Lecture #4

Introduction to the kinetics of electrochemical reactions, the slow-discharge theory

Goal

This lecture introduces the fundamental principles of electrochemical kinetics, focusing on the slow-discharge (or rate-determining step) theory. Students will learn to distinguish between thermodynamically feasible and kinetically controlled reactions and to apply rate equations to describe charge-transfer processes at electrode surfaces.

Electrode kinetics describe the rate at which charge transfer occurs across the electrode - electrolyte interface. In an electrochemical system, the overall current is governed by the rate of the elementary step that is slowest within the reaction sequence. When the limiting stage is the electron transfer between an electrode and a redox-active species, the system is under activation control, known as the slow-discharge regime. At equilibrium, oxidation and reduction proceed at equal rates, and the net current is zero. A small deviation from equilibrium potential (the overpotential, η) breaks this balance, and the resulting current density (*i*) is expressed by the Butler–Volmer equation:

$$i \;=\; i_0\,[\,e^{\frac{\alpha nF\eta}{RT}} \;-\, e^{-\frac{(1-\alpha)\,nF\eta}{RT}}\,]$$

(i_0) — exchange current density, characterizing the intrinsic rate of charge transfer;

(α) — transfer coefficient (typically 0.3–0.7);

(n) — number of electrons transferred;

(F), (R), (T) — Faraday constant, gas constant, and temperature.

For systems with small (i_0), a considerable overpotential is required to produce measurable current — the hallmark of slow discharge. The first exponential term $e^{\frac{\alpha nF\eta}{RT}}$, represents the cathodic (reduction) current. The second exponential term, $e^{-\frac{(1-\alpha)\,nF\eta}{RT}}$, represents the anodic (oxidation) current. At equilibrium (η=0), both terms are equal, and the net current is zero — the system is at dynamic equilibrium (oxidation = reduction).

When an overpotential is applied:

A negative η increases the reduction current (cathodic process)

A positive η increases the oxidation current (anodic process)

Small overpotentials (|η| < 10–20 mV):

Both exponential terms can be linearized using the first-order Taylor expansion. The current changes linearly with η — this is the polarization resistance region.

Large overpotentials:

One exponential term dominates and the equation simplifies to the Tafel equation:

$$\eta = a + b \, log i$$

where $b = \frac{2.303 \, RT}{\alpha n F}$ is the Tafel slope.

The Butler–Volmer and Tafel equations describe how the current depends on overpotential when the electron-transfer step controls the rate of an electrochemical reaction. These quantitative relationships are fundamental for understanding activation control at the electrode surface.

However, when we study more complex systems — especially catalytic or EC′-type mechanisms — the electron-transfer kinetics interact with diffusion and chemical regeneration processes. To describe how these effects combine, the ***slow-discharge theory*** was developed.

This theory extends the concept of activation control to a broader picture: it explains how the system gradually transitions from a diffusion-limited regime to a kinetic (catalytic) regime as the electron transfer and subsequent chemical steps become faster. When ions from the solution reach the electrode surface, they must accept or donate electrons to form new species. If this electron transfer occurs slowly, the reaction is said to be under slow-discharge conditions. In this case, the current is small, even if the concentration of ions near the surface is high. As the applied potential becomes more negative (for reduction) or more positive (for oxidation), the rate of electron transfer increases. The current grows until all arriving ions are discharged immediately upon reaching the surface. At this point, the current reaches a steady-state plateau, which reflects the kinetic limit of the system.

This gradual transition from slow to fast electron transfer can be represented by a sequence of kinetic zones:

$$D \rightarrow KT \rightarrow KG \rightarrow K \rightarrow KD \rightarrow KS$$

The kinetic behavior of electrochemical systems can be visualized using a kinetic map (Figure 1), which shows how current response changes as electron-transfer and catalytic steps accelerate.

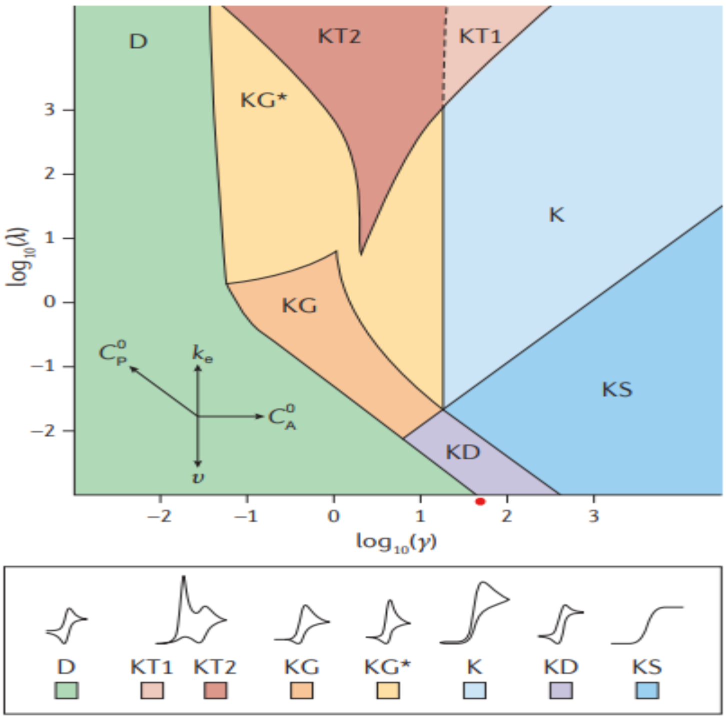

Figure 1. Kinetic map of electrochemical catalytic regimes according to the slow-discharge theory (adapted from Lee et al., 2017).

The theory's purpose is to connect molecular-level reaction kinetics with measurable experimental data such as the shape of cyclic voltammograms (CVs). By interpreting how the current evolves from a narrow diffusion peak (zone D) to an S-shaped catalytic plateau (zone KS), one can determine which process — diffusion, electron transfer, or chemical step — controls the overall rate. The main features of each zone illustrated in Figure 1 are summarized in Table 1 below.

Learning Outcomes

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

1. *Explain the concept of electrochemical reaction kinetics and identify the factors influencing reaction rates (related to LO 1.2).*
2. *Describe the slow-discharge theory and its significance in determining rate-limiting steps in electrode reactions (related to LO 1.2 and 2.3).*
3. *Apply rate laws and kinetic parameters (e.g., exchange current density, transfer coefficient) to analyze experimental data (related to LO 1.2 and 1.3).*

Questions and Self-study Assignments

1. *Define the term rate-determining step and explain its role in the overall kinetics of an electrochemical reaction.*
2. *Derive the relationship between electrode potential and current density using the Butler–Volmer equation for a one-electron transfer reaction.*
3. *Discuss how overpotential and activation energy influence the kinetics of charge transfer.*
4. *Solve a problem involving calculation of reaction rate constants using experimental current–potential data.*
5. *Prepare a short literature review on modern kinetic models extending the slow-discharge theory (e.g., Marcus theory of electron transfer).*

Table 1. Regions of behavior in catalytic voltammetry

Zone	Process Characteristics	Typical CV Shape	Description
D (Diffusion-controlled)	No catalysis; current limited by diffusion	Narrow peak	No chemical step follows electron transfer.
KT1 / KT2 (Kinetic–Transient)	Fast but incomplete catalytic response	Asymmetric peaks	Intermediate regime between diffusion-limited and catalytic behavior.
KG / KG* (Kinetic–Growth)	Growing catalytic current	Extended waves	System has not yet reached steady-state; mixed kinetic-diffusion control.
K (Kinetic)	Steady catalytic current	High current, no peak	Reaction rate governed by catalyst regeneration kinetics (k_{obs}).
KD (Kinetic–Diffusion transition)	Transition region between kinetic and diffusion control	S-shaped curve	Balance between diffusion and catalytic reaction rate.
KS (Steady-state catalytic region)	Catalytic plateau current	Ideal S-shaped wave	Current independent of scan rate; determined solely by catalytic kinetics.

In practice, the slow-discharge theory provides the conceptual basis for analyzing EC′-type mechanisms and for extracting the observed rate constant ($k_{o\beta_s}$) from catalytic plateau currents. It therefore links theory and experiment, helping researchers understand and quantify the kinetics of electrochemical catalysis.

References

1. Lee K. J. et al. Electrochemical and spectroscopic methods for evaluating molecular electrocatalysts //Nature Reviews Chemistry. – 2017. – T. 1. – №. 5. – C. 0039