# Potentiostatic current transients of new-phase formation

## Lecture 7 | Electrochemical nucleation and crystal growth

Al-Farabi Kazakh National University

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Discipline: Modern research methods in electrochemistry

Educational program: 7M05301 Chemistry

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# Purpose and learning outcomes

## Purpose

Understand how potential-step current transients reveal nucleation, three-dimensional growth, and diffusion-zone overlap.

## By the end, students can

Identify $j_m$ and $t_m$; distinguish instantaneous and progressive nucleation; normalize transients; evaluate model assumptions; interpret additives and overpotential.



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# Lecture trajectory: from signal to mechanism

### 1. Experiment

Potential step and current response

### 2. Physics

Nuclei form, grow, and diffusion fields overlap

### 3. Models

Scharifker–Hills normalization

### 4. Research

Indium deposition ± tetrabutylammonium

### 5. Practice

Fit, compare, and critically interpret

**Applications: electrodeposition • coating quality • catalyst synthesis • battery metal deposition**



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# Physical stages of electrocrystallization

### I. Initial response

Double-layer charging and early electroreduction

### II. Nucleation

Stable nuclei appear at active sites

### III. 3D growth

Hemispherical diffusion zones expand

### IV. Overlap

Mass transport becomes effectively planar

A smooth nucleation maximum may arise from the competition between increasing active area and depletion of reactant near the electrode.



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# Instantaneous versus progressive nucleation

### Instantaneous nucleation

A fixed population of nuclei forms rapidly after the potential step; subsequent current evolution reflects their growth and diffusion-zone overlap.

### Progressive nucleation

New nuclei continue appearing over time, alongside growth of existing nuclei. The early-time current rises more gradually.

**Both models assume idealized 3D diffusion-controlled growth; real surfaces may deviate.**



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# How to read an experimental transient

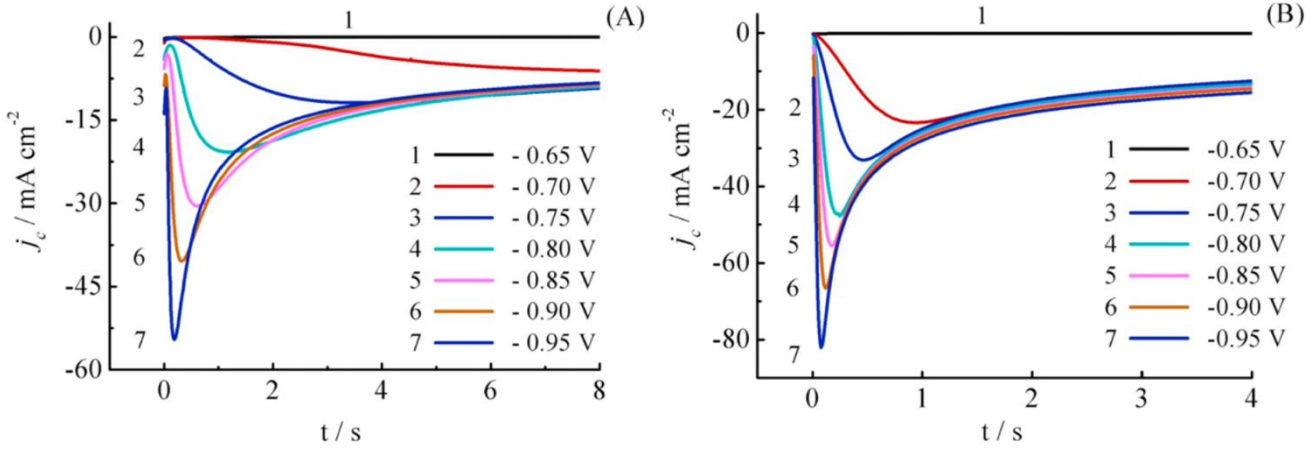


Figure 1. Potentiostatic transients for the deposition of indium on GC electrode. At 35°C temperature from a blank electrolyte (A); from a blank electrolyte +$10^{-4}$ M TBACh solution (B) for different applied potentials [1].

Identify the peak:

- $j_m$ = peak current density
- $t_m$ = time at the maximum
- Early response: charging and nucleation
- Late response: diffusion and possible side reactions

Curves are schematic; peak values are from the supplied lecture.

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.



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# Scharifker–Hills: dimensionless test

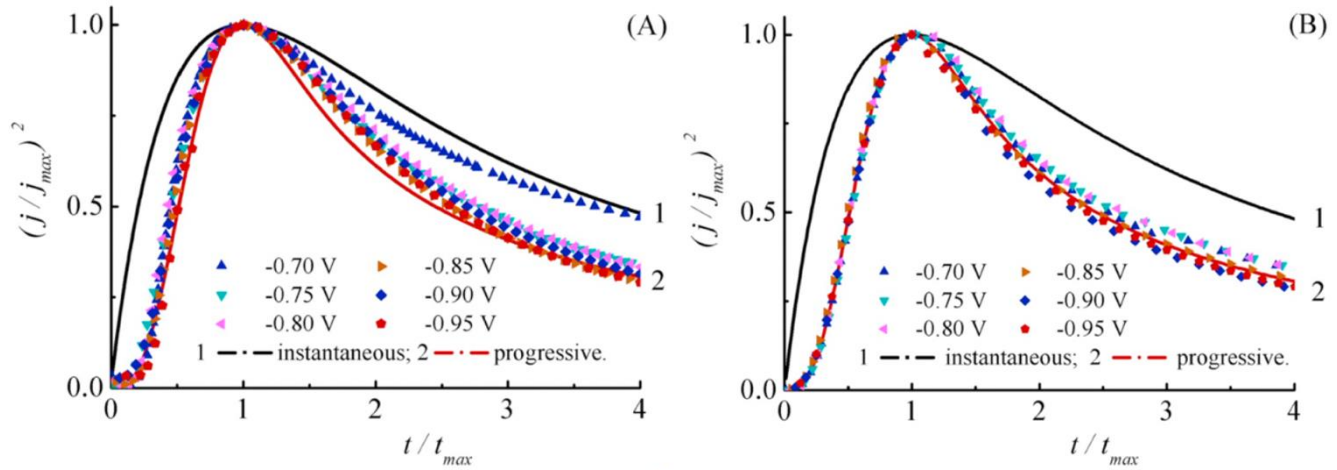


Figure 2. Dimensionless curves, $(j/j_{max})^2$ vs $t/t_{max}$ experimental (the symbols) and theoretical (the solid lines) for instantaneous and progressive for the indium nucleation at 35°C on GC electrode in a blank electrolyte (A) and a blank electrolyte $+10^{-4}$ M TBACh solution (B).

Define $\tau = t/t_m$ and $Y = (j/j_m)^2$.

Instantaneous:

$$Y = (1.9542/\tau)[1-\exp(-1.2564\tau)]^2$$

Progressive:

$$Y = (1.2254/\tau)[1-\exp(-2.3367\tau^2)]^2$$

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# Case study: indium on glassy carbon

- Electrolyte: 0.05 M $InCl_3$; experiments at 35 °C (source lecture).
- At −0.70 V without additive: $|j_m|$ = 6.3 mA $cm^{-2}$; $t_m$ = 10.61 s.
- With $10^{-4}$ M tetrabutylammonium chloride: $|j_m|$ = 23.3 mA $cm^{-2}$; $t_m$ = 0.93 s.
- The reported normalized curves agree most closely with progressive 3D nucleation.
- Interpret additive effects cautiously: adsorption, nucleation-site density, kinetics, and transport can all contribute.


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# Beyond SH: fitting and model limitations

### Scharifker–Hills (SH)

Uses dimensionless transient shape and peak coordinates to classify ideal instantaneous/progressive limits.

### Scharifker–Mostany (SM)

Fits more of the time-dependent response; useful for estimating nucleation parameters under model assumptions.

### MNHT

Includes short-time corrections; assess parameter sensitivity and goodness of fit.

**Critical checks: background subtraction • charging • side reactions • reproducibility • residuals • substrate effects**



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# Conclusions: what the transient can tell us

- Potential-step chronoamperometry probes nucleation, growth, and diffusion in real time.

- A current maximum reflects competing growth of electroactive area and mass-transfer depletion under appropriate conditions.

- Dimensionless SH curves help distinguish ideal instantaneous and progressive nucleation.

- Indium experiments suggest progressive nucleation, with strong transient changes after TBACl addition.

- Mechanistic assignments require controls and full-curve analysis—not peak position alone.



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# Homework and research problems

- 1. Explain why a 3D nucleation transient may exhibit a smooth current maximum.
- 2. Calculate $\tau$ and Y for t = 2.0 s, j = −4.0 mA $cm^{-2}$ when $t_m$ = 10.61 s and $j_m$ = −6.3 mA $cm^{-2}$.
- 3. Plot both SH equations over $0.05 \leq \tau \leq 4$; identify where the models differ most.
- 4. Propose three experiments to distinguish additive-induced nucleation changes from altered mass transport.
- 5. Discuss when an observed current maximum cannot be interpreted using SH theory.

Reading: Scharifker & Hills, Electrochim. Acta 28 (1983) 879–889; Avchukir et al., J. Electroanal. Chem. 842 (2019) 176–183.


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