Lecture #1

Principles of electrochemical measurements, apparatus, and definitions

Goal

This lecture introduces students to the fundamental aspects of electrochemical measurements. It aims to develop an understanding of the key components of an electrochemical cell, fundamental definitions such as potential, current, and charge transfer, and the principles underlying accurate and reproducible electrochemical experiments.

At the foundation of electroanalytical chemistry lies an understanding of core electrochemical concepts that elucidate the interactions between electrons and chemical species. These concepts not only govern the principles of electroanalytical methods but also provide insight into a vast array of electrochemical phenomena.

Key concepts include oxidation and reduction, and electrochemistry is fundamentally based on redox (reduction-oxidation) reactions, where the transfer of electrons between reactants occurs. In a redox reaction, one substance undergoes oxidation (loses electrons) while another undergoes reduction (gains electrons).

The tendency of a chemical species to gain or lose electrons is quantified by its **electrochemical potential**, often represented in volts (V). The Nernst equation relates this potential to the concentrations of the oxidized and reduced forms of a substance:

The Nernst equation is expressed as follows:

$$E = E^0 - \frac{RT}{nF} ln \frac{[Ox]}{[Red]}$$

where, E is the electrode potential; E° is the standard electrode potential; and [Ox], [Red] are concentrations of oxidized and reduced species.

This relationship not only aids in understanding the feasibility of electrochemical reactions but also sets the stage for the development of various analytical techniques based on these reactions.

Electrode is the interface where the electrochemical reactions take place, electrode design and material significantly influence the efficiency and selectivity of electroanalytical methods. Common types include: **working electrode** (WE), where the reaction of interest occurs; **reference electrode**

(RE) maintains a constant potential against which the working electrode is measured; **counter electrode or auxiliary electrode** (CE) completes the circuit by allowing a current to flow (Figure 1).

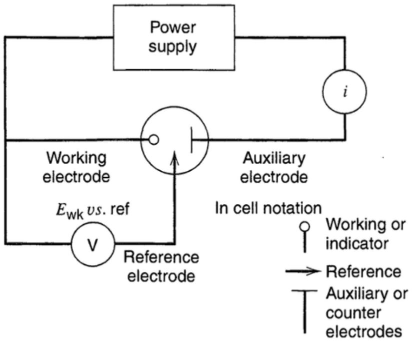

Figure 1. Three-electrode cell and notation for the different electrodes [1].

In experiments where iRs (Ohmic drop) may be high (e.g., in large-scale electrolytic or galvanic cells or in experiments involving nonaqueous solutions with low conductivities), a three-electrode cell (Figure 2) is preferable. In this arrangement, the current is passed between the working electrode and a counter (or auxiliary) electrode. The auxiliary electrode can be any convenient one, because its electrochemical properties do not affect the behaviour of the electrode of interest. It is usually chosen to be an electrode that does not produce substances by electrolysis that will reach the working electrode surface and cause interfering reactions there. Frequently, it is placed in a compartment separated from the working electrode by a sintered-glass disk or other separator. The potential of the working electrode is monitored relative to a separate reference electrode, positioned with its tip nearby [1].

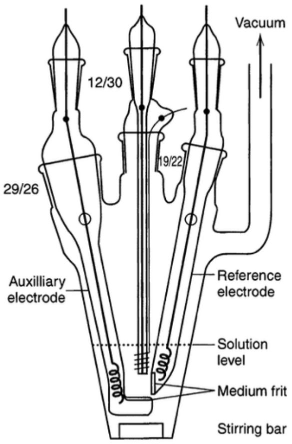

Figure 2. Three-electrode cell designed for studies with nonaqueous solutions at a platinum-disk working electrode, with provision for attachment to a vacuum line [2].

The electrochemical measurements

An investigation of electrochemical behavior consists of holding certain variables of an electrochemical cell constant and observing how other variables (usually current, potential, or concentration) vary with changes in the controlled variables. The parameters of importance in electrochemical cells are shown in following picture (Figure 3). For example, in potentiometric experiments, $i = 0$ and E is determined as a function of C. Since no current flows in this experiment, no net faradaic reaction occurs, and the potential is frequently (but not always) governed by the thermodynamic properties of the system. Many of the variables (electrode area, mass transfer, electrode geometry) do not affect the potential directly.

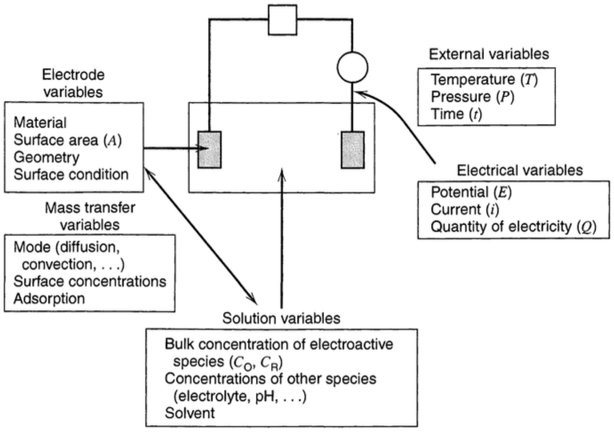

Figure 3. Variables affecting the rate of an electrode reaction.

Another way of visualizing an electrochemical experiment is in terms of the way in which the system responds to a perturbation. The electrochemical cell is considered as a "black box" to which a certain excitation function (e.g., a potential step) is applied, and a certain response function (e.g., the resulting variation of current with time) is measured, with all other system variables held constant (Figure 4).

The **aim of the experiment** is to obtain information (thermodynamic, kinetic, analytical, etc.) from observation of the excitation and response functions and a knowledge of appropriate models for the system.

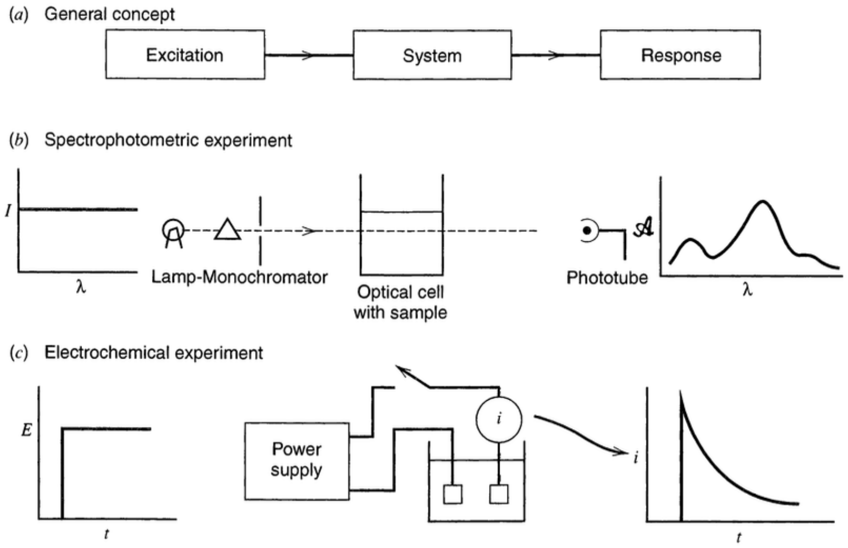

Figure 4. (a) General principle of studying a system by application of an excitation (or perturbation) and observation of response, (b) In a spectrophotometric experiment, the excitation is light of different wavelengths, and the response is the absorbance curve, (c) In an electrochemical (potential step) experiment, the excitation is the application of a potential step, and the response is the observed i-t curve.

Information about an electrode reaction is often gained by determining current as a function of potential (by obtaining i-E curves). Certain terms are sometimes associated with features of the curves. If a cell has a defined equilibrium potential, that potential is an important reference point of the system. The departure of the electrode potential (or cell potential) from the equilibrium value upon passage of faradaic current is termed polarization.

Electrochemical instrumentation generally consists of a potentiostat, for enforcing a controlled potential at an electrode (or a galvanostat, for controlling the current through the cell), along with a function generator, to produce the desired perturbation, and a recording and display system for measuring and presenting i, E, and t. The instrument is connected to the electrochemical cell, typically a three-electrode cell consisting of working, counter, and reference electrodes.

Electrochemical instrumentation, apparatus

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From an electronic standpoint, an electrochemical cell can be regarded as a network of impedances like those shown in the equivalent circuit of Figure 5a, where Z_c and Z_{wk} represent the interfacial impedances at the counter and working electrodes, and the solution resistance is divided into two fractions, R_Ω and R_u, depending on the position of the reference electrode's contact with the current path. This representation can be distilled further into that of Figure 5 b.

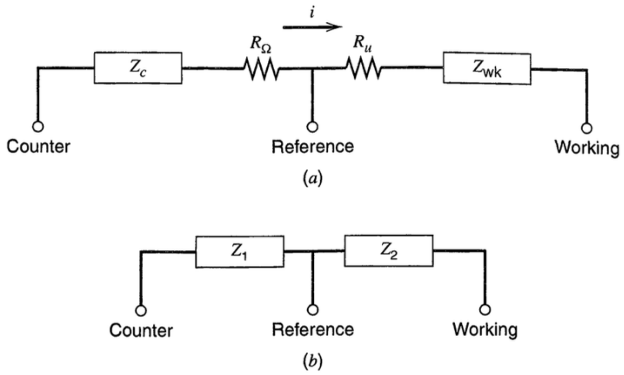

Figure 5. Views of an electrochemical cell as an impedance network tapped by connections to the three electrodes.

The potentiostat of Figure 6 illustrates the basic principles of potential control and will accomplish that task as well as any of several other designs. Its drawbacks concern its input requirements. First, note that neither terminal of the potential source is a true ground; hence the function generator supplying the waveform for potential control would have to possess a differential floating output. Most waveform sources would not meet that demand.

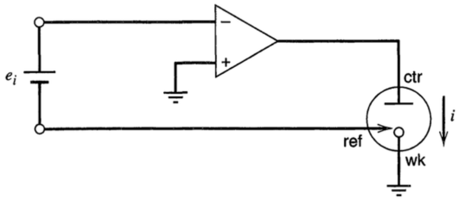

Figure 6. A simple **potentiostat** based on the control circuit of Figure 7.

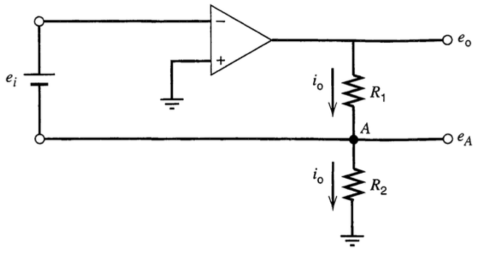

Figure 7. A circuit for controlling the potential at point A regardless of changes in R_1 and R_2. Note that the feedback circuit passes through the voltage source,

which is shown for simplicity as a
battery.

Learning Outcomes

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

1. *Explain the fundamental principles and terminology used in electrochemical systems (related to LO 1.1).*
2. *Identify the main components and functions of electrochemical measurement apparatus (related to LO 1.1 and 1.2).*
3. *Describe procedures ensuring reliable and reproducible electrochemical measurements (related to LO 4.2).*

Questions and Self-study Assignments

1. *Define and differentiate between galvanic and electrolytic cells.*
2. *Explain how reference, working, and counter electrodes function in a typical three-electrode setup.*
3. *Discuss major sources of error in electrochemical measurements and how they can be minimized.*
4. *Prepare a schematic diagram of an electrochemical cell, labeling all essential components.*
5. *Read one recent journal article (published within the last 3 years) that reports new electrochemical measurement techniques and summarize the main methodological advancements.*

References

1. Bard, Allen J., Larry R. Faulkner, and Henry S. White. *Electrochemical methods: fundamentals and applications*. John Wiley & Sons, 2022.
2. A. Demortier and A. J. Bard, /. Am. C hem. Soc, 95, 3495 (1973).