b)$$

In the atomistic model $\Phi(n^*)$, the excess surface energy, and n^* are constants in a given supersaturation interval and then $\ln J$ depends linearly on $\Delta\mu$ for each interval [6, 27], showing discontinuities when passing from one interval to another. Considering J_0 as a practically supersaturation independent term, we have for each interval:

$$n^* = \frac{d \ln J}{d \ln \beta} \quad (7a)$$

$$m^* = \frac{d \ln J}{d \ln S} \quad (7b)$$

When we deal with electrocrystallization, as $\ln \beta = zF\eta/RT$, where η is the overpotential, we can write [1, 9, 17, 27]:

$$n^* = \frac{RT d \ln J}{zF d \eta} \quad (7c)$$

Results and discussion

As can be seen from eq. (4a) and eq. (6a), nucleation models predict certain dependence between the nucleation rate and supersaturation, but one of the serious problems concerned with nucleation theories is their experimental test. In most of the works the nucleation rate J is obtained. In those systems where the number of nuclei N were reported for an instantaneous nucleation, it was assumed that $J \propto N$ [1, 17] and then similar equations to eqs. (7a-7c) were used. In some cases the nucleation rate can be related to the induction time t_i . The induction time includes the time for nucleation, t_n , and the time for nucleus growth until a detectable size, t_g . When exits a nucleation control $t_n \gg t_g$, and then

$$t_i \approx t_n \propto \frac{1}{J} \quad (8)$$

For a simplicity in the data treatment, it will be assumed that this consideration holds and then, in eqs. (4b), (5b), (7a-7c), the term $d \ln J$ can be substituted by $(-d \ln t_i)$:

$$n^* = -\frac{d \ln t_i}{d \ln \beta} \quad (9a)$$

$$n^* = -\frac{d \ln t_i}{d \ln S} \quad (9b)$$

$$n^* = -\frac{RT d \ln t_i}{zF d \eta} \quad (9c)$$

In most systems, $T=298$ K and thus $RT/F= 0.0257$ V. For the atomistic model, plots of $\ln J$ or $\ln N$ or $\ln t_i$ versus $\ln \beta$ or $\ln S$ or versus the overpotential η were done, and from the slope and the corresponding equations the value of n^* was determined. For the classical model, plots of $\ln J$ or $\ln N$ or $\ln t_i$ versus $1/\ln^2 \beta$ or $1/\ln^2 S$ were treated, and from the slope and the corresponding equations the value of n^* was determined. These models have been tested from experimental systems (Table 1 and Table 2). Table 1 shows the results of both the classical and the atomistic model, meanwhile Table 2 shows the results obtained only with the atomistic model. Some of the reported values have been calculated by the author from original data, but others were yet reported in the original paper.

The values of the critical nucleus size obtained with both classical and atomistic models agree (Table 1) and indicate that a small or very small critical nucleus is formed. This agreement is not strange since from eq. (4b) and eq. (2b) of the classical model it is obtained that $n^*= d \ln J / d \ln \beta$, which coincides with eq. (7a) of the atomistic model. Small values of the critical nucleus were also compiled by Krumm et al. (see Table 1 in ref [37]), with values ranging from 0 to 18, and by Budevski et al. (see Table 4.1 in ref [16]), with values ranging from 0 to 14, for other systems in electrodeposition. The small values of n^* obtained in electrocrystallization are due to the higher supersaturations usually attained in this case and

to the heterogeneous character introduced by the electrode surface, with the presence of defects. These small values seem to reinforce that the atomistic model is more realistic.

Critical nucleus sizes of zero, which appears in some electrocrystallization systems at high overpotentials, can be explained by the presence of active sites on the electrode surface. The active sites play the role of the critical nucleus [10], and when the necessary overpotential or supersaturation is reached, nucleation occurs at these centres. Nanoscopic structural defects, ions, impurity molecules and foreign nanoparticles in the volume of the old phase or on the substrate surface are examples of such active centres [1]. The data in Table 2 clearly show that the higher values for the critical nucleus size occur at single crystals or at well defined crystalline faces, and at low enough overpotentials (systems E, F, K, R, S, U, V and b in Table 2), as a consequence of a lower density of defects in the substrate.

From the plot of $\ln J$ or $\ln t_i$ vs. $\ln \beta$ or η it is seen, in several systems, a change in the slope (systems A and E in Table 1 and systems F, L, P and R in Table 2) that according to the atomistic model indicates a change in the critical nucleus size, but in a discrete way. The existence of nucleus sizes more stable than others is predicted by the atomistic models [2, 6]. Taken into consideration the very small determined critical nucleus size, it seems that magnitudes used by the classical models, as the interfacial tension, are without sense or meaning. But, on the other hand, the sizes predicted by the classical models agree with those of the atomistic model. This result seems to justify the formal use of classical models but the meaning of the magnitudes they use should be revised. Recently, Mostany et al. [60] have considered this point and proposed the temperature dependence of the nucleation rate, the interfacial tension and the exchange current densities as a way to analyse it. Small values of n^* were also obtained by the author [61] in the precipitation of calcium carbonate from supersaturated solutions. It was also observed a linear dependence in the plot of $\ln t_i$ vs. $\ln S$ with a change in the slope at a certain value of supersaturation, indicating a change in the value of n^* , as has been reported here for some systems in electrocrystallization.

From considerations of the atomistic model [8, 17], when the critical nucleus size change $\Delta G(n_1^*) = \Delta G(n_2^*)$, and according to eq. (6b), it is possible to calculate $\Phi(n_1^*) - \Phi(n_2^*)$. Particularly, when n^* change from 1 to 0, the values of $\Phi(1)$ and $\Delta G(1)$ can be obtained. From the systems and values reported in Table 1 and Table 2, the results shown in Table 3 arise. The obtained values of $\Phi(1)$ indicate a certain correlation with the overpotential, being necessary higher overpotentials when the excess surface energy increases. Lower values of $\Phi(1)$ indicate a strong interaction with the substrate, as is the case of electrocrystallization of PbSO_4 on Hg/Pb amalgam (system G in Table 3). Due to the connection between the excess surface energy, of the atomistic model, and the interfacial tension, of the classical models, this low value can be related to a low value of the interfacial tension for this system.

Some studies on nucleation and growth at the initial stages of metal electrodeposition and nanoparticle formation have used Scanning Probe Microscopy (SPM) techniques, as STM and ECSTM [30, 52, 62-65] or AFM [39, 48, 66-67]. These nanometric techniques yield information on an atomic scale and provide a view of the electrodeposition process in a nanometric scale. Aspects such as the spatial distribution of nuclei, 2D or 3D dimensional growth, influence of defects and influence of additives or surface-capping agents, can be undertaken now in a more precise way. In particular, the number of nuclei, or the nucleation rate, as a function of the overpotential can be obtained more precisely with recent fast SPM than using other microscopy techniques as Scanning Electron Microscopy (SEM) [44, 46, 56, 68]. Furthermore, some of these techniques can be applied in-situ. A revision of the impact of these techniques on the analysis of electrochemical nucleation is out of the target of the present work.

Conclusions

It can be concluded that the atomistic model can be applied to the electrochemical nucleation phenomenon, and that small values for the critical nucleus size are obtained. These small values are due to the high attained supersaturations and also to the presence of defects in the electrode surface. The presence of intervals where $\ln J$ depends linearly on $\Delta\mu$, according to the atomistic model, has been observed in several systems.

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Table 1. Critical nucleus size, n^* , calculated in electrocrystallization from both the classical and the atomistic models. Supersaturation expressed as potential or overpotential in V, except for D) and E) where the values between () are expressed as $S=a/a_{\text{sat}}=IAP/K_{\text{SP}}$; ^a values reported in the original paper.

System	Supersat.	n^* clas.	n^* atom.	reference
A) Ag on C	$\eta=0.09-0.24$	3-1 ^a		28
	$\eta=0.09-0.16$		1 ^a	
	$\eta=0.16-0.24$		0 ^a	
B) Cd on Pt	$\eta=0.022-0.038$	5-1		29
C) Cu on Au(111)	$\eta=0.071-0.082$	3-2 ^a	3-2 ^a	30
D) PbCl ₂ on Hg/Pb	$\eta=0.067-0.117$	2-0	1	31
	(190-6720)			
E) PbSO ₄ on Hg/Pb	$\eta=0.025-0.100$	2-0		31
	(7-2450)			
	$\eta=0.025-0.060$		1	
	(7-110)			
	$\eta=0.060-0.100$		0	
	(110-2450)			

Table 2. Critical nucleus size, n^* , calculated in electrocrystallization from the atomistic model. Supersaturation expressed as potential or overpotential in V; ^a values reported in the original paper.

System	Supersat.	n^* atom.	reference
A) Ag on Si	-E=0.8-0.9	1-0 ^a	32
Ag on C	-E=0.7-0.9	1-0 ^a	
B) Ag on C	$\eta=0.110-0.120$	2	33
C) AgO on Ag	E=0.63-0.74	1	34
D) Bi on C	-E=0.1-0.35	0 ^a	35
E) Cd on Cd(0001)	$\eta=0.015-0.045$	5 ^a	36
F) Cd on Si(111)	$\eta=0.015-0.021$ 0.474-0.520	6 1-0	37
G) Co on C	-E=1.2-1.5	0	38
H) Co on C	-E=0.83-0.88	1-0	39
I) Co on C	-E:1.22-1.27	0 ^a	40
J) Cu on n-Si/TiN	-E=0.05-0.25	1-0	41
K) Cu on Pt	$\eta=0.022-0.032$	11 ^a	42
Cu on W	$\eta=0.040-0.055$	4 ^a	
L) Cu on Pd	$\eta=0.040-0.054$ $\eta=0.054-0.082$ $\eta=0.082-0.200$	4 ^a 1 ^a 0 ^a	43
M) Cu on n-GaAs	-E=0.49-0.56	0-1 ^a	44
N) Cu on n-GaAs	-E=0.6-0.9	0 ^a	45
O) Cu on C	E=-0.18-0.10	0 ^a	46
P) Cu on C	$\eta=0.060-0.074$ $\eta=0.074-0.124$	3 ^a 1 ^a	47
Q) Cu on Si(111)	-E=0.50-0.75	0-1	48
R) Hg on Pt	$\eta=0.084-0.094$ 0.094-0.106	10 6	49
S) Hg on Pt	$\eta=0.083-0.093$	5 ^a	50
T) Ni on C	-E=0.93-0.98	1-0	39
U) Pb on Ag(111)	$\eta=0.013-0.019$	11 ^a	51
Pb on Ag(100)		13 ^a	
V) Pb on n-Si(111)	$\eta=0.006-0.010$	11 ^a	52
Pb on HOPG(0001)	$\eta=0.004-0.007$	11	
W) Pt on W	-E=0.54-0.76	0 ^a	53
X) Pt on Ti	-E=0.56-0.68	0 ^a	54
Y) Rh on Au	E=0.2-0	1-0 ^a	55
Z) Rh on PG	-E=0.17-0.30	0 ^a	56
a) Sn on C	$\eta=0.160-0.410$	1-0	57
b) Tl on Si(111)	$\eta=0.003-0.007$	18 ^a	37
c) Zn on C	-E=1.35-1.70	1-0	58
d) Zn on HOPG	$\eta=0.22-0.37$	1 ^a	59

Table 3. Values of $\Phi(n_1^*) - \Phi(n_2^*)$, $\Phi(1)$ and $\Delta G(1)$ for some systems. η is the overpotential at the point of change of n^* , expressed in V.

System	$\Phi(n_1^*) - \Phi(n_2^*) 10^{20}/J$	$\Phi(1) 10^{20}/J$	$\Delta G(1) 10^{20}/J$	η/V	ref. Table n
A) Ag on C	$\Phi(1) - \Phi(0) = 2.6$	2.6	1.1 - 0	0.160	A Table 1
B) Ag on Pt	$\Phi(1) - \Phi(0) = 3.8$	3.8	0.6 - 0	0.240	17
C) Cu on C	$\Phi(3) - \Phi(1) = 4.7$			0.074	P Table 2
D) Cu on Pd	$\Phi(4) - \Phi(1) = 5.2$			0.054	L Table 2
	$\Phi(1) - \Phi(0) = 2.6$	2.6	0.9 - 0	0.082	
E) Hg on C	$\Phi(1) - \Phi(0) = 7.7$	7.7	0.7 - 0	0.242	17
F) Hg on Pt	$\Phi(10) - \Phi(6) = 6.0$			0.094	R Table 2
G) PbSO ₄ on Hg/Pb	$\Phi(1) - \Phi(0) = 1.9$	1.9	1.1 - 0	0.060	E Table 1