Lecture #5

Mechanism of the electrochemical reactions

Goal

This lecture focuses on understanding the stepwise mechanisms of electrochemical reactions, including electron transfer, chemical transformations, and coupled processes at the electrode interface. Students will learn how to identify intermediates, determine rate-determining steps, and interpret experimental data to propose plausible reaction pathways.

Electron transfer processes are at the center of the reactivity of inorganic complexes. Molecular electrochemistry has become a central tool of research efforts aimed at developing renewable energy technologies.

Cyclic voltammetry (CV) is a powerful and popular electrochemical technique commonly employed to investigate the reduction and oxidation processes of molecular species. CV is also invaluable to study electron transfer-initiated chemical reactions, which includes catalysis.

Several processes can give rise to voltammograms more complicated than the data seen for simple, reversible, one-electron transfer reactions. In the simplest cases, the voltammogram is modified by **slow electron transfer** or multielectron transfers, and cyclic voltammetry can provide useful information for these pure electron transfer reactions. Further, when electron transfers are **coupled to chemical reactions**, cyclic voltammetry can provide kinetic and **mechanistic information**.

In many cases, these coupled reactions can be related to a specific type of mechanism that has been previously described; as such, careful examination of a voltammogram can assist in diagnosing which homogeneous reaction mechanism is occurring as well as the kinetics of these reactions. The notation used to describe various coupled reaction scenarios deserves a brief explanation: ***E*** indicates an electron transfer step, ***C*** indicates a homogeneous chemical reaction (a chemical step). In addition, the subscript ***r*** indicates reversibility, and subscript ***i*** indicates irreversibility. Each reaction is described for the reduction of the analyte Ox to Red. The same concepts can be readily extended to oxidative reactions.

When **electron transfer** at the electrode surface is slow compared to **mass transport**, the process is termed “electrochemically **irreversible**.” As a result, peak-to-peak separation is larger than the 57 mV anticipated for an electrochemically reversible one-electron redox couple.

Many metal complex compounds can undergo multiple reversible redox processes. The voltammogram appearance is dependent upon the difference in formal potential of the two electrochemical steps.

$$\mathrm{Ox} + e^- \rightleftharpoons \mathrm{Red}$$
$$\mathrm{Red} + e^- \rightleftharpoons \mathrm{Q}$$

If the second electrochemical step is thermodynamically more favourable than the first, the voltammogram appears identical to a Nernstian two-electron transfer, and the peak-to-peak separation (ΔE_p) will be 28.5 mV instead of the 57 mV predicted for a one-electron process. As the second electron transfer becomes less thermodynamically favourable, ΔE_p grows until it reaches a maximum value of just over 140 mV; at that point, the wave separates into two resolvable waves, each with ΔE_p = 57 mV (Figure 1). See reference 28 for an experimental example of a two-electron wave in the voltammogram of an inorganic complex.

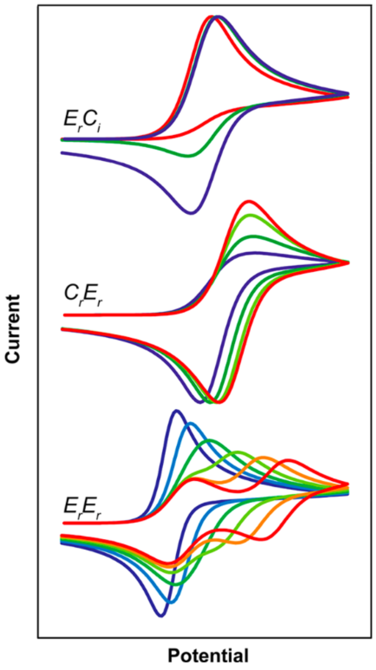

Figure 1. Examples of voltammograms modeled using DigiElch simulation software for three common mechanisms. **E_rC_i mechanism:** increasing the scan rate (from υ = 0.1 (**red**) to 1 (**green**) to 10 V s^{-1} (**blue**)) restores

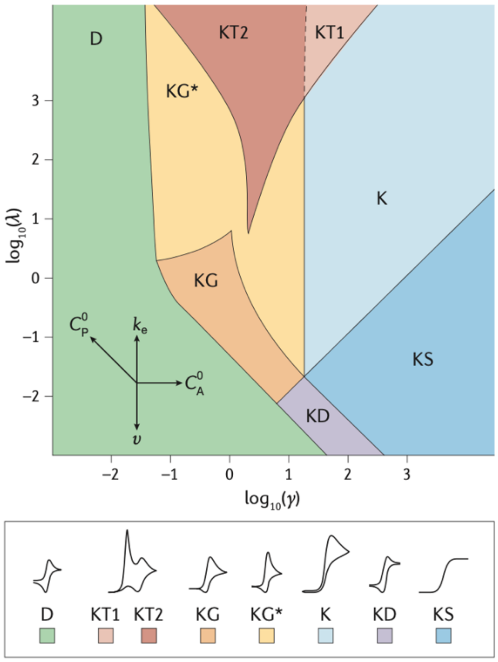

Figure 2. Kinetic zone diagram describing the expected voltammetric responses for electrocatalysts operating by a EC' mechanism.

To move between the zones, the kinetic parameter λ and excess factor γ must be tuned by changing reversibility (rate constant for the C_i step $k = 5\ s^{-1}$).

C_rE_r mechanism: the faster the forward rate constant of the C_r step, the more reversible the voltammogram ($K_{eq} = 0.1$, $k_f = 1$ (blue), 10 (**dark green**), 100 (**lime green**), 1000 s^{-1} (**red**)).

E_rE_r mechanism: as the separations between the two reduction potentials ($\Delta E_{1/2}$) decreases, the peaks merge to become a single two-electron peak. $\Delta E_{1/2} = -0.05$ (**dark blue**), 0 (**light blue**), 0.05 (**dark green**), 0.1 (**lime green**), 0.15 (**orange**), and 0.2 V (**red**) [1].

parameters according to the compass rose.
The parameters include initial catalyst concentration (C_P^0), the initial substrate concentration (C_A^0), scan rate (υ), and the rate constant for homogenous electron transfer from the reduced catalyst to the substrate (k_e). EC' denotes a one-electron, one-substrate catalytic system [2].

The simple case of a reduction followed by an irreversible chemical reaction is the **E_rC_i mechanism**

$$\mathrm{Ox} + e^- \rightleftharpoons \mathrm{Red}$$
$$\mathrm{Red} \rightarrow^{k} \mathrm{Z}$$

A slow homogeneous chemical reaction (compared to the electron transfer) results in a voltammogram that appears reversible, because the amount of Red that reacts to form Z is negligible (Figure 1). As the rate constant (k) of the homogeneous reaction increases, the amount of Red consumed in the chemical reaction increases, thereby moving the system from equilibrium and leading to a non-Nernstian response. The ratio of the anodic to cathodic peak currents decreases because the reduced species Red is consumed by the subsequent chemical reaction, resulting in fewer species to oxidize on the anodic scan.

Experimentally, the response can be modified by varying the scan rate. As the scan rate is increased, the time scale of the experiment competes with the time scale of the chemical step, and more Red is left for reoxidation. For sufficiently fast scan rates, the electrochemical feature will regain reversibility as oxidation outcompetes the chemical reaction.

Another simple case is the **C_rE_r mechanism**

$$\mathrm{Z} \rightleftharpoons \mathrm{Ox}$$
$$\mathrm{Ox} + e^- \rightleftharpoons \mathrm{Z}$$

In this example, the amount of Ox available for the reduction is dictated by the equilibrium constant of the first step. The greater the equilibrium constant, the more reversible the voltammogram (Figure 1). In the extreme case where the equilibrium constant is so large as to be considered an irreversible reaction, the voltammogram becomes completely reversible.

Another example of electrochemical reaction mechanism explanation in electrocatalysis application is given in Figure 2 and discussed in [2].

Learning Outcomes

1. *By the end of this lecture, students will be able to:*
2. *Explain the general principles governing electrochemical reaction mechanisms and distinguish between simple and complex electrode processes (related to LO 2.1 and 2.3).*
3. *Describe various types of coupled chemical and electrochemical reactions (e.g., EC, CE, ECE mechanisms) (related to LO 2.3).*
4. *Analyze experimental data from voltammetric or kinetic studies to infer reaction mechanisms and identify intermediates (related to LO 2.2 and 2.3).*

Questions and Self-study Assignments

1. *Define and classify electrochemical reactions according to their mechanism (e.g., charge transfer, adsorption, catalytic, or coupled chemical reactions).*
2. *Explain the differences between EC and CE mechanisms with the help of reaction schemes.*
3. *Interpret a given cyclic voltammogram to identify evidence of a coupled chemical step.*
4. *Solve a kinetic problem illustrating how the rate of a chemical step affects the shape of a voltammetric curve.*
5. *Review one research paper that investigates an electrochemical reaction mechanism and summarize the analytical methods used to determine the mechanism.*

References

1. Elgrishi, Noémie, et al. "A practical beginner’s guide to cyclic voltammetry." *Journal of chemical education* 95.2 (2018): 197-206.
2. Lee, Katherine J., et al. "Electrochemical and spectroscopic methods for evaluating molecular electrocatalysts." *Nature Reviews Chemistry* 1.5 (2017): 0039.