Lecture #7

Potentiostatic current transients of a new-phase formation

Goal

This lecture aims to provide an in-depth understanding of current transients observed during the nucleation and growth of a new phase under potentiostatic conditions. Students will learn how to interpret current–time responses to distinguish between instantaneous and progressive nucleation processes and how these processes influence the overall electrochemical kinetics.

Potentiostatic current transients are the measure of current over time during an electrochemical process where the potential is held constant. When a new phase forms on an electrode, the transient current-time plot typically shows an initial rise, reaching a maximum, and then falling off as diffusion becomes the rate-limiting factor. This shape is used to analyze the nucleation and growth mechanisms of the new phase, which can be instantaneous or progressive, and to determine parameters like nucleation rate and ion diffusivity.

To determine the kinetic parameters of electrocrystallization and the mechanism of a new phase formation (nucleation), potentiostatic current transients - chronoamperograms for the electrodeposition of indium on GC electrode in 0.05M $InCl_3$ containing solutions were obtained and given in Figure 1. It can be seen from the chronoamperograms that, at a potential of −0.65V, indium electrodeposition is not observed (Figure 1 A, B). At a potential of −0.70 V, electroreduction of In^{3+} ions occurs and the current maxima are observed (j_{max}=−6.3 mA cm^{-2}; t_{max}=10.61s), which is associated with the overlapping of the diffusion zones of individual crystallites and hemispherical mass-transfer gives way to linear mass-transfer to a effectively planar surface. The further course of the current transients is explained by the diffusion limitation.

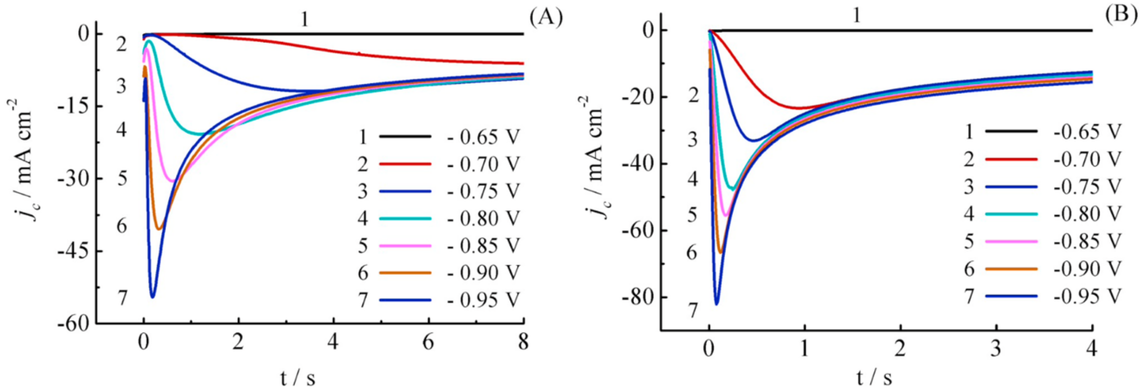


Figure 1. Potentiostatic transients for the deposition of indium on GC electrode. At 35°C temperature from a blank electrolyte (A); from a blank electrolyte +10^{-4} M TBACh solution (B) for different applied potentials [1].

Additions of tetrabutylammonium to deposition electrolyte significantly shift the chronoamperogram maxima to the region of small times (t_{max}=0.93s; j_{max}=−23.3 mA cm^{-2}). The shape of the experimental potentiostatic transients in the nondimensional coordinates (($(j/j_{max})^2$–t/t_{max}) depends on the nature of the rate-determining stage and the type of nucleation. In the case of diffusion-controlled processes, the approach to analyzing the above transients has been developed by B.R. Scharifker and G.J. Hills [2].

Experimental transients are compared in Figure 2A, B to transients calculated according to the Scharifker-Hills (SH) model for **instantaneous** and **progressive** three-dimensional nucleation according to following equations [3]:

$$\frac{j^2}{j_{\max}^2} = \frac{1.9542}{\frac{t}{t_{\max}}}\left\{1 - \exp\left[-1.2564\left(\frac{t}{t_{\max}}\right)\right]\right\}^2$$ **instantaneous**

$$\frac{j^2}{j_{\max}^2} = \frac{1.2254}{\frac{t}{t_{\max}}}\left\{1 - \exp\left[-2.3367\left(\frac{t}{t_{\max}}\right)^2\right]\right\}^2$$ **progressive**

The experimental curves obtained without tetrabutylammonium chloride are in good agreement with a 3D progressive nucleation (Figure 2A). Same type of nucleation has been pointed out with TBACh additives. The stationary nucleation rate – AN_∞ and saturation nucleus density – N_{sat} for 3D progressive nucleation with diffusion control are calculated from the current maxima of the potentiostatic transients [2].

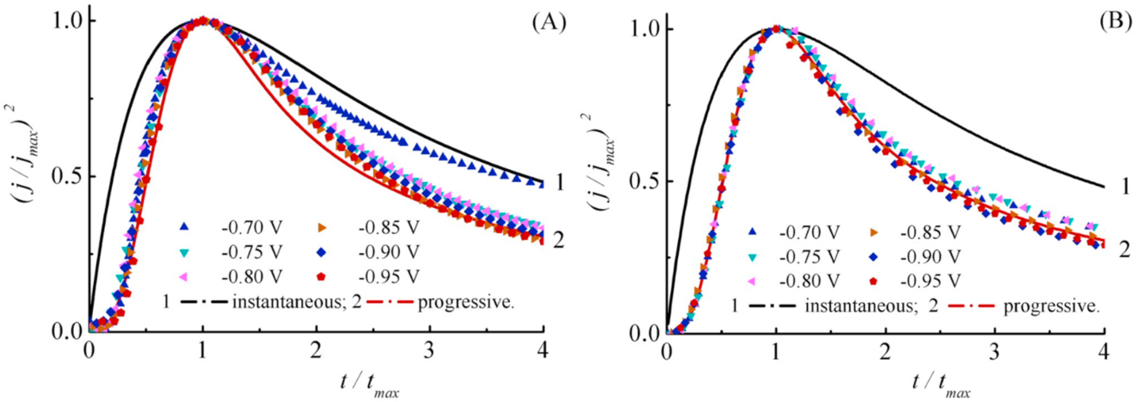
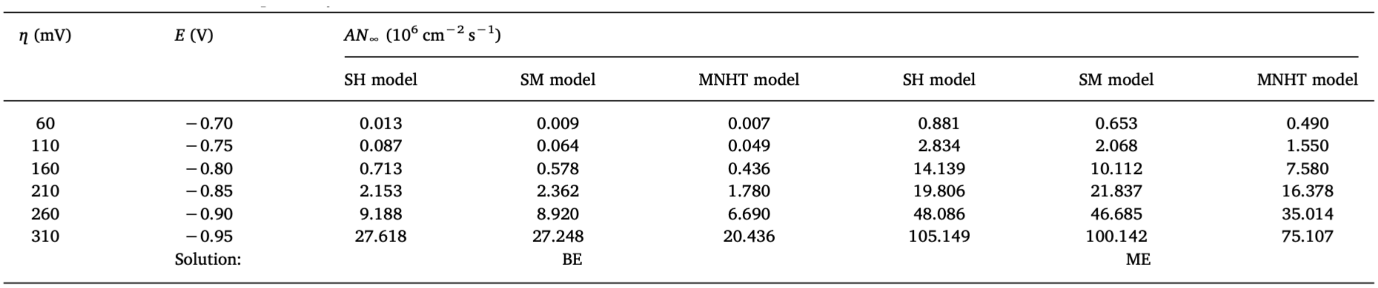


Figure 2. Dimensionless curves, $(j/j_{max})^2$ vs t/t_{max} experimental (the symbols) and theoretical (the solid lines) for instantaneous and progressive for the indium nucleation at 35°C on GC electrode in a blank electrolyte (A) and a blank electrolyte +10^{-4} M TBACh solution (B).

In the SH model, the estimation of the nucleation parameters is based only on one point (t_{max} and j_{max}). For a more accurate assessment of the kinetic parameters of indium crystallization on glassy carbon, more appropriate models have been used, such as the. Scharifker-Mostany (SM)model and the Mirkin-Nilov-Heerman-Tarallo (MNHT) model. According to the literature, the accuracy of the SM model depends on the time interval, and this model well describes theoretical dependence of j vs. t just in the limit. Of a longer time. The MNHT model includes a correction to the SM model for short periods of time.

The values of the stationary nucleation rate, obtained by fitting the theoretically calculated j_c–t curve using the SM and MNHT models are presented in Table 1.

Table 1. Calculated values of the stationary nucleation rate, AN_∞ for the 3D progressive nucleation according to SH model, SM and MNHT models, respectively.



η (mV)	E (V)	AN_∞ (10^6 cm^{-2} s^{-1})					
		SH model	SM model	MNHT model	SH model	SM model	MNHT model
60	− 0.70	0.013	0.009	0.007	0.881	0.653	0.490
110	− 0.75	0.087	0.064	0.049	2.834	2.068	1.550
160	− 0.80	0.713	0.578	0.436	14.139	10.112	7.580
210	− 0.85	2.153	2.362	1.780	19.806	21.837	16.378
260	− 0.90	9.188	8.920	6.690	48.086	46.685	35.014
310	− 0.95	27.618	27.248	20.436	105.149	100.142	75.107
	Solution:		BE			ME	

Learning Outcomes

By the end of this lecture, students will be able to:

1. *Explain the principles of nucleation and growth mechanisms in electrochemical phase formation (related to LO 1.3).*
2. *Analyze potentiostatic current–time transients to differentiate between instantaneous and progressive nucleation (related to LO 2.2).*
3. *Apply mathematical models to describe and interpret electrocrystallization processes during new-phase formation (related to LO 3.2 and 4.2).*

Questions and Self-study Assignments

1. *Define nucleation and growth in the context of electrochemical phase formation.*
2. *Compare instantaneous and progressive nucleation, and illustrate the characteristic current–time transients for each.*
3. *Derive the Scharifker–Hills model and explain how it is used to analyze potentiostatic current transients.*
4. *Solve a numerical problem calculating the number of active nucleation sites from given experimental data.*
5. *Find and summarize one research article applying potentiostatic methods to study metal electrodeposition or thin-film growth.*

References

1. Avchukir, Khaisa, et al. "Influence of tetrabutylammonium chloride on the electrodeposition of indium from chloride solution on a glassy carbon electrode." *Journal of Electroanalytical Chemistry* 842 (2019): 176-183.
2. Scharifker, Benjamin, and Graham Hills. "Theoretical and experimental studies of multiple nucleation." *Electrochimica acta* 28.7 (1983): 879-889.

3. Bekey, Akbayan, Florence Vacandio, and Khaisa Avchukir. "Influence of Acetonitrile on Cu Electrochemical Nucleation and Growth: Preliminary Test of Catalytic Activity for eCO2RR." *Electrocatalysis* 16.3 (2025): 513-525.