Lecture #6

Basic concepts of potentiostatic measurement

Goal

This lecture introduces students to the fundamental principles and experimental techniques of potentiostatic measurements. Emphasis is placed on the control of electrode potential, recording of current–time responses, and interpretation of data to study reaction kinetics and mechanisms under constant potential conditions.

Potentiostatic measurement is an electrochemical technique where the potential (voltage) of a working electrode is precisely controlled and maintained constant or varied in a defined manner, while the resulting current flowing through the electrochemical cell is measured. This allows researchers to study the specific electrochemical reactions occurring at the working electrode interface.

Figure 1. is a picture of the basic experimental system. An instrument known as a potentiostat has control of the voltage across the working electrode-counter electrode pair, and it adjusts this voltage to maintain the potential difference between the working and reference electrodes in accord with the program defined by a function generator.

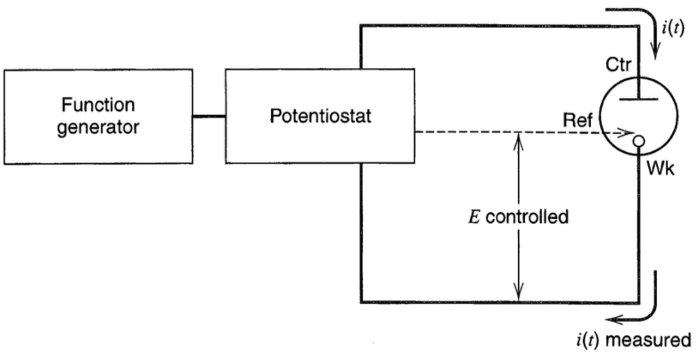


Figure 1. Experimental arrangement for controlled-potential measured experiments [1].

Since the current and the potential are related functionally, that current is unique. Chemically, it is the flow of electrons needed to support the active electrochemical processes at rates consistent with the potential.

Figure 2a is a diagram of the waveform applied in a basic potential step experiment. Let us consider its effect on the interface between a solid electrode and an unstirred solution containing an electroactive species. As an example, take anthracene in deoxygenated dimethylformamide (DMF). We know that there generally is a potential region where faradaic processes do not occur; let E_1 be in this region. On the other hand, we can also find a more negative potential at which the kinetics for reduction of anthracene become so rapid that no anthracene can coexist with the electrode, and its surface concentration goes nearly to zero. Consider E_2 to be in this "mass-transfer-limited" region.

First, the electrode must reduce the nearby anthracene to the stable anion radical:

$$An + e^- = An^*$$

This event requires a very large current, because it occurs instantly. Current flows subsequently to maintain the fully reduced condition at the electrode surface. The initial reduction has created a concentration gradient that in turn produces a continuing flux of anthracene to the electrode surface. Since this arriving material cannot coexist with the electrode at E_2, it must be eliminated by reduction. The flux of anthracene, hence the current as well, is proportional to the concentration gradient at the electrode surface. Note, however, that the continued anthracene flux causes the zone of anthracene depletion to thicken; thus the slope of the concentration profile at the surface declines with time, and so does the current. Both of these effects are depicted in Figure 2b and Figure 2c. This kind of experiment is called chronoamperometry, because current is recorded as a function of time.

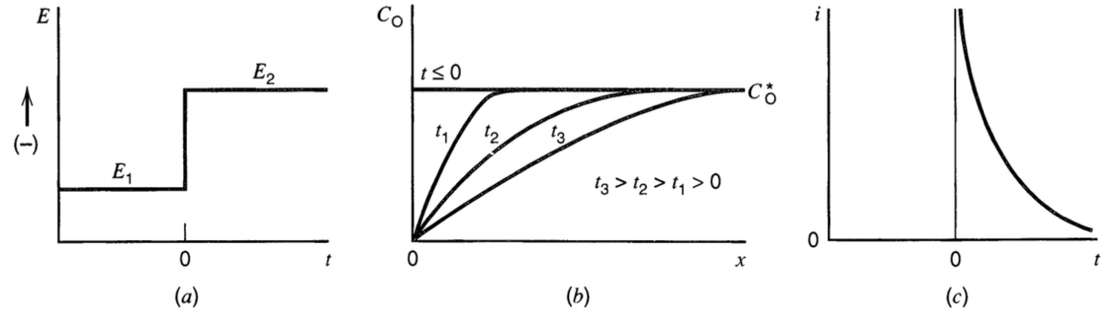


Figure 2. (a) Waveform for a step experiment in which species O is electroinactive at E_1, but is reduced at a diffusion-limited rate at E_2, (b) Concentration profiles for various times into the experiment, (c) Current flow vs. time [1].

For example, the chronoamperometric technique makes it possible to find the kinetic mode of the process in the system studied, calculate the diffusion coefficients and the effective mass-transfer constant [2]. For determining the diffusion coefficients and the mass transfer constant the measured chronoamperograms of indium reduction from chloride electrolytes at the varied concentration of indium salt were used (Figure 3 a).

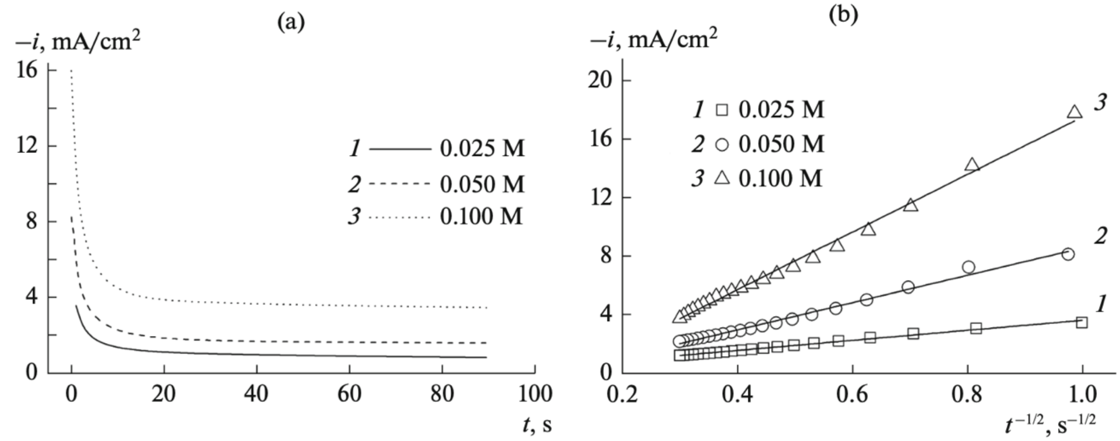
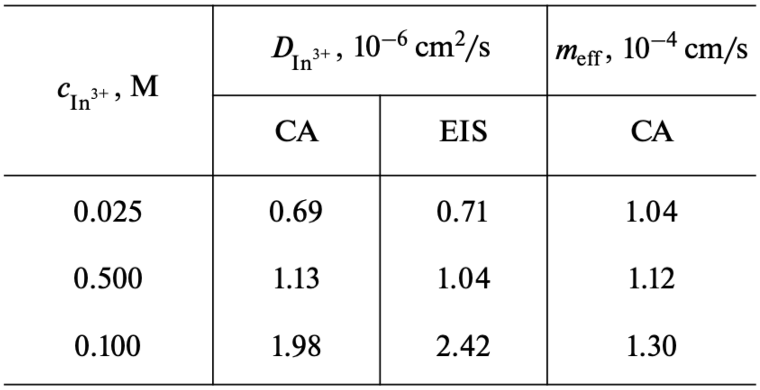


Figure 3. (a) Chronoamperograms of indium electrodeposition at 25°C on indium electrode from 2.0 M NaCl solution with different content of $In(ClO_4)_3$ at E = –0.9 V; (b) the dependence i - $t^{-1/2}$ [2].

The diffusion coefficient of the electroactive substance can be found based on chronoamperametric data from the slope of the line i - $t^{-1/2}$ (Figure 3 b), and calculated values of the diffusion coefficient and an effective mass-transfer constant are given in Table 1.

Table 1. Diffusion coefficient of indium ions and effective mass-transfer constant for electroreduction of indium in 2.0 M NaCl solution obtained by chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) methods [2].



$c_{In^{3+}}$, M	$D_{In^{3+}}$, 10^{-6} cm^2/s		m_{eff}, 10^{-4} cm/s
	CA	EIS	CA
0.025	0.69	0.71	1.04
0.500	1.13	1.04	1.12
0.100	1.98	2.42	1.30

Learning Outcomes

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

1. *Explain the principle of potentiostatic control and describe the function of a potentiostat in an electrochemical system (related to LO 1.3 and 2.1).*
2. *Analyze current–time transients obtained during potentiostatic experiments and relate them to reaction mechanisms (related to LO 1.3 and 2.3).*
3. *Design and conduct potentiostatic experiments for studying electrode kinetics and diffusion processes (related to LO 2.1 and 4.2).*

Questions and Self-study Assignments

1. *Describe the working principle of a potentiostat and explain how potential control is achieved in a three-electrode system.*
2. *Sketch and interpret a typical current–time curve obtained from a potentiostatic experiment.*
3. *Explain how potentiostatic measurements can be used to distinguish between activation-controlled and diffusion-controlled processes.*
4. *Calculate the diffusion coefficient from potentiostatic data using the Cottrell equation.*
5. *Review a scientific publication where potentiostatic methods were used to investigate electrode reactions and summarize the main findings.*

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.