Lecture #8

Fundamentals of the polarization methods. Potential sweep methods.

Goal

This lecture introduces the fundamental principles of polarization methods and potential sweep techniques used to investigate electrochemical systems. Students will learn how potential sweep methods, including linear and cyclic voltammetry, provide valuable insights into electrode kinetics, diffusion control, and reaction mechanisms.

Polarization methods in electrochemistry involve applying an external potential or current to an electrode and measuring the system's response (current or potential) to study reaction kinetics, mechanisms, and material properties like corrosion resistance. The goal is to induce a deviation, or overpotential, from the natural equilibrium state of the electrode.

The core principles of polarization methods are rooted in the relationship between electrode potential and current density, described by the Butler-Volmer equation, and mass transfer processes.

Measurements typically use a three-electrode cell: a working electrode (where the reaction of interest occurs), a reference electrode (for potential control and measurement), and a counter (auxiliary) electrode (to balance the current). A potentiostat or galvanostat is used to control the potential or current, respectively.

The results of polarization measurements are typically plotted as a current-potential curve (voltammogram), which provides kinetic and thermodynamic information about the electrochemical system.

Potential Sweep Methods

Potential sweep methods (also known as potentiodynamic methods) are a type of polarization technique where the potential of the working electrode is varied linearly with time, and the resulting current is measured. The main potential sweep methods include:

- **Linear Sweep Voltammetry (LSV).** The electrode potential is scanned linearly at a constant rate from an initial potential to a final potential (in one direction). It produces a current peak (or trough) at the potential where the analyte begins to be oxidized or reduced. The peak current is proportional to the concentration of the species, and the peak potential can provide information about the reaction kinetics (especially for irreversible systems).
- **Cyclic Voltammetry (CV).** The potential is swept linearly from an initial potential to a switching potential, and then the sweep direction is reversed back to the initial potential, often repeating the cycle multiple times. CV is highly versatile and provides significant information about reaction mechanisms, reversibility of reactions, stability of reaction products, and diffusion coefficients. Reversible systems show distinct oxidation and reduction peaks with a specific potential difference.
- **Potentiodynamic Polarization (PDP) Test.** This method is widely used in corrosion studies. The potential is scanned over a wide range (e.g., ±500 mV from the corrosion potential) while the current is measured. It determines parameters like the corrosion potential, corrosion current density, Tafel slopes, and the susceptibility to localized corrosion (pitting) by analyzing the current-potential curve (Tafel plot).

Other advanced potential sweep methods often use pulse techniques superimposed on a linear or stepped potential, such as **Differential Pulse Voltammetry** (DPV) and **Square Wave Voltammetry** (SWV), to improve sensitivity and detection limits.

A typical LSV response curve for the anthracene system considered in Lecture #6 is shown in Figure 1 b. If the scan is begun at a potential well positive of $E^{0'}$ for the reduction, only nonfaradaic currents flow for a while. When the electrode potential reaches the vicinity of E° the reduction begins and current starts to flow. As the potential continues to grow more negative, the surface concentration of anthracene must drop; hence the flux to the surface (and the current) increases. As the potential moves past E°, the surface concentration drops nearly to zero, mass transfer of anthracene to the surface reaches a maximum rate, and then it declines as the depletion effect sets in. The observation is therefore a peaked current-potential curve like that depicted.

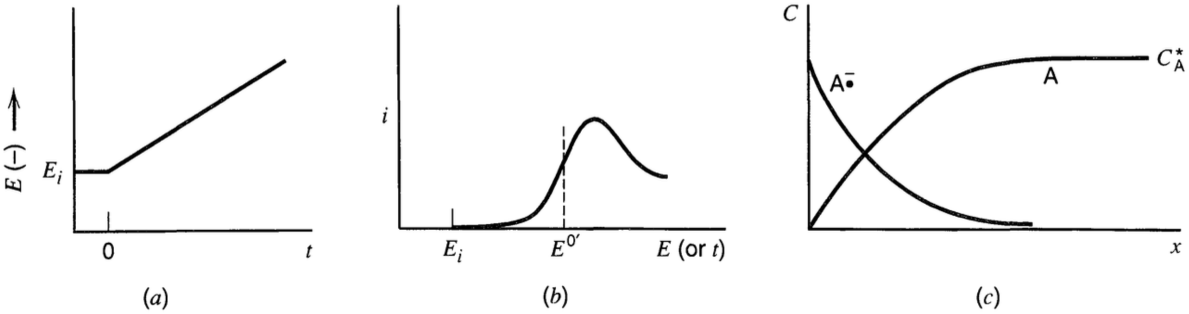

Figure 1. (a) Linear potential sweep or ramp starting at E_i (b) Resulting i-E curve, (c) Concentration profiles of A and A^* for potentials beyond the peak [1].

At this point, the concentration profiles near the electrode are like those shown in Figure 1c. Let us consider what happens if we reverse the potential scan (see Figure 2). Suddenly the potential is sweeping in a positive direction, and in the electrode's vicinity there is a large concentration of the oxidizable anion radical of anthracene. As the potential approaches, then passes, E°', the electrochemical balance at the surface grows increasingly favourable toward the neutral anthracene species. Thus, the anion radical becomes reoxidized and an anodic current flow. This reversal current has a shape much like that of the forward peak for essentially the same reasons.

Cyclic voltammetry (CV) is a reversal technique and is the potential-scan equivalent of double potential step chronoamperometry (Lecture #6). Cyclic voltammetry has become a very popular technique for initial electrochemical studies of new systems and has proven very useful in obtaining information about fairly complicated electrode reactions.

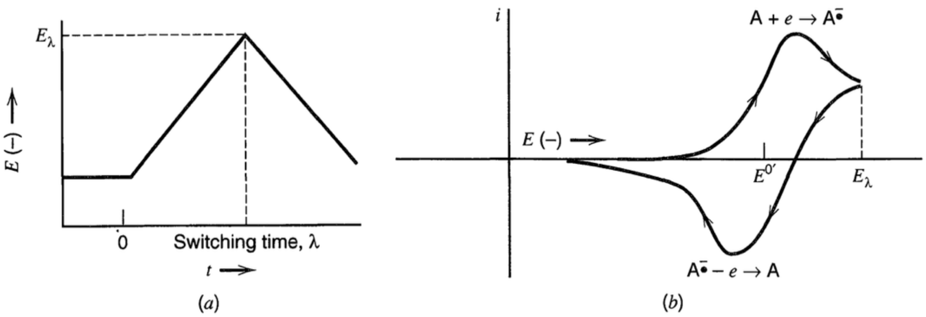

Figure 2. (a) Cyclic potential sweep, (b) Resulting cyclic voltammogram.

An analytical approach based on an integral equation is used here, because it has been widely applied to these types of problems and shows directly how the current is affected by different experimental variables (e.g., scan rate and concentration). However, in most cases, particularly when the overall reactions are complicated by coupled homogeneous reactions, digital simulation methods (Lecture #6) are used to calculate voltammograms.

Using experimental LSV (Figure 3) and CV (Figure 4) curves a kinetic characteristic of the reaction can be found as demonstrated in work [2].

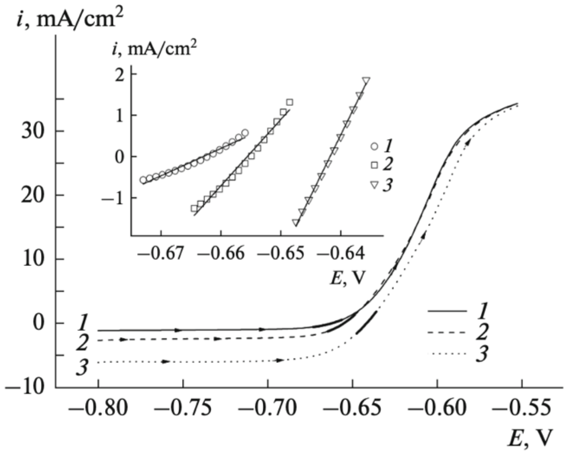

Figure 3. Polarization curves of indium discharge-ionization on indium electrode at 25°C, v = 5 mV/s in 2.0 M NaCl solution with different content of $In(ClO_4)_3$: (1) 0.025 M; 2) 0.050 M; (3) 0.100 M.

Insert: linear segment, region of low overpotentials.

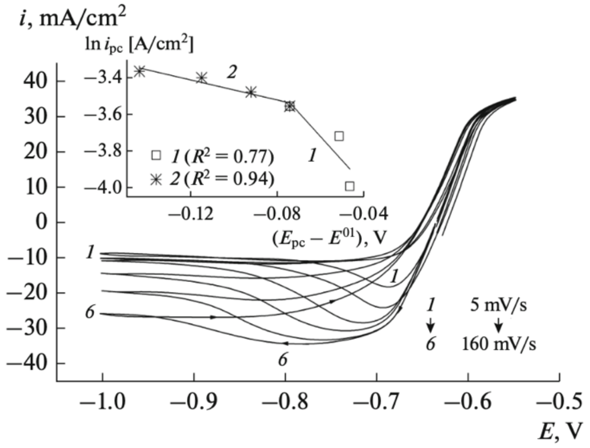

Figure 4. Cyclic voltammograms of indium at 25°C on indium electrode in 0.1 M $In(ClO_4)_3$+ 2.0 M NaCl solution at different polarization rates.

Insert: dependence of $\ln(i_{pc})$ on $(E_{pc}-E^{o'})$ at different potential sweep rates: (1) low (5–20 mV/s), (2) high (20–160 mV/s).

Learning Outcomes

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

1. *Explain the theoretical background and objectives of polarization and potential sweep methods (related to LO 1.2 and 1.3).*

2. *Describe the operation and data interpretation of linear sweep voltammetry (related to LO 1.3 and 2.1).*
3. *Analyze polarization curves to identify activation, ohmic, and diffusion-controlled regions in electrochemical systems (related to LO 1.2 and 4.3).*

Questions and Self-study Assignments

1. *Define polarization and explain its role in understanding electrochemical reaction kinetics.*
2. *Describe the differences between linear sweep voltammetry and cyclic voltammetry in terms of technique and information obtained.*
3. *Sketch a typical polarization curve and label its key regions (activation, ohmic, diffusion).*
4. *Solve a problem involving the determination of Tafel parameters from polarization data.*
5. *Read and summarize one scientific article where potential sweep methods were used to study corrosion or battery electrode materials.*

References

1. Bard, Allen J., Larry R. Faulkner, and Henry S. White. Electrochemical methods: fundamentals and applications. John Wiley & Sons, 2022.
2. Avchukir, Kh, et al. "The kinetics of indium electroreduction from chloride solutions." Russian Journal of Electrochemistry 54.12 (2018): 1096-1103.