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***Study and Development of Measurement and Acquisition
Circuits for Characterising Potentiostat for Electroplating
Solutions***

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الملخص

يعتبر potentiostat أداة إلكترونية تلعب دورًا مهمًا في الطلاء الكهربائي من خلال تنظيم الإمكانيات المطبقة على الركيزة وتوفير قياسات دقيقة للمعاملات الكهروكيميائية المعنية. في هذا المشروع ، هدفنا هو دراسة وتصميم الدائرة الأساسية لأداة potentiostat. بدأ الجزء المختلف من أداة الجهد الكامل بدائرة قياس الجهد الكهربائي للتيار الذي يمر عبر النظام. يجب أن تقوم الدائرة المصممة المهمة الثانية بمراقبة عملية الطلاء الكهربائي والتحكم فيها. بالإضافة إلى ذلك ، في تحليلنا وتصميمنا الإلكتروني ، أخذنا في الاعتبار قدرة potentiostat على قياس ومراقبة المعاملات الكهروكيميائية التي تساعد في تحليل عملية الطلاء الكهربائي وتحسينها. علاوة على ذلك ، قمنا بنمذجة خلية كهروكيميائية باستخدام نموذج مجمع للعديد من المواضيع في منحنى I-V لإكمال حلقة تحليلنا. أداة تصميم المحاكاة المستخدمة في المحاكاة لدينا هي - PCB Design and Circuit Simulator Software - Proteus.

Abstract

A potentiostat is an electronic instrument that plays a critical role in electroplating by regulating the potential applied to the substrate and providing accurate measurements of the electrochemical parameters involved. In this project, our purpose is to study and design the basic fundamental circuit of potentiostat instrument. The different part of the complete potentiostat instrument began with the potentiostat measuring circuit of the current passing through the system. A second important designed circuit have to monitor and control of the electroplating process. Additionally in our electronic analysis and design we have taken account of the potentiostat's ability to measure and monitor electrochemical parameters aids in the analysis and optimization of the electroplating process. Above this, we have modelized electrochemical cell using a lumped model for several position in the I-V curve to complete the loop of our analysis. The simulator design tool used in our simulation is PCB Design and Circuit Simulator Software – Proteus .

Résumé

Le potentiostat est un instrument électronique qui joue un rôle essentiel dans la galvanoplastie en régulant le potentiel appliqué au substrat et en fournissant des mesures précises des paramètres électrochimiques impliqués. Dans ce projet, notre objectif est d'étudier et de concevoir le circuit fondamental de base de l'instrument potentiostat. Les différentes parties de l'instrument complet du potentiostat commencent par le circuit de mesure du potentiostat du courant passant à travers le système. Un deuxième circuit important a été conçu pour surveiller et contrôler le processus de galvanoplastie. En outre, dans notre analyse et notre conception électroniques, nous avons tenu compte de la capacité du potentiostat à mesurer et à contrôler les paramètres électrochimiques, ce qui facilite l'analyse et l'optimisation du processus de galvanoplastie. En outre, nous avons modélisé la cellule électrochimique à l'aide d'un modèle forfaitaire pour plusieurs positions de la courbe I-V afin de compléter la boucle de notre analyse. L'outil de conception de simulateur utilisé dans notre simulation est le logiciel de conception de PCB et de simulation de circuit - Proteus.

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DEDICATION

This thesis is dedicated to:

my parents, who raised me with a love of science

and supported me in all my pursuits.

my sister and brothers, whom I am truly grateful for

having in my life.

My loving Wife and encouraging family.

My dedication also goes out to everyone with

whose effort the completion of this thesis was made

possible.

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Glossary of Terms

J: is the diffusion flux

D: is the diffusion coefficient

C: is the concentration, **Z** is the distance from the electrode.

J: is the current density

J₀: is the exchange current density

α: is the anodic transfer coefficient

n: is the number of electrons exchanged in the reaction

F: is Faraday's constant

R: is the perfect gas constant

T: is the temperature

η: is the electrochemical overpotential.

E₀: standard potential under standard conditions.

F: Faraday constant (96500 C.mol⁻¹).

n: number of electrons involved.

R: perfect gas constant (8,314 J.mol⁻¹ .K⁻¹).

T: temperature (o K).

n_o: bulk concentration

z: charge on the ion

e: charge on a proton

k: Boltzmann constant

RE: Reference Electrode,

CE: CounterElectrode,

WE: Working Electrode,

R: Summing resistors,

U1: Control amplifier,

U2: Reference buffer amplifier,

R_c: Compensated cell resistance,

R_u: Uncompensated cell resistance.

i: represents the electric current.

V: represents the voltage.

R: represents the resistance.

V_{max}: Maximum scan rate value (Vs⁻¹)

E_w: DAC potential window width (V)

RC_t: DAC RC filter rise time (s)

PWM: Pulse-width modulation

DAC: Digital to analog converter

ADC: Analog to digital converter

General Introduction

Introduction

Electrochemistry is the scientific discipline concerned with the relationship between chemistry and electricity. It describes chemical phenomena coupled with reciprocal exchanges of electrical energy. Electrochemistry includes all the technologies and techniques resulting from its scientific work, such as electrolysis, corrosion, batteries, fuel cells, accumulators, batteries and electroplating . [1]

Today, electrochemistry is playing an increasingly important role at both fundamental and industrial levels. This is due to its low cost and ease of implementation.

Electroplating offers the possibility of obtaining thick deposits with record operating times compared with physical techniques. compared with physical techniques.

Among these devices, we distinguish the potentiostat, a device used in drawing intensity-potential curves which are a very interesting tool to illustrate, for example, corrosion phenomena in aqueous solution.

The purpose of this theses is to give a description of the functional and structural aspects of a potentiostat. This manuscript is divided into three chapters:

- The first chapter is devoted to bibliographical research aiming at the bases of electrochemistry and its techniques.
- The second & third chapter presents the experimental conditions and measurement techniques used in this study. then describe the experimental approach test beds and the electrochemical methods used.
- The final chapter presents and analyses the experimental results obtained during this study.
- We end with a general conclusion summarising the main results obtained.

CHAPTER 1:

THEORETICAL AND TECHNICAL STUDIES OF ELECTRODEPOSITION

1.1 Electroplating

Electroplating is a method that involves imposing an electric current between two or three electrodes immersed in a solution containing a metal salt containing a metal salt of the metal to be deposited. Depending on the processing conditions (electrolysis bath, pH, conductivity, temperature, additives, current density, continuous or pulsed mode, etc.), it is possible to obtain nanometric grain sizes. This production technique may have the disadvantage of incorporating into the coating impurities present in the electrolytic solution. These impurities have a strong influence on the physio-chemical behaviour of the deposit. [2]

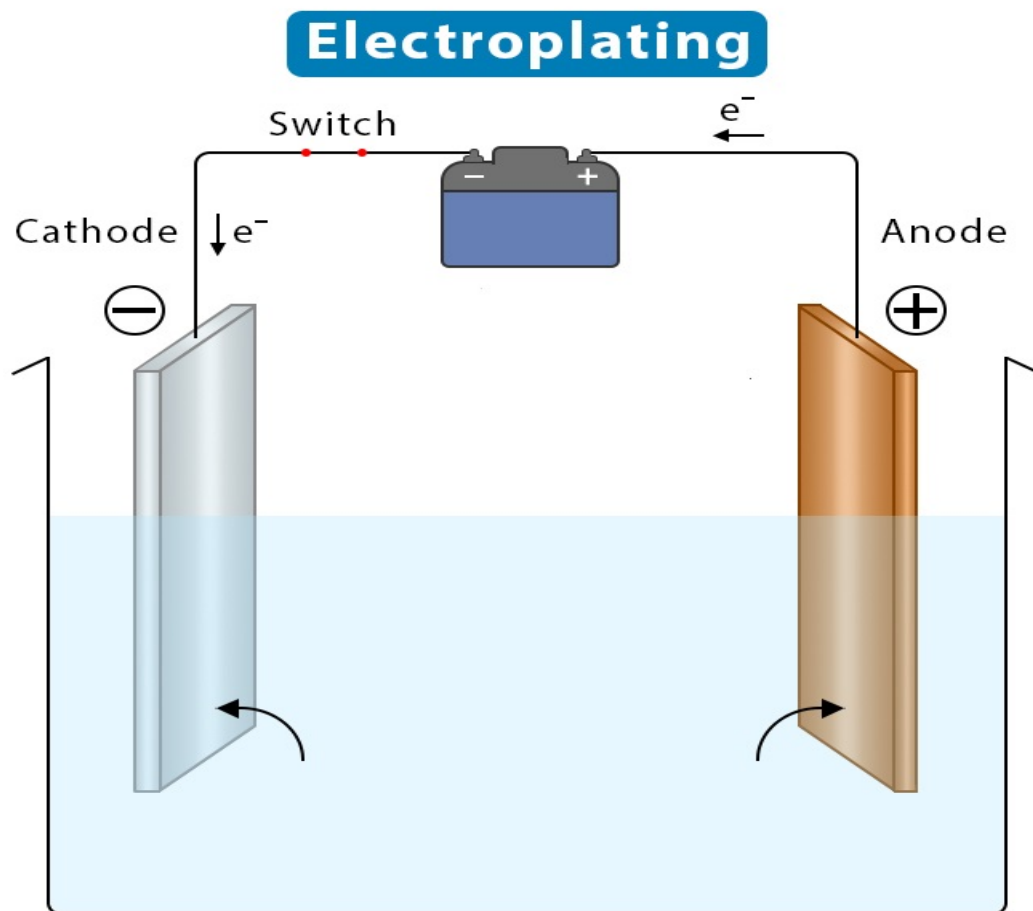


Figure 1.1: Showing anod cathod Electroplating Cell. [3]

1.1.1 Principle of electroplating

The aim of electroplating is to apply a surface layer to a metal to give it the desired properties: aesthetic, magnetic and/or electrical. The principle of electroplating is very simple: it is electrolysis. It involves redox (oxidation-reduction) reactions, which are triggered by a current source. [4]



This electrochemical method is often based on traditional electroplating baths. The electrolysis bath is usually the critical component of the cell.

It contains the appropriate metal salt (sulphates, chlorides or other salts). The substrate (working electrode) on which the deposit is to be made forms the cathode of an electrolytic assembly, the electrolyte in which it is immersed containing positively charged Mn^{+} metal ions.

Polarisation of the electrodes will cause these ions to migrate towards the cathode, substrate. The metal ion is neutralised by the electrons supplied by the cathode and is deposited on the cathode in the form of metal M according to the reaction see figure 1.2

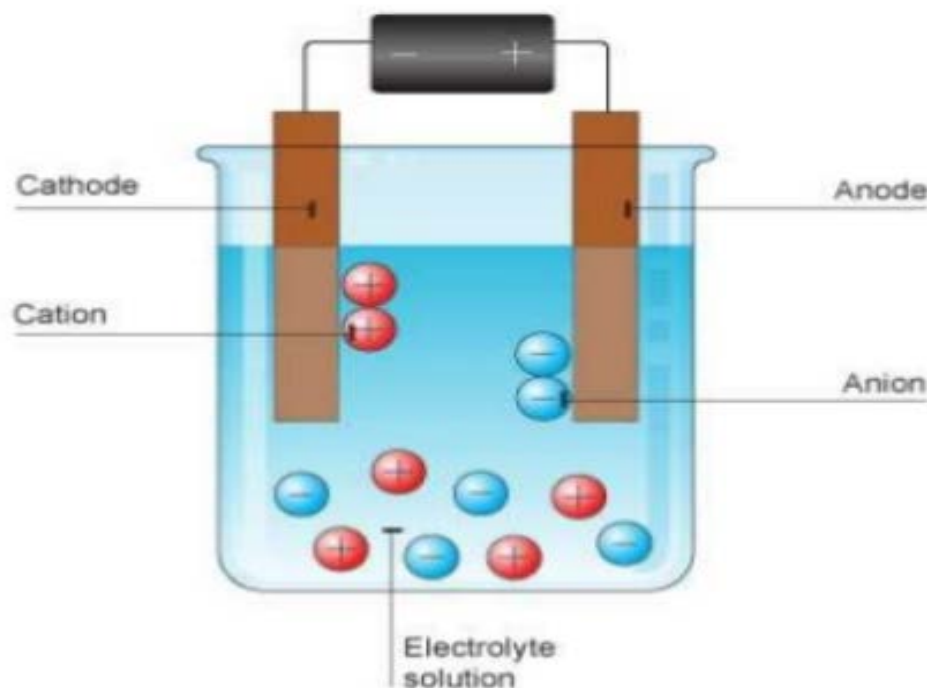


Figure 1.2: Principle of electroplating. [5]

1.1.2 Principle of electroplating and Faraday's law:

When an element of a molar mass M is deposited by electrolysis from its ions or from species in which this element is at the oxidation number n , the value of the mass m deposited during time t can be calculated with the Faraday expression [6]:

$$m = \frac{M.I.t}{n.F} \quad (1.2)$$

where I is the intensity of the electrolysis current used to deposit the metal and F is Faraday's constant. The mass m can be expressed as a function of the density ρ of the metal and the surface S of the substrate

$$m = \rho.S.\varepsilon \quad (1.3)$$

Using the relationship between I and the current density i ($I=iS$), equations 1 and 2 are used to determine the deposition velocity according to the following relation:

$$V = \frac{\varepsilon}{t} = \frac{M I}{n F \rho} \quad (1.4)$$

ε being the thickness of metal deposited for a time t which is deduced from this last relation. Metal anode and cathode When an M metal is in contact with a solution of its ions, two phenomena can occur Atoms of the metal oxidize by each losing n electrons:



The Mn^+ ions then go into solution, while the electrons remain in the metal and an electric current can be extracted from them. The metal is an electrode in this case. By definition, an electrode that is the seat of an oxidation is called an anode.

Electrons from the metal reduce Mn^+ ions in solution and are deposited on the solid as atoms



The metal is in this case the seat of a reduction and the electrode is called cathode.see figure 1.3.

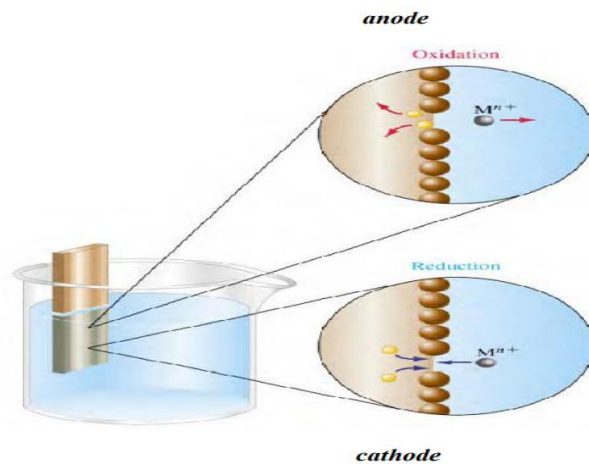


Figure 1.3: Oxidation and reduction reactions. [6]

1.2 Electroplating mechanisms

The electrodeposition of a metal on a substrate is a complex phenomenon composed of a succession of elementary steps in series, the slowest of which determines the overall speed of the process. Electroplating processes include the following steps [7]:

1.2.1 Mass transport

In this process, substances consumed or produced during the electrode reaction are transported from the electrolyte to the electrode surface or from the surface to the electrolyte. The transport of ions in solution can result from:

- Diffusion, which is a movement of species charged or not under the effect of a concentration gradient.
- Migration which is a transport of charged species, created by an electrical potential gradient.
- Convection is a forced or natural movement of fluid. [8]

1.2.2 Crystallization

The adatoms will, during this crystallization stage, either consolidate the crystalline edifice under construction, thus promoting the growth of large crystals, or give birth to new crystallites. If the growth rate of the germs is lower than that of nucleation (germination), the deposit will consist of small crystals. [9]

1.2.3 Other reactions involved in the electrode process

Charge transfer and material transport are not the only decisive steps in electrochemical kinetics, it sometimes comes to meet chemical reactions that take place on the surface of the electrode and that can influence the speed of the reaction as an example electrochemical deposition from a complexed ion. [10]

1.2.4 Temperatures

The rise in temperature produces two opposite effects on the structure of the deposit. It leads to an increase in the diffusion speed, which opposes the depletion of the diffusion layer, thus favouring a fine-grain structure, and a decrease in the overvoltage, and therefore in the cathodic polarisation. However, fine deposits are always accompanied by lifting polarisation, so it is a coarse-grained deposit that tends to form at high temperatures (in general, at medium temperatures, the first action prevails, while at high temperatures, the second predominates). [11]

1.2.5 Organic additives

In electroplating, inorganic additives are used to change the conditions of electrocrystallisation and the properties of electrolytic deposits. These substances can be inorganic anions or cations: Inorganic anions or cations.[11]

Oxides and hydroxides.

- Organic cations (amine).
- Organic anions (sulfuric acid).
- Neutral organic molecules with a large deposition

1.3 Basics of electrochemical

1.3.1 Electrolysis-electrolyte interface

1.3.1.1 Electrolysis

Electrolysis is the chemical transformation of a substance by the passage of an electric current. During electrolysis, ionic species migrate towards the electrodes in the direction of the electrolyte and an electrochemical reaction takes place. Electrolysis is manifested by the circulation of an electric current, the intensity of which can be measured. [12]

1.3.1.2 Electrolyte

An electrolyte is obtained by dissolving or melting a salt, an acid or a base. It consists of a polar solvent (water or organic solvent) and a solute (salt, acid, base). The polar solvent, through the phenomenon of solvation of ions by one or more molecules of this solvent, ensures both the dissolution of the solute and its ionic dissociation into negatively charged anions and positively charged cations. As the electrolytic solution is electrically neutral. [13]

1.3.2 Steps in an electrochemical reaction

1.3.2.1 Mass transfer

It is the transfer of matter from the core of the solution to the surface of the electrode and vice versa. This mode of transport can be classified into three different processes:

- Transport by migration: concerns the movement of ions under the effect of an electric potential gradient, i.e. under the effect of an electric field E .
- Transport by diffusion: concerns the movement of matter under the effect of a chemical potential gradient, i.e. from the most concentrated regions to the least concentrated regions.
- Transport by convection: concerns the displacement of the material under the effect of a gradient of temperature or pressure or mechanical agitation. [14]

1.3.2.2 Chemical reactions

These can include acid-base reactions, complexations and dehydration. These reactions take place before or after the electrode reactions described below.. [15]

1.3.2.3 Surface reactions

These are the phenomena of adsorption, desorption or growth of crystalline germs. [16]

1.3.2.4 Transfer of charges

It is the transfer of electrons to the surface of the electrode and more precisely in the double-layer (the interface area containing the separation of charges). The speed of an electrochemical reaction therefore depends on the speed of the reaction steps. The step that limits the current by its slowness and creates a polarization of the electrode is called the "kinetically limiting step". It is she who imposes the overall speed of the reaction. [17]

1.4 Electrochemical Cell

1.4.1 What is an electrodes?

An “electrode” is any electronic conductor (metal, semiconductor, metalloid) in contact with an electrolyte. The following figure illustrates some examples of electrodes used in electrochemistry. [19]

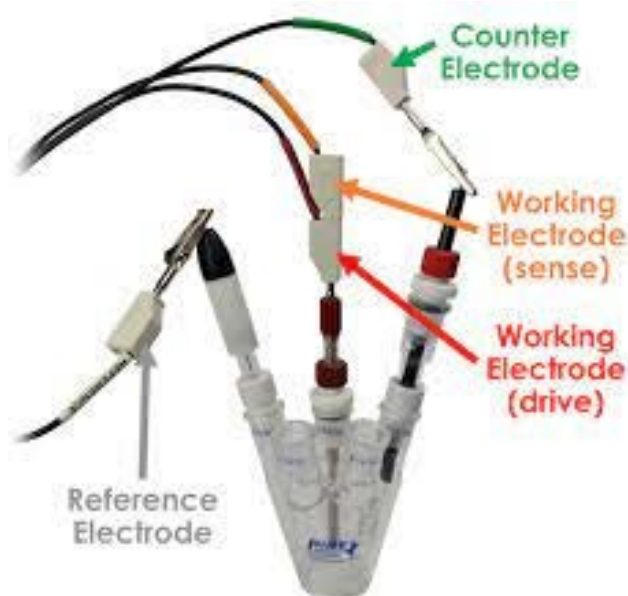


Figure 1.4: Some examples of electrodes. [19]

1.4.2 Different types of electrodes

The electrodes used in electrochemical assemblies can be classified into three categories: measurement (or indicator) electrodes, reference electrodes and working electrodes. [18]

- Indicator electrodes
- References electrodes
- Working electrodes

1.4.2.1 Indicator electrodes

Indicator electrodes are generally ideally polarizable electrodes, that is to say whose potential can be varied (compared to a reference) over a wide range (typically several volts). This implies that, in the absence of electroactive species in solution, the current which crosses the electrode-electrolyte interface remains negligible throughout this range of potential.

The materials used in the production of the indicator electrodes are either noble metals

(platinum, palladium, gold), or certain allotropic forms of carbon (graphite, glassy carbon). However, other materials such as mercury and certain metal oxides (titanium oxide **TiO₂**) are also used but in more restricted potential domains.



Figure 1.5: Photograph of counter electrode. [18]

1.4.2.2 Reference electrodes

Contrary to the indicator electrodes, the reference electrodes must present characteristics allowing them to be ideally non-polarizable, that is to say to keep a constant potential whatever the current which crosses them.

Current reference electrodes are therefore based on redox couples of the form **M|MX_n|X⁻**

Where **M** designates a metal and **X** generally a halogen so that the compound **MX_n** (oxidant of the couple) is insoluble. The two reference electrodes very commonly used in an aqueous medium are:

- The saturated calomel electrode (**SCE**): Hg(l)|Hg₂Cl₂(s)|KCl(sat) (see Fig.2)
- The silver chloride electrode: Ag(s)|AgCl(s)|KCl(sat)

The potential of the reference electrode is defined with respect to the standard hydrogen electrode (**SHE**) considered as the absolute reference electrode for which the potential is zero. The table below gives the values of the potentials at **25°C** of some reference electrodes with respect to the **ESH**.

In certain measurement configurations where space is limited, a pseudo-reference electrode is used, consisting of a simple metal wire (**Ag, Pt**) whose potential should be calibrated by measuring it against a real reference electrode. [17]

Table 1.1: Redox potentials of some reference electrodes in water (25°C).

Électrode de référence	E (V)
$\text{Hg}_{(l)} \text{Hg}_2\text{Cl}_{2(s)} \text{KCl}_{\text{sat}}$ (ECS)	0,24
$\text{Ag}_{(s)} \text{AgCl}_{(s)} \text{KCl}_{\text{sat}}$	0,20
$\text{Hg}_{(l)} \text{Hg}_2\text{SO}_{4(s)} \text{K}_2\text{SO}_{4\text{sat}}$	0,64
$\text{Hg}_{(l)} \text{HgO}_{(s)} \text{NaOH } 0,1\text{M}$	0,93

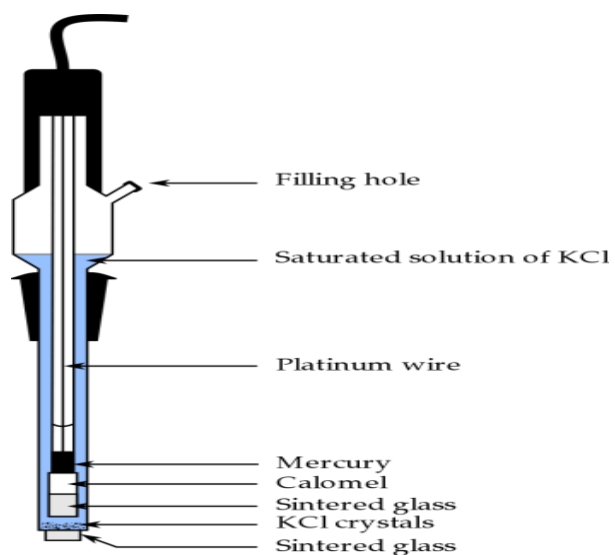


Figure 1.6: Calomel reference electrode schematic.



Figure 1.7: Photo of the reference electrode

1.4.2.3 Working Electrodes (WE)

Common working electrodes can consist of materials ranging from inert metals such as gold or platinum, to inert carbon such as glassy carbon, boron-doped diamond or pyrolytic carbon, and mercury drop and film electrodes. Chemically modified electrodes are employed for the analysis of both organic and inorganic samples. [22]



Figure 1.8: Working electrode

1.5 The electrochemical boundary layer

The electrochemical boundary layer, also known as the diffusion boundary layer, refers to a thin region near the electrode in an electrochemical system where chemical species are transported by diffusion. It forms as a result of the difference in concentration between the electrolyte and the electrode.

In an electrochemical cell, the electrochemical reaction occurs at the interface between the electrode and the electrolyte. When the reaction occurs, chemical species are consumed or produced at the electrode, creating a concentration difference between the electrode surface and the surrounding electrolyte.

The electrochemical boundary layer develops when these chemical species must diffuse to or from the electrode through the electrolyte. Due to diffusion resistance, the concentration of chemical species at the electrode may be different from that of the surrounding electrolyte. The electrochemical boundary layer therefore limits the flow of chemical species to the electrode and plays an important role in the kinetics of electrochemical reactions.

The size of the electrochemical boundary layer depends on various factors such as the rate of the reaction, the properties of the electrolyte, the geometry of the electrode and the experimental conditions. Reducing the thickness of the boundary layer can be achieved by stirring the electrolyte, increasing the surface area of the electrode or increasing the concentration of reactive species in the electrolyte.

Understanding the electrochemical boundary layer is crucial for optimising the performance of electrochemical cells such as fuel cells, batteries and electrochemical sensors. Mathematical models and experimental techniques are used to study and characterise the electrochemical boundary layer in order to improve the efficiency and reactivity of electrochemical systems.

The electrochemical boundary layer is generally divided into two distinct regions: the diffusion boundary layer and the reaction boundary layer. [29]

1.5.1 Diffusion boundary layer

- In this region, the transport of chemical species to the electrode occurs mainly by molecular diffusion.
- The concentration of chemical species gradually decreases as the electrode is approached.
- The concentration profile in the diffusion boundary layer can be represented graphically by a concentration profile as a function of distance from the electrode. This graph is often referred to as the "boundary layer concentration profile" or "diffusion concentration profile".
- The typical concentration profile is usually slope-shaped, with a maximum concentration at the electrode/electrolyte interface and a minimum concentration at the end of the diffusion boundary layer near the electrolyte [30]

1.5.2 Reaction boundary layer

- This region lies just above the electrode and is characterised by rapid consumption or production of chemical species due to electrochemical reactions.
- The reaction boundary layer is often very thin, of the order of a few nanometres.
- Another graph commonly used to represent the reaction boundary layer is the "current density profile". This graph shows the variation in electrochemical current density as a function of distance from the electrode.

➤ In the reaction boundary layer, the electrochemical current density increases rapidly with distance from the electrode, reaching a maximum value at the electrode/electrolyte interface.

To study the electrochemical boundary layer in an electrochemical experiment using a potentiostat, it is important to take into account certain specific conditions.

Here is more detailed information on the specific conditions to be taken into account when studying the electrochemical boundary layer using a potentiostat [36]:

1.5.2.1 Electrode geometry

When choosing the electrode geometry, you need to consider the kinetics of the electrochemical reaction you are studying. For example, disc electrodes are commonly used for fast reactions, while wire electrodes are suitable for slower reactions.

The surface area of the electrode can also influence the boundary layer. A larger surface area can reduce the thickness of the boundary layer and facilitate the diffusion of chemical species. [37]

1.5.2.2 Scanning speed

The potential slew rate is an important parameter to set on the potentiostat. A slow sweep rate allows more efficient diffusion of chemical species through the boundary layer. This can be particularly useful for studying slow reactions or systems where diffusion is limiting.

A fast scan speed can result in a thicker boundary layer and variations in concentration and current density profiles. This can be used to study fast reactions or to generate particular electrochemical regimes, such as the oxidation or reduction of specific reactants. [38]

1.5.2.3 Concentration of chemical species

The concentration of chemical species in the electrolyte can influence the thickness of the electrochemical boundary layer. High concentrations can reduce the thickness of the boundary layer by providing more chemical species available for the electrochemical reaction.

However, excessively high concentrations can also lead to overdiffusion effects, where the reaction becomes rate-limited rather than diffusion-limited. [39]

1.5.2.4 Electrolyte viscosity

The viscosity of the electrolyte can influence the diffusion resistance of chemical species and therefore the thickness of the boundary layer. A high viscosity can lead to a thicker boundary layer, which can have an impact on the kinetics of electrochemical reactions.

Electrolytes with different viscosities can be used to study the effect of viscosity on the boundary layer and adjust the experimental conditions accordingly. [40]

1.5.2.5 Temperature

The temperature of the electrolyte can affect the formation of the electrochemical boundary layer. In general, an increase in temperature increases the mobility of chemical species, which reduces the thickness of the boundary layer.

However, it is important to note that temperature can also have an impact on the kinetics of electrochemical reactions. [41]

1.5.3 Theoretical laws electrochemical boundary layer

There are several theoretical laws that describe the behaviour of the electrochemical boundary layer. Here are some of the most commonly used laws[42]:

1.5.3.1 Fick's law of diffusion

➤ Fick's law of diffusion describes the diffusion flux of chemical species across the boundary layer.see figure1.9.

➤ For a one-dimensional system, Fick's law of diffusion can be formulated as follows:

$$J = -D * \frac{dC}{dz} \quad (1.7)$$

Where:

- J is the diffusion flux
- D is the diffusion coefficient
- C is the concentration, Z is the distance from the electrode.

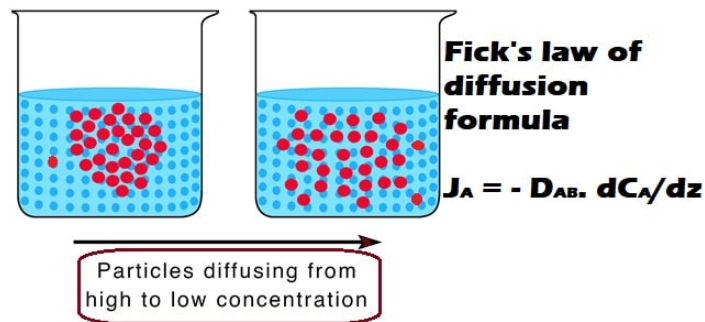


Figure 1.9: showing Diffusion Formula. [42]

1.5.3.2 The Butler-Volmer equation :

The Butler-Volmer equation is used to describe electrochemical reactions at the electrode/electrolyte interface. [43]

It relates the electrochemical current density to the electrode/electrolyte potential difference (see figure1.10) and to the kinetic coefficients of electron transfer. The Butler-Volmer equation is given by :

$$J = J_0 * \left(e^{\frac{\alpha * n * F * \eta}{RT}} - e^{-\frac{(1 - \alpha) * n * F * \eta}{RT}} \right) \quad (1.8)$$

Where:

- J is the current density
- J₀ is the exchange current density
- α is the anodic transfer coefficient
- n is the number of electrons exchanged in the reaction
- F is Faraday's constant
- R is the perfect gas constant
- T is the temperature
- η is the electrochemical overpotential.

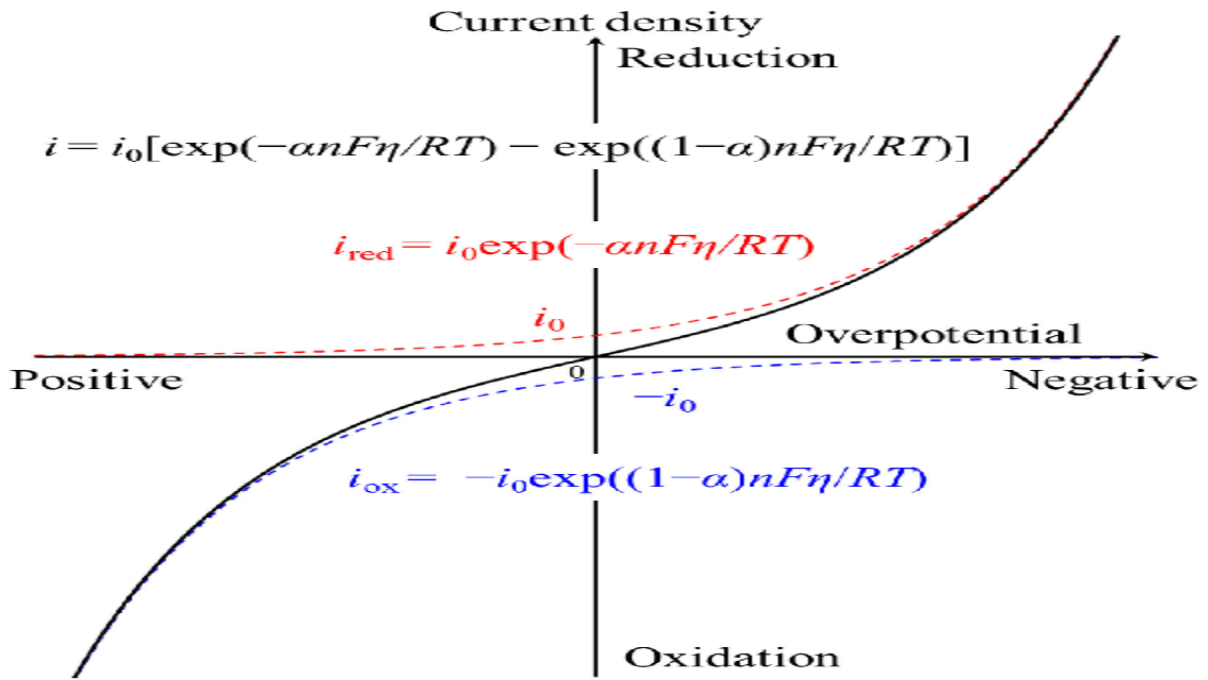


Figure 1.10: Current–potential curves based on Butler–Volmer equation. [43]

1.5.3.3 Nernst relation

The Nernst relation relates the thermodynamic equilibrium potential E of an electrochemical system in solution to its standard potential E^0 and the activities of the Ox and Red pairs involved in the electrode reaction. For an electrode at equilibrium, this relationship is given by[45] :

$$E_{Th} = E^0 + \frac{RT}{nF} + Ln \frac{a_{Ox}}{a_{Red}} \quad (1.9)$$

where :

- E^0 : standard potential under standard conditions.
- F : Faraday constant (96500 C.mol⁻¹).
- n : number of electrons involved.
- R : perfect gas constant (8,314 J.mol⁻¹ .K⁻¹).
- T : temperature (o K).

The production of an electrochemical reaction requires conditions to be met which make the electrode potential different from the equilibrium potential, i.e. the establishment of an electrode overpotential (overvoltage) (see figure 1.11):

$$\boxed{\eta = E - E_{th}} \quad (1.10)$$

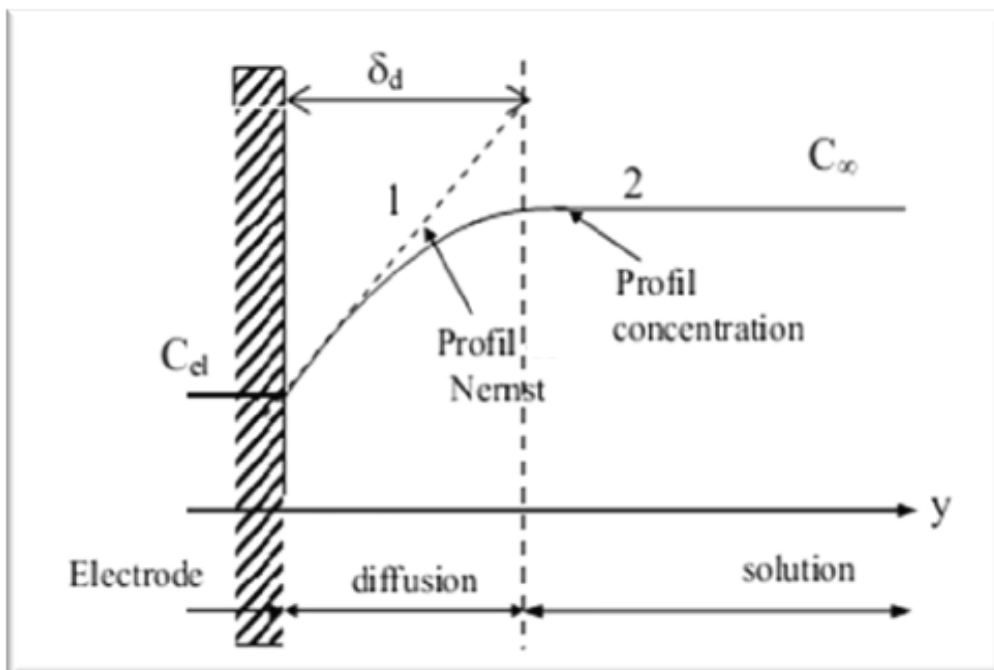


Figure 1.11: Variation in solution concentration as a function of distance from the electrode. [45]

These theoretical laws, combined with appropriate transport and reaction equations, are used to model and study the electrochemical boundary layer in different electrochemical configurations. However, it is important to note that the electrochemical boundary layer is a complex phenomenon and approximations and simplifications are often necessary to obtain analytical or numerical solutions.

1.5.3.4 Helmholtz Double Layer(1879)

This theory is a simplest approximation that the surface charge is neutralized by opposite sign counterions placed at an increment of d away from the surface.

The surface charge potential is linearly dissipated from the surface to the counterions satisfying the charge. The distance, d , will be that to the center of the counterions, i.e. their radius. The Helmholtz theoretical treatment does not adequately explain all the features, since it hypothesizes rigid layers of opposite charges. This does not occur in nature. [46]

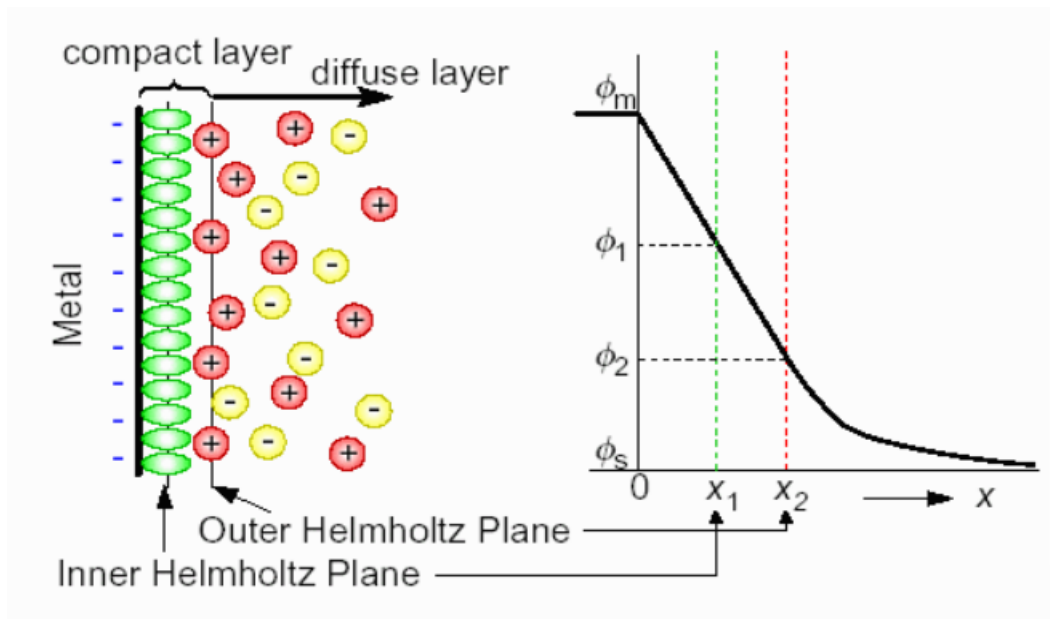


Figure 1.12: This diagram Helmholtz Plane. [46]

1.5.3.5 Gouy-Chapman Double Layer(1910-1913)

Gouy suggested that interfacial potential at the charged surface could be attributed to the presence of a number of ions of given sign attached to its surface, and to an equal number of ions of opposite charge in the solution. In other words, counter ions are not rigidly held, but tend to diffuse into the liquid phase until the counter potential set up by their departure restricts this tendency. The kinetic energy of the counter ions will, in part, affect the thickness of the resulting diffuse double layer.

Gouy and, independently, Chapman developed theories of this so called diffuse double layer in which the change in concentration of the counter ions near a charged surface follows the Boltzmann distribution[28]:

$$N = N_0 e^{-(zeY/KT)} \quad (1.11)$$

where:

- n_0 = bulk concentration
- z = charge on the ion
- e = charge on a proton
- k = Boltzmann constant

Now, since we have a diffuse double layer, rather than a rigid double layer, we must concern ourselves with the volume charge density rather than surface charge density when studying the coulombic interactions between charges. The volume charge density, r , of any volume, i , can be expressed as

$$r_i = Sz_i en_i \quad (1.12)$$

The coulombic interaction between charges can, then, be expressed by the Poisson equation. For plane surfaces, this can be expressed as

$$\frac{dy^2}{dx^2} = -\frac{4\pi r}{d} \quad (1.13)$$

where Y varies from Y_0 at the surface to 0 in bulk solution. Thus, we can relate the charge density at any given point to the potential gradient away from the surface.

Combining the Boltzmann distribution with the Poisson equation and integrating under appropriate limits, yields the electric potential as a function of distance from the surface. The thickness of the diffuse double layer:

$$I_{double} = [e_r KT / (4\pi e^2 S n_{i0} z_i^2)]^{1/2} \quad (1.14)$$

at room temperature can be simplified as

$$I_{double} = 3.3 * 10^6 e_r / (ZC^{1/2}) \quad (1.15)$$

in other words, the double layer thickness decreases with increasing valence and concentration.

The Gouy-Chapman theory describes a rigid charged surface, with a cloud of oppositely charged ions in the solution, the concentration of the oppositely charged ions decreasing with distance from the surface. This is the so-called diffuse double layer.

This theory is still not entirely accurate. Experimentally, the double layer thickness is generally found to be somewhat greater than calculated. This may relate to the error incorporated in assuming activity equals molar concentration when using the desired form of the Boltzmann distribution.

Conceptually, it tends to be a function of the fact that both anions and cations exist in the solution, and with increasing distance away from the surface the probability that ions of the same sign as the surface charge will be found within the double layer increase as well.

1.5.3.6 Stern Modification of the Diffuse double Layer(1924)

The Gouy-Chapman theory provides a better approximation of reality than does the Helmholtz theory, but it still has limited quantitative application. It assumes that ions behave as point charges, which they cannot, and it assumes that there is no physical limits for the ions in their approach to the surface, which is not true. Stern, therefore, modified the Gouy-Chapman diffuse double layer. His theory states that ions do have finite size, so cannot approach the surface closer than a few nm.

The first ions of the Gouy-Chapman Diffuse Double Layer are not at the surface, but at some distance d away from the surface. This distance will usually be taken as the radius of the ion. As a result, the potential and concentration of the diffuse part of the layer is low enough to justify treating the ions as point charges.

Stern also assumed that it is possible that some of the ions are specifically adsorbed by the surface in the plane d , and this layer has become known as the Stern Layer. Therefore, the potential will drop by $\psi_0 - \psi_d$ over the "molecular condenser" (i.e., the Helmholtz Plane) and by ψ_d over the diffuse layer. ψ_d has become known as the zeta (ζ) potential. [47]

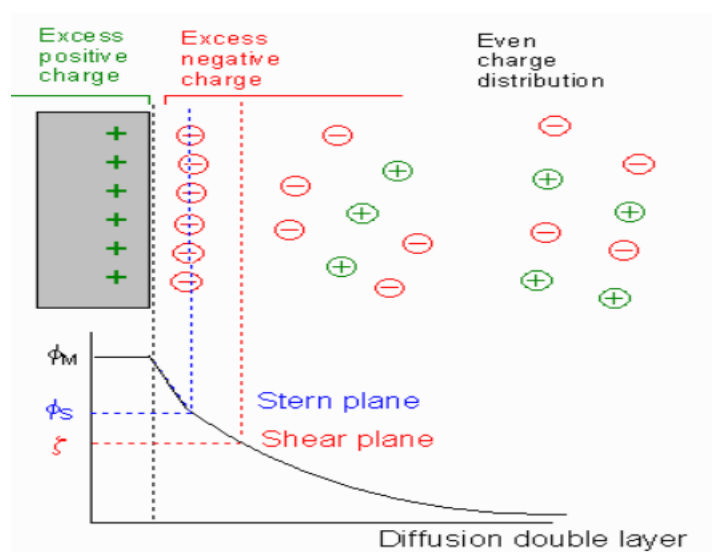


Figure 1.13: This diagram serves as a visual comparison of the amount of counterions in each the Stern Layer and the Diffuse Layer. [47]

Thus, the double layer is formed in order to neutralize the charged surface and, in turn, causes an electrokinetic potential between the surface and any point in the mass of the suspending liquid. This voltage difference is on the order of millivolts and is referred to as the surface potential. The magnitude of the surface potential is related to the

surface charge and the thickness of the double layer. As we leave the surface, the potential drops off roughly linearly in the Stern layer and then exponentially through the diffuse layer, approaching zero at the imaginary boundary of the double layer.

The potential curve is useful because it indicates the strength of the electrical force between particles and the distance at which this force comes into play. A charged particle will move with a fixed velocity in a voltage field. This phenomenon is called electrophoresis. The particle's mobility is related to the dielectric constant and viscosity of the suspending liquid and to the electrical potential at the boundary between the moving particle and the liquid.

This boundary is called the slip plane and is usually defined as the point where the Stern layer and the diffuse layer meet. The relationship between zeta potential and surface potential depends on the level of ions in the solution. The figure above represents the change in charge density through the diffuse layer. One shows considered to be rigidly attached to the colloid, while the diffuse layer is not. As a result, the electrical potential at this junction is related to the mobility of the particle and is called the zeta potential. Although zeta potential is an intermediate value, it is sometimes considered to be more significant than surface potential as far as electrostatic repulsion is concerned.

The equivalent electrical circuit for the cell has to represent all these features and can be described by the electrical model shown on the left. Here C_{dl} is the capacitance of the double layer and R_{rxn} is the resistance of the Faradaic reaction. Two double layers at the electrodes can be represented as one cell capacitance:

$$C_{cell} = \epsilon\epsilon_0 A / 2d_{dl} \quad (1.16)$$

and the Faradaic resistor, R_F , in parallel to it. The resistance of the solution to the motion of ions can be represented a series resistance R_{cell} . As a result, the equivalent electrical circuit for the cell (two electrodes and solution between them) can be presented as shown on the left.

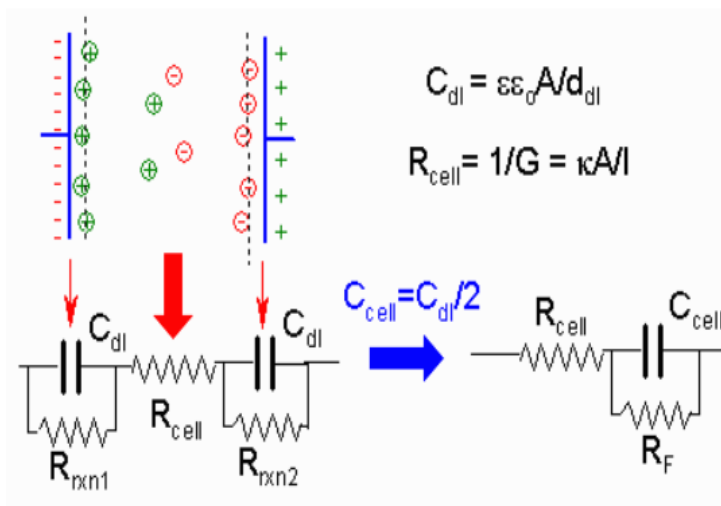


Figure 1.14: This diagram show Cell double layer. [48]

1.6 Electrochemical techniques

We will during this section present a number of electrochemical techniques is schematized by the figure for the study of reaction mechanisms such as:

- Voltametricyclic
- Chronoamperometry
- Chronopotentiometry

1.6.1 Cyclic voltammetry

Cyclic voltammetry (CV) is an electroanalysis technique based on the measurement of the current flow resulting from electrochemical phenomena occurring at the electrode surface under the effect of a controlled variation in the potential difference between two specific electrodes. difference between two specific electrodes . potential, allowing measurement of the $i = f(E)$ curves for oxidation and reduction of the compound. In particular, this technique makes it possible to study the speed of the redox reaction as a function of the measurement time. [9]

1.6.1.1 Operating principle

The potential is measured between the reference electrode and the working electrode but the current is measured between the working electrode and the counter electrode. This data is then plotted as current (i) versus potential (E).

The subsequent sweep produces a current peak for all that can be reduced within the sweep potential range.

The current increases as the potential reaches the reduction potential of the electrolyte, then falls as the electrolyte concentration decreases around the electrode surface. The oxidation peak will usually have a similar shape to the reduction peak similar shape to the reduction peak, so information on the redox potential and proportions of compounds obtained from the electrochemical reaction. The main characteristic values of a voltammogram are shown in the figure 1.15. [49]

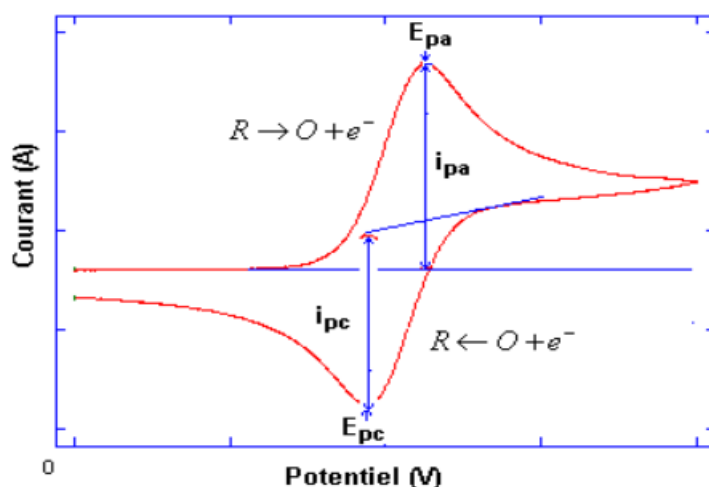


Figure 1.15: Cyclic voltammogram of a red/ox couple. [49]

- i_{pa} , i_{pc} : anodic and cathodic peak current
- E_{pa} , E_{pc} : anode and cathode peak potential.

When the potential is first applied, the imposed current is low because there is no red/ox reaction. When the imposed potential is increased, the oxidation reaction becomes favourable and the reduced species near the electrode are oxidised with electron transfer to the working electrode, leading to diffusion of reduced species towards the electrode.

the working electrode, causing diffusion of reduced species towards the electrode. As the imposed potential increases, electron transfer becomes increasingly favourable and rapid. The intensity of the current detected increases. This increase reaches a maximum (E_{pa}) because there is a progressive depletion of reagent in the solution near the electrode and the phenomenon of diffusion of reduced species becomes the limiting factor.

1.6.2 Chronoamperometry

It is a method that consists in imposing or fixing a potential and varying the current as a function of time with the formation of a new phase, (transient) nucleation phenomena and crystal growth. For the case of a diffusion-controlled system, the expression of current as a function of time is given by the Cottrell equation[50]:

$$i(t) = n \cdot F \cdot C \cdot \sqrt{\frac{D}{\pi t}} \quad (1.17)$$

Where:

- i : current density.
- t : time.
- n : number of electrons exchanged
- F : Faraday's constant.
- D : diffusion coefficient.
- C : concentration

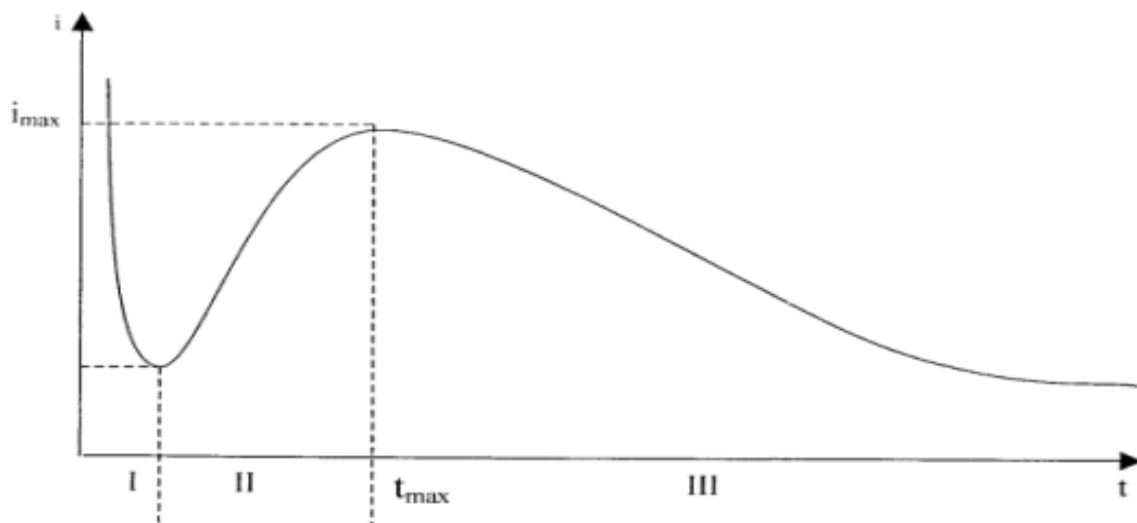


Figure 1.16: Current-time curve. [50]

The figure shows the current-time curve for three-dimensional germination includes three distinct areas:

- Zone I : Corresponds to the area of the double layer and the time required to form germs.
- Zone II: Corresponds to the growth of germs so to the increase of the active surface on the electrode.
- Zone III : Reflects the fact that the diffusion of ions in the solution becomes the limiting step for the growth reaction of the deposited film.

1.6.3 Chronopotentiometry

is a method of studying electrochemical systems which consists in imposing a constant current i and measuring the temporal evolution of the potential $E = f(t)$ of an electrode is schematized by the figure [1-17]. [51]

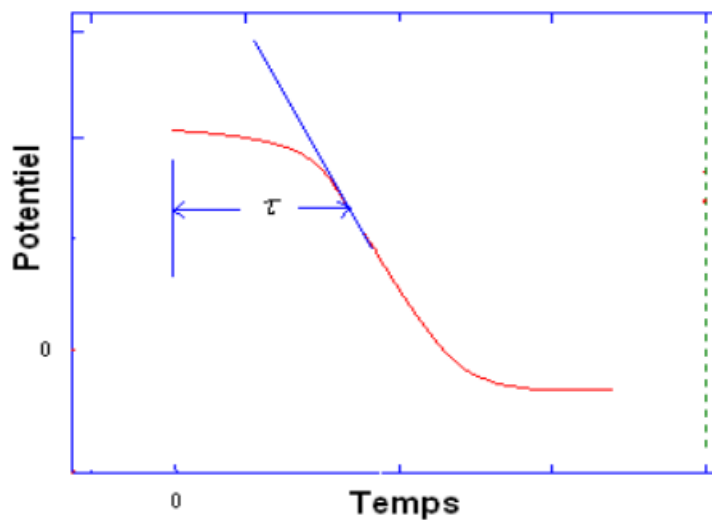


Figure 1.17: Constant current chronopotentiogram. [51]

Potential variations result from changes in the electrode and electrolyte at the interface due to the passage of current. They will be either brutal for example in the case of the complete disappearance of a layer of a reactant located on the electrode, or slower and more regular for example during the depletion of one of the dissolved reactants.

In the latter case, the absence of steady state is required; Indeed, if the supply of reactant by agitation or migration from the other electrode is sufficient, a regime can be achieved in which the concentrations of dissolved species are maintained at a constant value and consequently, the potential becomes independent of time.

Conclusions

In conclusion, electrochemistry is a vital field that explores the connection between chemical processes and electrical phenomena. It has diverse applications in energy storage, corrosion protection, electroplating, sensors, and environmental monitoring. Through electrochemical techniques and tools like the potentiostat, researchers have gained profound insights into reaction kinetics, material properties, and system performance. Electrochemistry has facilitated the development of innovative technologies, such as high-performance batteries and efficient fuel cells. Despite challenges like electrode fouling and reaction selectivity, ongoing research aims to advance materials, electrode designs, and measurement techniques.

CHAPTER 2:

Potentiostat

2.1 What is a Potentiostat?

In electrochemical measurements, it is important to be able to both control (resp. measure) the potential difference between the measuring electrode and the reference electrode and to measure (resp. control) the current flowing through the circuit. This double function cannot be realised with a simple stabilised power supply, as it requires feedback (the parameter to be controlled must be compared with its set value).

On the other hand, it is often useful, in addition to "simply" controlling the potential of the measuring electrode (in relation to the reference), to be able to impose a signal on it that varies over time. The potentiostat is a device that fulfils this dual role: signal generator on the one hand and imposition and control of parameters (voltage or current) on the other. [13]

2.2 Why a three-electrode arrangement ?

The simple fact of wanting to simultaneously control the voltage between the measurement electrode and the reference electrode and measure the current flowing through the measurement electrode poses a double difficulty[14]:

- The first difficulty is to precisely control the voltage across the two electrodes because of the large current flowing through them, due to the existence of a non-zero resistance in the part of the circuit separating the two electrodes.
- The second difficulty is that in a two-electrode circuit, the reference electrode carries the same current as the measurement electrode. This results in polarisation of the reference electrode and rapid degradation of its performance.

This double problem can be overcome by introducing a third electrode, the so-called auxiliary electrode (or counter electrode) into the circuit. The main function of this electrode is to allow the current to flow through the measuring electrode, without passing through the reference electrode. The schematic diagram of the three-electrode arrangement is shown above figure 2.1.

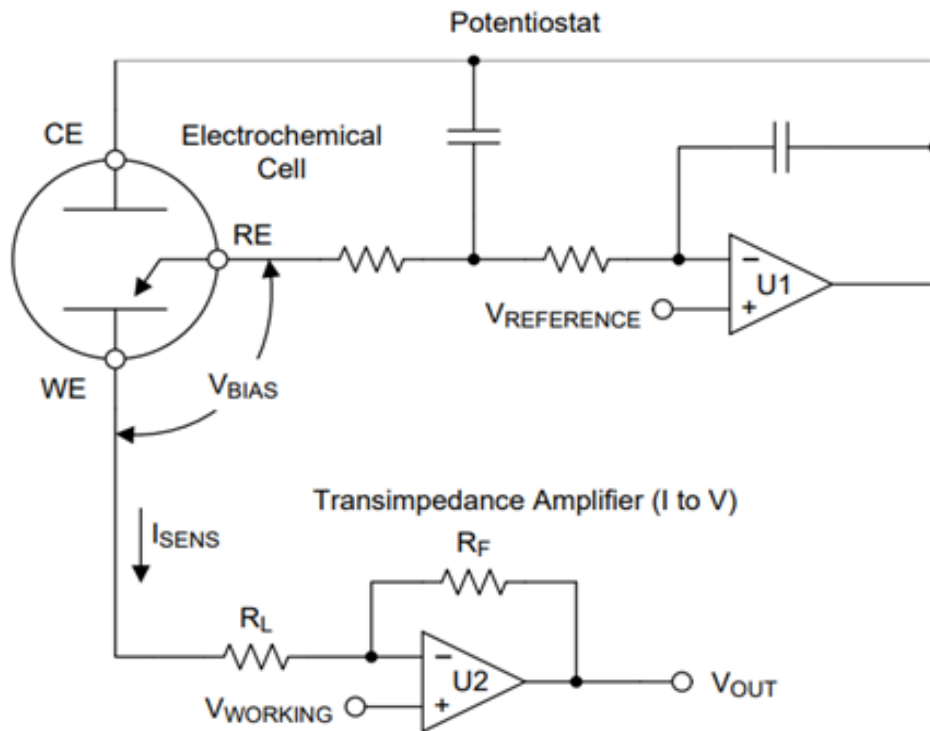


Figure 2.1: Schematic diagram of an electrochemical assembly using a potentiostat. [14]

In a 3-electrode set-up, the electrode whose potential is being monitored (or measured) in relation to the reference electrode is called the working electrode, while the other electrode is called the auxiliary or counter electrode.

2.3 Principle Schematic of a potentiostat.

Figure shows the schematic diagram of the operation of a potentiostat; there are mainly three operational amplifiers (AOP):

- The first (1) acts as a comparator between the set value of the voltage between working electrode (WE) and reference electrode (RE).
- The second (2) plays the role of voltage follower (inverter) and thus makes it possible to measure the voltage (-RE).
- The third (3) is a current-voltage converter: the variable resistor makes it possible to adjust the "current range" to obtain an output signal within the acceptable voltage range, regardless of the value of the measured intensity.

The schematic diagram in Figure 2-2 shows that the adjustable parameter of the circuit is the potential of the auxiliary electrode, and that the potentiostat is adjusted to maintain a short circuit between the inputs of the operational amplifier (1), i.e.

(WE-RE) equal to its set value. The performance of the potentiostat (in particular its ability to control the potential of the working electrode) depends directly on the maximum value that the potential of the auxiliary electrode can take.

Finally, the value of the potential imposed on the working electrode in relation to the reference electrode is either fixed or variable over time according to a predefined function:

ramp, sinusoid, square wave... which explains the presence of the function generator shown in the diagram in figure .2-3. [15]

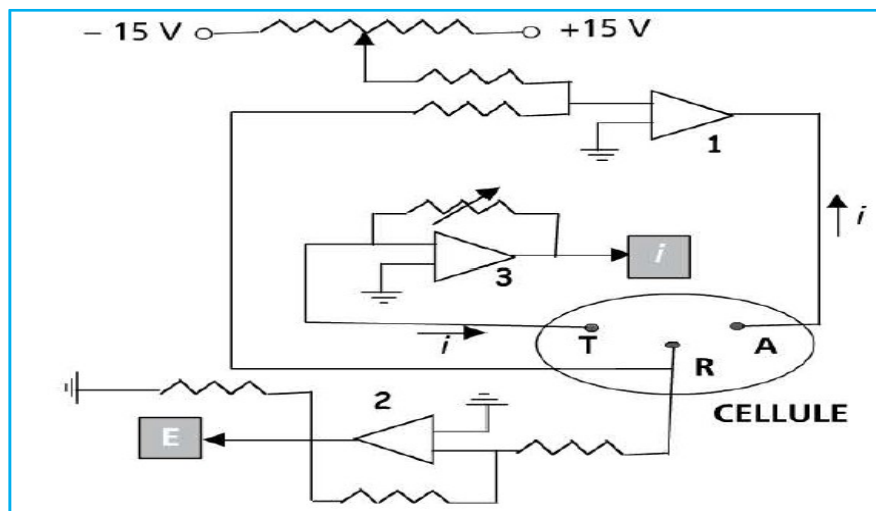


Figure 2.2: Schematic diagram of a potentiostat. [15]

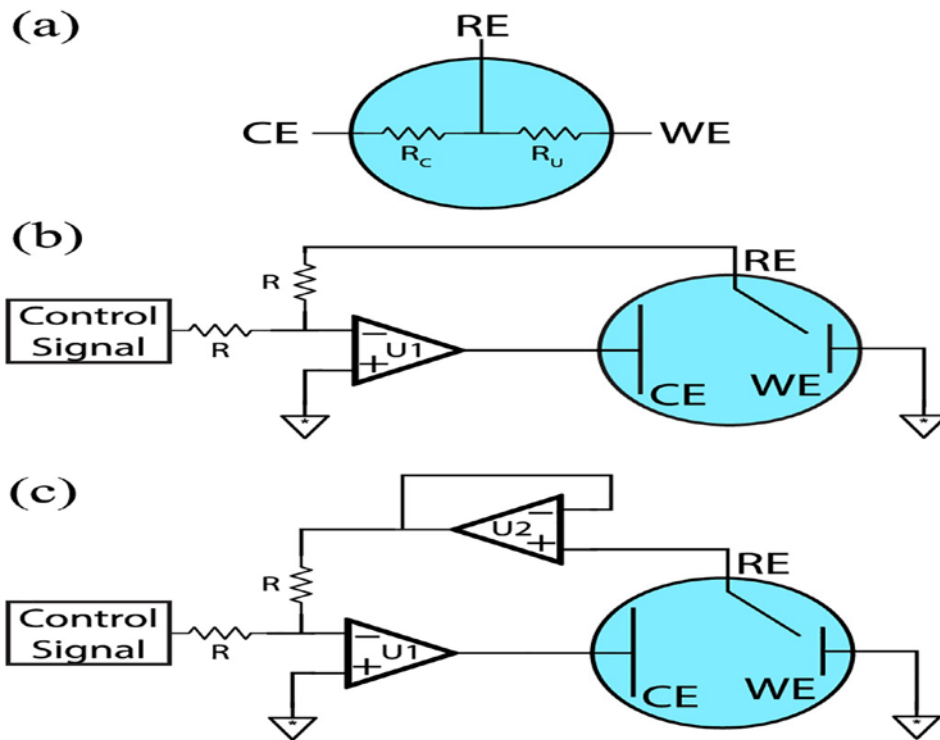


Figure 2.3: Electrochemical cells and potentiostatic circuits. [69]

- RE: Reference Electrode,
- CE: Counter Electrode,
- WE: Working Electrode,
- R: Summing resistors,
- U1: Control amplifier,
- U2: Reference buffer amplifier,
- R_c : Compensated cell resistance,
- R_u : Uncompensated cell resistance.
- (a) Simplified three electrode cell model.
- (b) Basic potentiostatic circuit.
- (c) DStat potentiostatic circuit.

2.4 Potentiostat & galvanostat

In contrast to a potentiostat, a galvanostat (or amperostat) is a device for imposing an electric current to measure the electrical potential of an electrochemical cell.

However, it should be noted that most potentiostats can also be used as galvanostats, since it is easier to control the current than the potential. A very simple circuit, such as that shown in Figure [2-4], is sufficient to control the current flowing through the cell. [16]

The latter is given by the following formula :

$$i = \frac{Ve}{R} \quad (2.1)$$

Where:

- i represents the electric current.
- V represents the voltage.
- R represents the resistance.

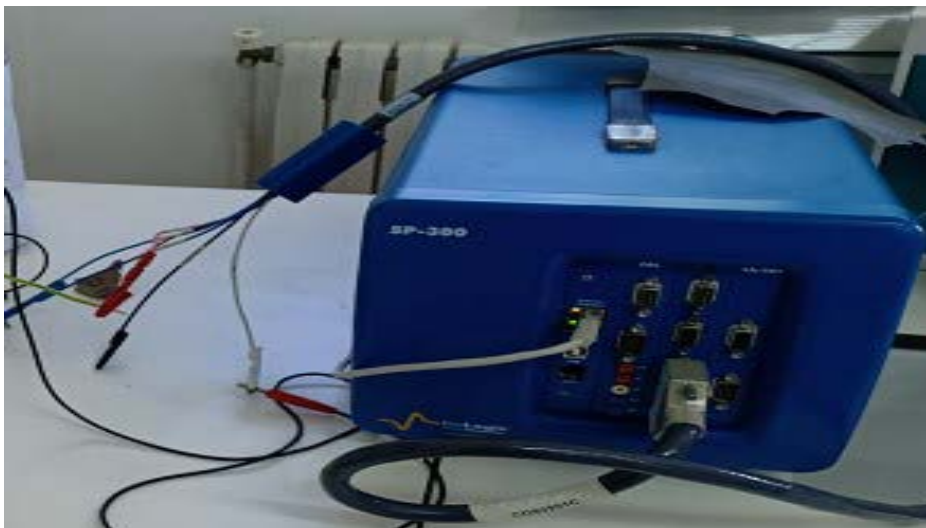


Figure 2.4: potentiostat. [16]

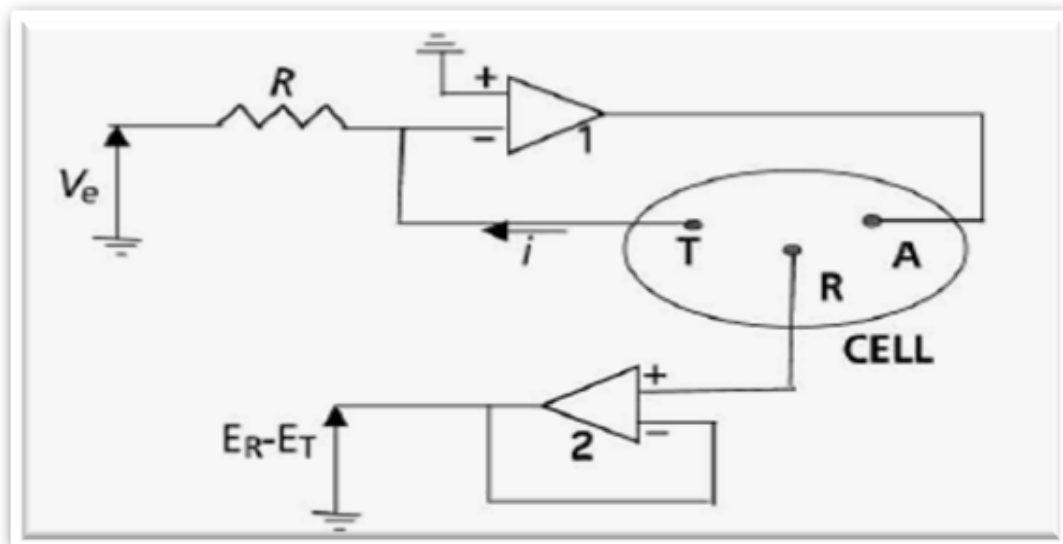


Figure 2.5: Schematic diagram of the galvanostat:

- T is the connection to the working electrode
- A to the auxiliary electrode, R to the reference. Operational amplifiers: 1 = inverting multiplier; 2 = follower. [17]

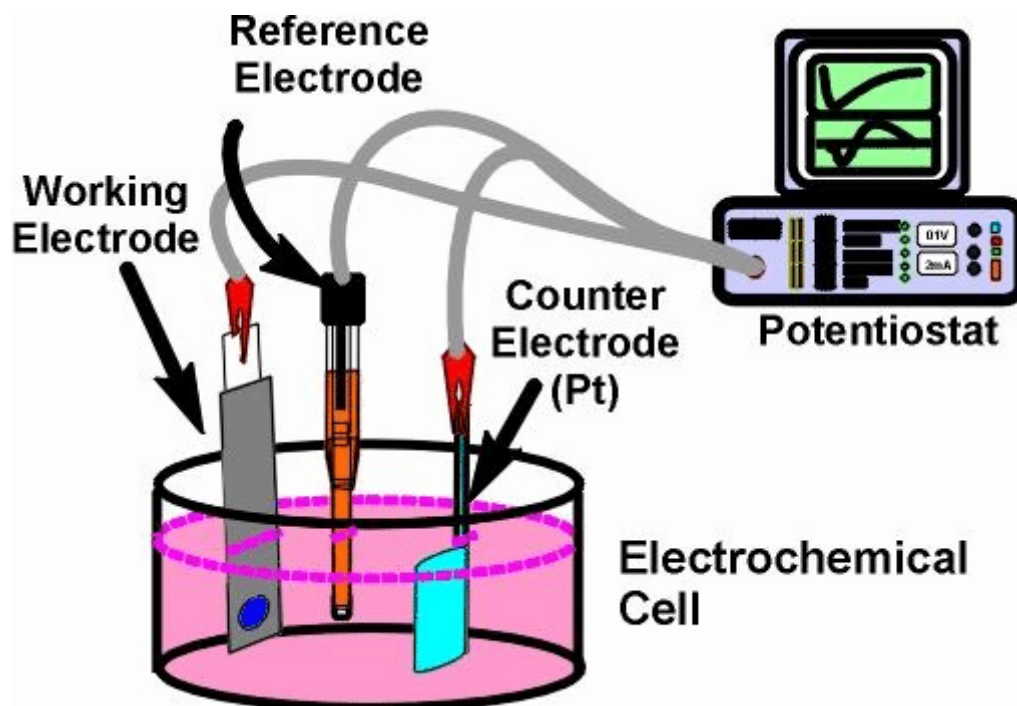


Figure 2.6: Schematic representation of an electrochemical cell for CV experiments.

2.5 How does it Work

2.5.1 Working Principles

Potentiostats operate based on three-electrode configurations. The three electrodes include a working electrode (WE), a reference electrode (RE), and a counter electrode (CE). The potentiostat applies a potential between the WE and the RE while measuring the current flowing through the electrochemical cell. By controlling the potential difference, the potentiostat can drive specific electrochemical reactions on the working electrode surface. [38] [39] [40] [41]

2.5.2 Components

2.5.2.1 Potentiostat Control Circuit

This circuitry generates the desired voltage waveform to control the potential of the working electrode. It ensures precise potential control and stability.

2.5.2.2 Current Measurement Circuit

It measures the current flowing through the cell using techniques such as amperometry, galvanostatic, or potentiostatic mode. The circuit converts the current to a measurable voltage for analysis.

2.5.2.3 Feedback Loop

The feedback loop continuously adjusts the applied potential to maintain a stable current. It compares the measured current with the desired value and adjusts the potential accordingly.

2.5.2.4 Potential Control

The potentiostat's control circuit generates a desired voltage waveform, which is applied between the working electrode (WE) and the reference electrode (RE). The control circuitry adjusts the potential to maintain the desired voltage. This potential control is critical for driving specific electrochemical reactions at the working electrode surface

2.5.2.5 Reference Electrode (RE)

The RE provides a stable reference potential for the working electrode. Common reference electrodes include the Ag/AgCl electrode, saturated calomel electrode (SCE), and silver/silver sulfate electrode.

2.5.2.6 Counter Electrode (CE)

The CE completes the electrical circuit by allowing current to flow. Typically, a large-area electrode, such as a platinum or graphite electrode, is used as the counter electrode.

2.5.2.7 Working Electrode (WE)

The WE is the electrode where the electrochemical reaction of interest takes place. It can be a metal, an alloy, or a modified electrode surface specific to the application.

2.5.2.8 Voltage-Current Relationship

The potentiostat operates based on Ohm's Law and Faraday's laws of electrolysis. According to Ohm's Law, the current flowing through the electrochemical cell is directly proportional to the potential difference applied across the working electrode and the reference electrode. Faraday's laws relate the amount of charge transferred during an electrochemical reaction to the measured current.

By maintaining a constant potential and measuring the resulting current, the potentiostat enables researchers to investigate the electrochemical behavior of the system, including reaction kinetics, redox processes, charge transfer mechanisms, and other electrochemical properties.

2.5.3 Key Features

2.5.3.1 Voltage Control

Potentiostats provide precise control over the applied potential, allowing researchers to investigate electrochemical processes at specific voltages.

2.5.3.2 Current Measurement

Potentiostats offer high-precision current measurement capabilities, enabling accurate analysis of electrochemical reactions.

Simultaneously, the potentiostat's current measurement circuit continuously monitors the current flowing through the electrochemical cell. The current can be measured using various techniques, such as amperometry or potentiostatic/galvanostatic modes. The current measurement circuit converts the current into a measurable voltage signal, which is used for analysis.

2.5.3.3 Impedance Spectroscopy

Advanced potentiostats often include impedance spectroscopy functionality, allowing researchers to characterize the electrical properties of electrochemical systems over a range of frequencies.

2.5.3.4 Multiple Electrode Support

Potentiostats can be equipped with multiple channels, enabling simultaneous measurements on multiple electrodes or multiple cells.

2.5.3.5 Versatility

Potentiostats are versatile instruments that can be used for a wide range of applications, including cyclic voltammetry, chronoamperometry, chronopotentiometry, and impedance spectroscopy.

2.5.3.6 Software Control and Data Analysis

Many potentiostats come with dedicated software that provides control over the instrument, data acquisition, and advanced data analysis tools.

2.5.4 Advanced Features

Some advanced potentiostats offer additional features and capabilities:

2.5.4.1 Potential Scan Rates

Potentiostats may provide adjustable potential scan rates, allowing researchers to vary the rate at which the potential is swept during cyclic voltammetry experiments. This feature enables the study of reaction kinetics and electrochemical processes.

2.5.4.2 Pulse Techniques

Certain potentiostats support pulse techniques, such as chronoamperometry with potential pulses or pulse voltammetry. These techniques enable the investigation of fast electrochemical reactions and transient phenomena.

2.5.4.3 Multi-Channel Support

High-end potentiostats can have multiple independent channels, allowing researchers to perform simultaneous measurements on different working electrodes or multiple cells. This feature enhances productivity and enables parallel experimentation.

2.5.4.4 Low Current Measurement

Some potentiostats offer ultra-low current measurement capabilities, allowing detection of currents in the picoampere (pA) or even femtoampere (fA) range. This feature is valuable for sensitive electrochemical measurements and analysis of low-conductivity systems.

2.5.4.5 Automation and Integration

Potentiostats can be integrated into automated systems or controlled remotely through computer interfaces. This integration facilitates high-throughput experiments, data acquisition, and integration with other analytical techniques.

2.6 Applications

- Electrochemical Analysis
- Corrosion Studies
- Battery Testing
- Sensor Development
- Electroplating and Surface Modification
- Biosensors and Bioelectrochemistry
- Environmental Analysis
- Electrochemical Energy Conversion

2.7 Experimental Setup

2.7.1 Potentiostat

Start by selecting a suitable potentiostat based on the desired specifications and experimental requirements. Ensure that the potentiostat has the necessary capabilities for the desired electrochemical technique (e.g., cyclic voltammetry, chronoamperometry, impedance spectroscopy).

2.7.2 Experimental Design

Define the objectives of your experiment and design the specific electrochemical technique or measurement protocol accordingly (e.g., cyclic voltammetry, chronoamperometry, impedance spectroscopy). Consider factors such as potential range, scan rate, time duration, and any additional parameters specific to your technique.

2.7.3 Instrument Calibration

Before starting the experiment, calibrate the potentiostat to ensure accurate potential and current measurements. This may involve verifying the accuracy of the reference electrode, setting the reference potential, and performing any necessary adjustments or calibrations.

2.7.4 Electrode Conditioning

Condition the working electrode before starting the experiment, if required. This may involve cleaning the electrode surface, polishing, or modifying it as per your experimental needs.

2.7.5 Experimental Procedure

Follow the experimental procedure specific to your chosen electrochemical technique. This may include steps such as:

- Applying a potential waveform (e.g., potential sweep, potential pulse) and recording the resulting current.
- Monitoring the current at a fixed potential and recording the time-dependent behavior (chronoamperometry).
- Applying an AC signal and measuring the impedance at different frequencies (impedance spectroscopy).

2.7.6 Data Analysis

After acquiring the experimental data, analyze and interpret the results using appropriate data analysis techniques. This may involve plotting current-potential curves, analyzing voltammograms, fitting impedance spectra, or extracting relevant electrochemical parameters.

2.7.7 Validation and Reproducibility

Validate your experimental results by performing replicates or control experiments to ensure the reproducibility and reliability of your findings.

2.7.8 Data Presentation and Reporting

Summarize and present your results, including figures, tables, and statistical analyses. Interpret your findings and discuss their implications in the context of your research objectives.

It's important to note that the above methodology is a general guideline, and specific variations and considerations may apply depending on your research objectives, technique.

Conclusions

In conclusion, potentiostats are essential devices for precise control and measurement of electrochemical processes. They enable accurate analysis of electrochemical properties, offer versatility with different working modes, and provide high sensitivity for detecting low currents. With advanced features and portability, potentiostats facilitate research in various fields and contribute to scientific and technological advancements

CHAPTER 3:

MATERIAL EXPERIMENTAL

3.1 Introduction

"Now, let's shift our focus to the design and methodology employed in our study/experiment. Also, we will delve into the details of our experimental setup and methodology. Next, I will outline the specific design considerations and experimental procedures we implemented in our research."

In the following sections, we will discuss the design aspects and methodology adopted for our study."

3.2 Experimental setup & Methodology

3.2.1 what is proteuse

Proteus is a software suite developed by Labcenter Electronics for electronic circuit design, simulation, and PCB layout. It provides a comprehensive set of tools that enable engineers and designers to create and test electronic circuits before physically implementing them. Proteus consists of two main components[42] [43]:

3.2.2 Proteus Design Suite

3.2.2.1 ISIS schematic capture

This module allows users to design electronic circuits using a graphical interface. It provides a vast library of electronic components, including microcontrollers, sensors, passive components, and more.

3.2.2.2 Virtual Instruments

Proteus includes a range of virtual instruments that can be added to the circuit design, such as oscilloscopes, function generators, and logic analyzers. These virtual instruments facilitate real-time analysis and testing of the circuit's behavior.

3.2.2.3 Simulation

The Proteus simulator enables engineers to simulate and analyze the behavior of the designed circuit. It supports both analog and digital simulation, allowing users to evaluate circuit performance, verify functionality, and identify potential issues or design flaws.

3.2.2.4 Mixed-mode simulation

Proteus supports the simulation of mixed analog and digital circuits, enabling users to test the interaction between different components and analyze system-level behavior.

3.2.3 Proteus PCB Design

3.2.3.1 PCB Layout

Proteus offers a powerful PCB design module that allows users to create and design printed circuit boards (PCBs) based on their circuit schematics. The module supports various features like component placement, track routing, copper pour, and design rule checking (DRC).

3.2.3.2 3D Visualization

Proteus includes a 3D visualization tool that enables users to visualize the PCB in a three-dimensional view, aiding in checking component clearances, identifying design errors, and assessing the overall layout.

3.2.3.3 Manufacturing Outputs

Once the PCB design is completed, Proteus facilitates the generation of manufacturing outputs, including Gerber files, bill of materials (BOM), and assembly drawings, which can be used for PCB fabrication and assembly.

Proteus is widely used in the electronics industry and educational institutions for circuit design, simulation, and PCB layout. It offers an integrated platform that allows designers to seamlessly move from schematic capture to simulation and PCB design.

The ability to simulate circuits and test their functionality before fabrication helps reduce design iterations, saves time and costs, and enhances the overall quality and reliability of electronic systems.

3.3 Our Gather Materials

- Breadboard.
- Arduino.
- Function Generator.
- DC Power Supply.
- Computer.
- Conducting cell.
- Electrodes
- Wires and cables.
- 5 op-amps (I used LM741's).
- Capacitors:
 - 100nF, 470nF, 1 μ F.
- Resistors:
 - 200 Ω , 510 Ω , 100 Ω , 1k Ω , 10k Ω , 12k Ω , 24k Ω , 5 k Ω , 1M Ω ,
- Liquid Crystal LCD (I used LM016L).

3.4 Power supply

Most operational amplifiers (Op-Amp), such as the LM741 used in this report, typically require symmetrical power supplies. This means they need both positive and negative voltages, relative to ground, to operate correctly.

In the proposed circuit, the +/- 6.5V supply is designed to provide a +/- 5V output on the Op-Amp (accounting for the typical internal voltage drop of 1.5V). This output range aligns with the capabilities of the microcontroller, as explained in more detail. While not essential, this setup serves as a failsafe to protect the microcontroller by including a 5.1V Zener diode connected between the output of the Analog-to-Digital Converter (ADC) and ground.

The LM741 quad Op-Amp can be powered by a dual power supply ranging up to +/- 18V, relative to a common ground. One option to achieve this power supply is by utilizing the +12V and -12V rails of a PC ATX power supply. These power supplies are readily available and can often be salvaged from old PCs without incurring any additional costs for the project.

To ensure stability and precision, the -5V supplied to the summing amplifier and current-to-voltage converter in the main manuscript needs to be reliable. Any fluctuations in this voltage can cause offsets in both the applied potential to the electrochemical cell and the current reading. To provide a stable -5V, a voltage regulator such as the LM741 can be employed, utilizing the -12V rail of the ATX power supply.

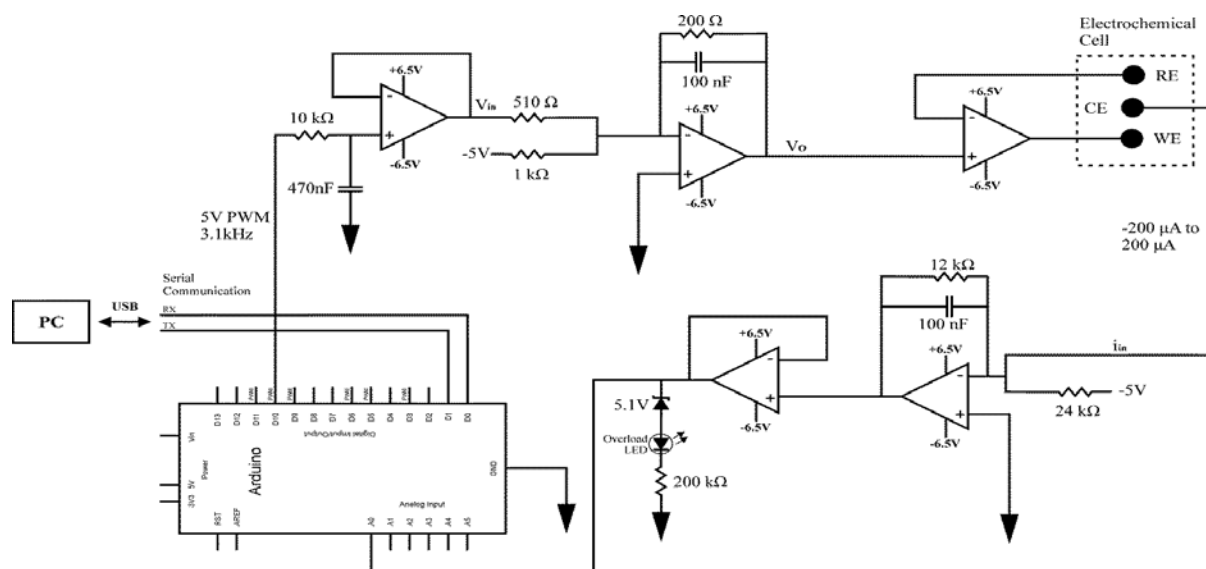


Figure 3.1: Full schematic design of the potentiostat including the Arduino board pin connections. All the components values are the ones used on the electrochemical experiments.

3.5 Description

The LM741 series are general-purpose operational amplifiers which feature improved performance over industry standards like the LM709. They are direct, plug-in replacements for the 709C, LM201, MC1439, and 748 in most applications.

The amplifiers offer many features which make their application nearly foolproof: overload protection on the input and output, no latch-up when the common mode range is exceeded, as well as freedom from oscillations.

The LM741C is identical to the LM741 and LM741A except that the LM741C has their performance ensured over a 0°C to +70°C temperature range, instead of -55°C to +125°C see figure 3.2. [44] [45] [46]

3.5.1 LM741 Op-Amp Datasheet Specifications

	LM741A	LM741	LM741C
Supply Voltage	±22V	±22V	±18V
Power Dissipation (Note 3)	500 mW	500 mW	500 mW
Differential Input Voltage	±30V	±30V	±30V
Input Voltage (Note 4)	±15V	±15V	±15V
Output Short Circuit Duration	Continuous	Continuous	Continuous
Operating Temperature Range	-55°C to +125°C	-55°C to +125°C	0°C to +70°C
Storage Temperature Range	-65°C to +150°C	-65°C to +150°C	-65°C to +150°C
Junction Temperature	150°C	150°C	100°C
Soldering Information			
N-Package (10 seconds)	260°C	260°C	260°C
J- or H-Package (10 seconds)	300°C	300°C	300°C
M-Package			
Vapor Phase (60 seconds)	215°C	215°C	215°C
Infrared (15 seconds)	215°C	215°C	215°C

Figure 3.2: Show data sheet of LM741.

3.5.2 Features

- Overload Protection on the Input and Output
- No Latch-Up When the Common-Mode Range is Exceeded

3.5.3 Applications

- Comparators
- Multivibrators
- DC Amplifiers
- Summing Amplifiers
- Integrator or Differentiators
- Active Filters

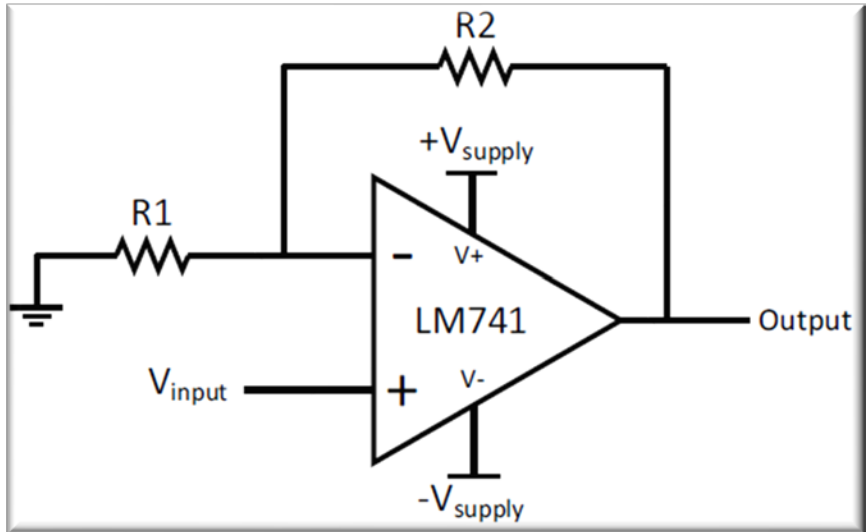


Figure 3.3: Show Schematic LM741.

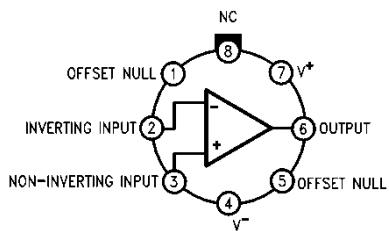


Figure 3.4: LMC Package 8-Pin TO-99

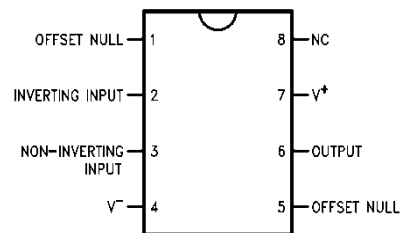


Figure 3.5: NAB Package 8-Pin TO-99
8-Pin CDIP or PDIP.

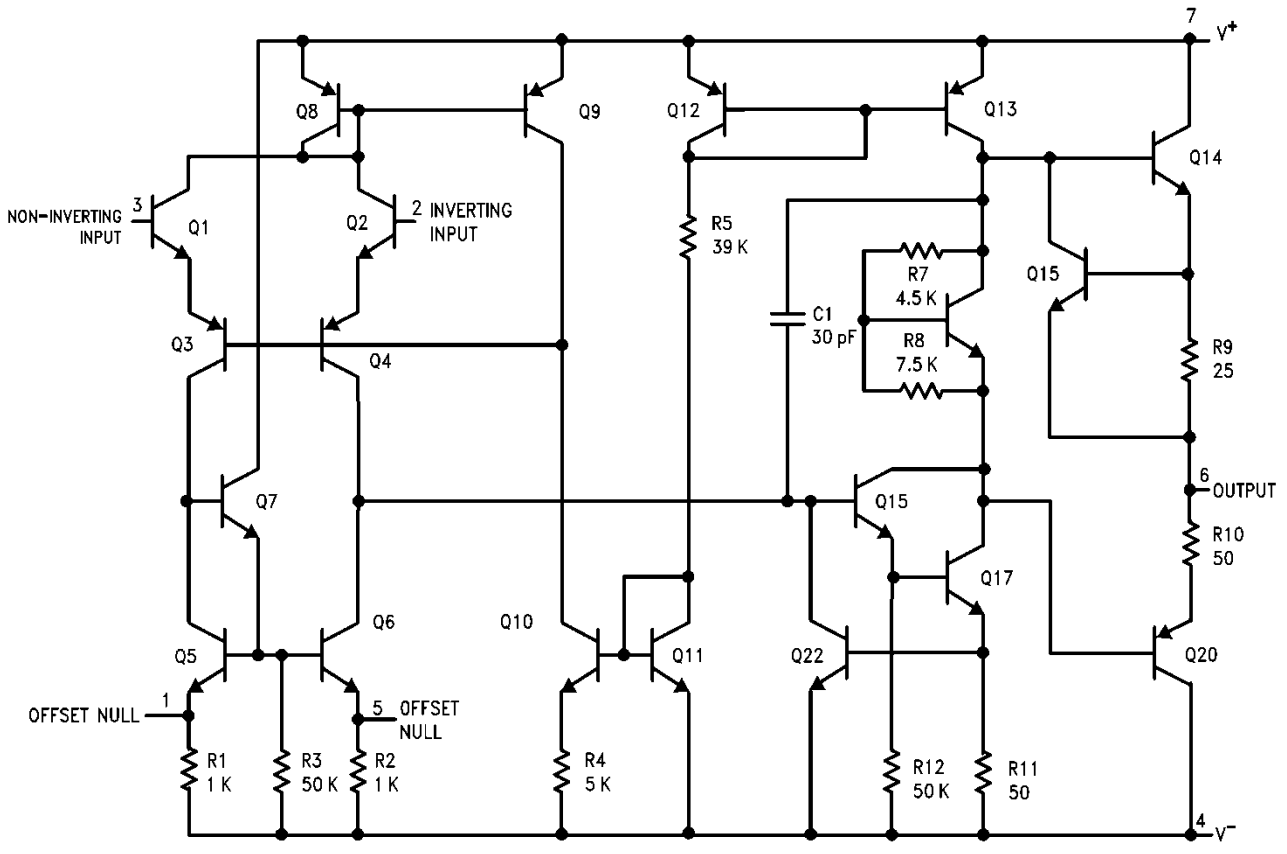


Figure 3.6: schematic of Functional Block Diagram.

3.6 Digital to analog converter (DAC)

As the Arduino Uno boards do not have a true digital to analog converter (DAC) but only pulse-width modulation (PWM) and for a cyclic voltammetry experiment, a potential ramp should be applied on the potential controller, the square wave generated by the PWM must be converted into a potential ramp.

One alternative is to use an RC filter to convert PWM values into true analog values. The drawback of using this approach is that for a Uno board the PWM has an 8-bit resolution, generating only 256 discrete potential values. This might result in poorly defined voltammograms, especially if performing experiments with less than the maximum and minimum potential limit of the equipment.

The summing amplifier gives those limits. Besides the resolution problem, most Arduino boards have low frequency PWM signal, ranging from 400 Hz to 960 Hz, resulting in a high time constant for the RC filter.

These frequencies are determined by an integer divider on the internal clock of the board, meaning that the frequency can be changed by changing the divider value, resulting in frequencies up to 3.1 kHz, much more suitable for the intended application. Table 3.2 lists the truth table for the PWM based DAC. Table lists the truth table for the PWM based DAC. [47]

Table 3.2 : for the summing amplifier, showing its voltage output as a function of the DAC voltage/PWM level

Input (V/PWM level)	Output (V)
0/0	1
2.5/127	0
5/255	-1

The PWM voltage of the Uno board is 5V and the DAC can only provide voltages from 0 to 5V. Thus, a summing Op-Amp is needed for cyclic voltammetry experiments as we are interested to vary the potential between negative and positive values. As most of the teaching experiments in electrochemistry are performed in water and the electrochemical window for water is not greater than 1.5V for most working electrode (WE) materials, there is no point in sweeping the potential up to 5V. Thus, the summing amplifier can be designed to output voltages in a more usable range. As the 8-bit resolution will be used in the whole span of the potential window, the design of the summing amplifier is a compromise between the potential resolution and potential window width.

The width of the window can be adjusted by changing the values of Vb1, R2, R3, and R4. Applying Kirchhoff's law and Ohm's law on the inverting input of the summing amplifier, it can be easily seen that the relation between VO, Vin, Vb1, R2, R3, and R4 is given by:

$$V_0 = -R_4 \left(\frac{V_{in}}{R_3} + \frac{V_{b1}}{R_2} \right) \quad (3.1)$$

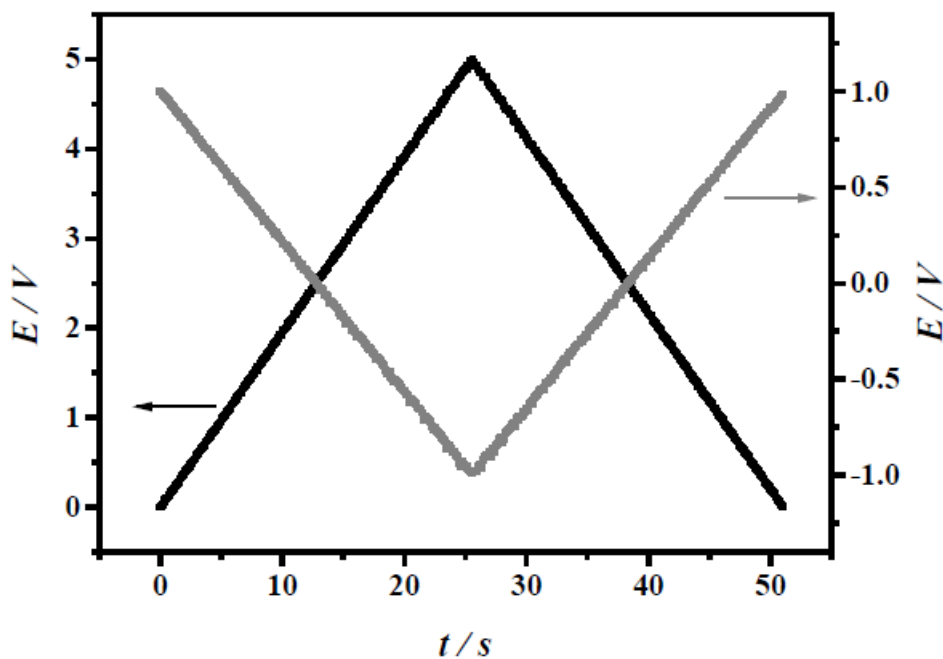


Figure 3.7: E vs. t plot of the DAC output (black line) and summing amplifier output (grey line).

3.7 Scan rate

The maximum scan rate for the designed device is dependent on the rise time of the RC filter used on the ADC. In addition, the potential window and resolution will affect the maximum scan rate.

All those parameters can be changed allowing for some experimental setup flexibility. As the DAC bit resolution is fixed (8-bit) the DAC can generate 256 different levels. With a potential window of 2V (from -1V to 1V) as used for the electrochemical experiments, the DAC resolution is 0.0078V.

With a DAC RC filter rise time of 0.01s (10k Ω resistor and 470nF capacitor and 3.1kHz PWM) the maximum scan rate on the setup used for the electrochemical experiments would be 0.780 Vs⁻¹.

The maximum scan rate of the device is defined by[48]:

$$V_{max} = \left(\frac{E_w}{2^{56}} / RC_t \right) \quad (3.2)$$

Where:

Vmax: Maximum scan rate value (Vs^{-1})

Ew: DAC potential window width (V)

RCt: DAC RC filter rise time (s)

3.8 Analog to digital converter (ADC)

The current reading part of the equipment is highlighted in the main manuscript and it consists of an Op-Amp in a current to voltage converter setup (transimpedance amplifier) connected to the counter electrode (CE). The current to voltage converter (CVC), as its name suggests, converts the current that flows through the electrochemical cell into a potential that the microcontroller can read. To avoid any damage to the microcontroller the Op-Amps are supplied with +6.5 V, which is within the microcontroller limits. This means that an overload in the current reading will only result in a saturated amplifier and not cause damage to the equipment. The current limit is given by the resistor R_6 connected to the trans-impedance amplifier feedback loop.

Using the property of Op-Amps and Ohm's law, one can easily see that the current limit is given by:

$$V_{cvc} = i_{in} \times R_6 \quad (3.3)$$

where V_{cvc} is the output voltage of the converter. The potentiostat was designed to use the maximum dynamic range of potential reading from the microcontroller (0-5 V) and engineered taking into account that the Arduino Uno board does not read negative potentials, meaning that a value of 0 A on the current to voltage converter should result in 2.5 V (Table 3.3).

This was achieved by the addition of a bias potential on the inverting input of the amplifier. [49]

Table 3.3: Truth table of the current to voltage converter, showing its voltage output and ADC level as a function of the current flowing through the counter electrode.

Input (μA)	Output (V)	ADC level
-200	0	0
0	2.5	511
200	5	1023

Table 3.4: Current and voltage limits for the potentiostat used during the experiments performed in the main manuscript.

	Min.	Max.
Potential (V)	-1	1
Current (μA)	-200	200
Voltage compliance (V)	-5	5
Scan rate (Vs^{-1})		0.780

Conclusion

In conclusion, The potentiostat enables precise control over the electrochemical reactions. Overall, the potentiostat plays a crucial role in advancing our understanding of electrochemical processes and has significant implications across various scientific and technological fields.

CHAPTER 4:

EXPERIMENT *RESULTS*

4.1 POTENTIOSTAT CONCEPTION

Potentiostats are simple devices that rely on operational amplifiers to keep a desired potential difference between two electrodes (working and reference electrodes) immersed in a solution while recording the electrical current that flows between them.

Normally a third electrode (counter electrode) is added to the system in order to isolate the electrode used as a potential reference (reference electrode) from the charge transfer reaction.

A basic potentiostat can be assembled using a handful of simple electronic components consisting of some resistors, capacitors, and operational amplifiers. A circuit diagram of the electronic components used in the simulation of the proposed can be seen in Figure4.1.

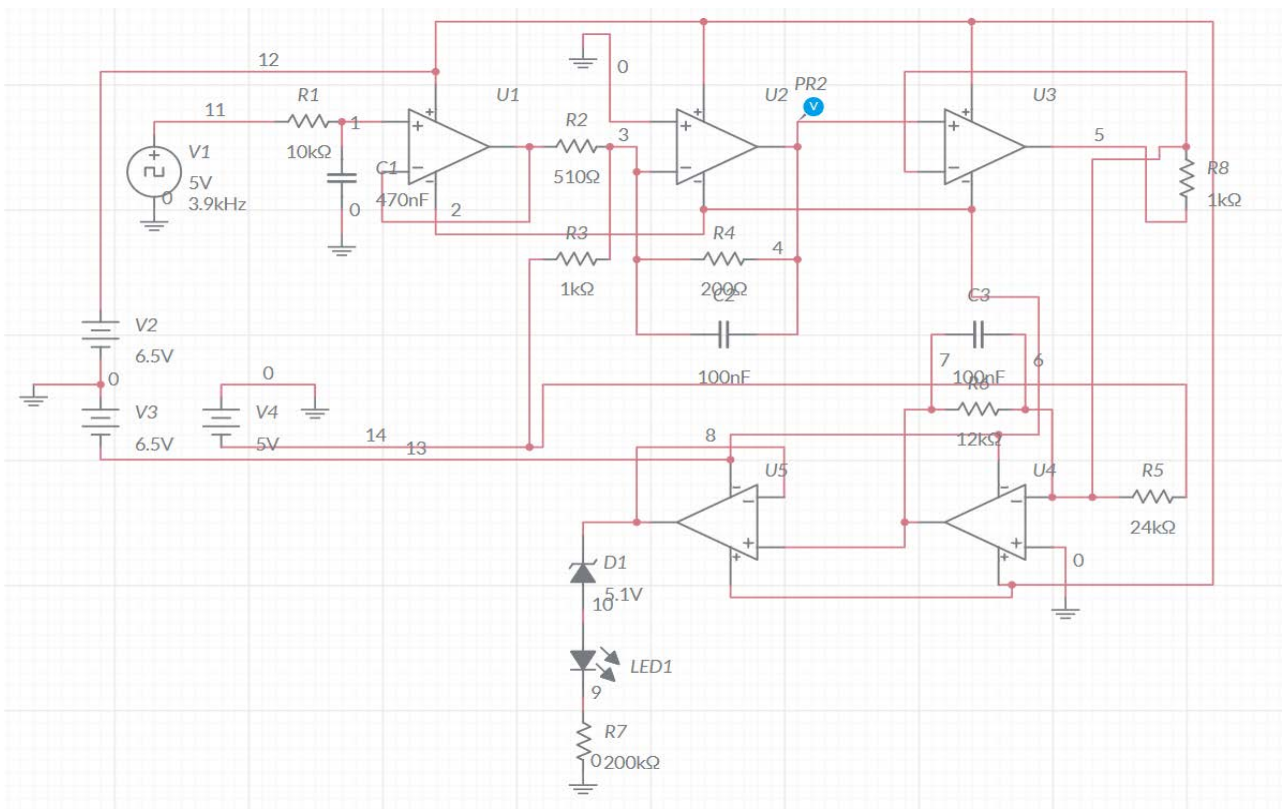


Figure 4.1: Schematic of our potentiostat

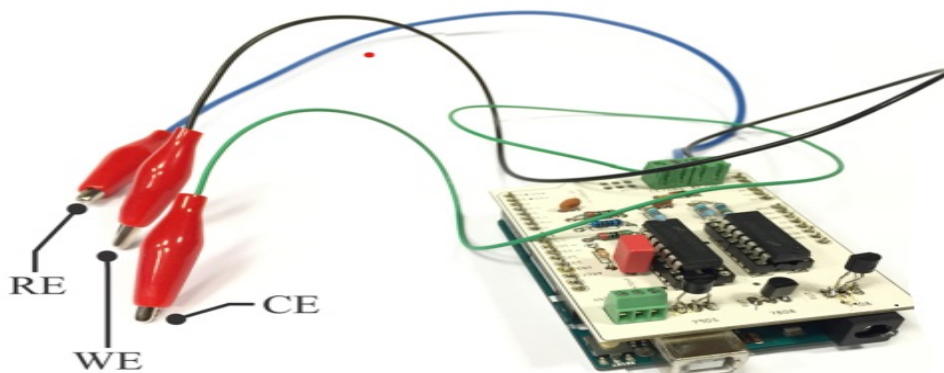


Figure 4.3: Show Fabrication potentiostat using Arduino

4.2 Data acquisition

The proposed data acquisition device presents a flexible and affordable solution, benefiting from the support of the open-source and do-it-yourself (DIY) community. It takes advantage of the Arduino IDE's serial communication capabilities to streamline data reception and transmission.

The collected data can be conveniently transmitted by the Arduino board in a tab-separated value (tsv) format, allowing for easy manipulation using any data processing software. Furthermore, users have the ability to visualize the data as a graph directly within the Arduino IDE version 2.1.0 and above.

This straightforward serial communication method empowers users with programming skills to develop customized communication programs using their preferred programming language.

4.3 Diffusion coefficient calculation

$$i_p = 268.600n^{\frac{3}{2}}AD^{\frac{1}{2}}Cv^{\frac{1}{2}} \quad (4.1)$$

Randles–Sevcik equation at 25°C where:

- D: Diffusion coefficient cm^2/s
- N: Number of electrons involved on the reaction
- A: Area of the electrode cm^2
- C: Concentration of the electroactive species mol/cm^3
- v: Scan rate
- i_p : Peak current **Amper**

4.4 Arduino sketch

Basic Arduino script used to perform electrochemical experiments. The latest version of Arduino IDE can be downloaded from: <https://www.arduino.cc/en/Main/Software>.

The script shown below was used to automatically perform cyclic voltammetry experiments at different scan speeds, as discussed in the Diffusion Coefficient Determination section of the main manuscript. All parameters (slew rate and potential window) can be set in the software.

This shows the flexibility and versatility of the design (both hardware and software) in allowing multiple experiments to be performed and repetitive procedures to be automated[51].

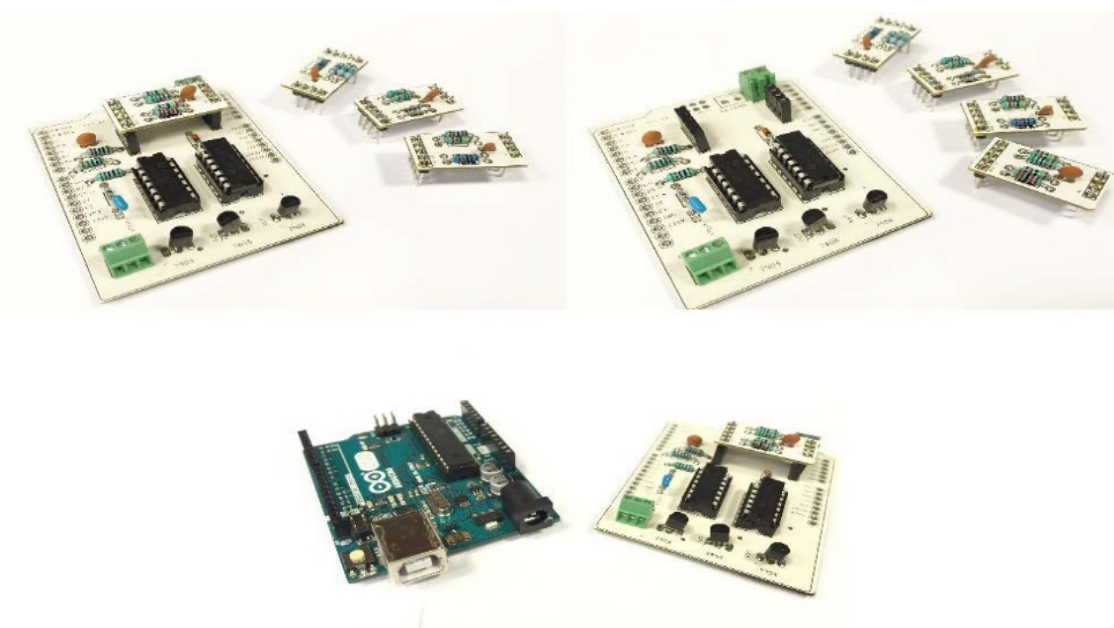


Figure 4.4: Multiple pictures of the proposed potentiostat design fabricated using a custom etched PCB in an “Arduino shield” configuration. The small PCBs on the top pictures are shield that can be attached to the main PCB to allow for current range changing.

4.5 Cyclic Voltammograms Explained

In the example of the cyclic voltammogram described above, the scan begins at -1V and proceeds forward towards more positive, oxidative potentials. Initially, the potential is insufficient to oxidize the analyte (a).

As the potential approaches several kT of the standard potential, it reaches the onset of oxidation (E_{onset}). At this point, the current starts to exponentially increase (b) as the analyte undergoes oxidation at the working electrode surface. In reversible processes, the current initially rises without a change in the oxidant concentration. It depends on the rate of oxidant diffusion to the electrode and the proportion converted to the reduced form, as explained by the Nernst equation.

As the scan continues, the oxidant gradually depletes, resulting in a change in the concentration gradient. This leads to the formation of a peak in the voltammogram. The decrease in current due to oxidant depletion outweighs the increase caused by altering the proportion of oxidant being oxidized at the electrode.

The current reaches its maximum peak at point c, known as the anodic peak current (i_{pa}) corresponding to oxidation at the anodic peak potential (E_{pa}). At this stage, increasing potentials result in an increased current, although limited by a diminishing flux of analyte from greater distances away from the electrode surface.

Beyond this point, the current becomes limited by the mass transport of analyte from the bulk to the double-layer interface, which is slow on the electrochemical timescale. Consequently, the current decreases (d) as the potentials are scanned more positively. This decline continues until a steady-state is achieved, where further increases in potential have no effect.

When reversing the scan to negative potentials (reductive scan), the analyzer continues to undergo oxidation until the applied potential reaches a value where the accumulated oxidized analyte at the electrode surface can be re-reduced (e).

The reduction process mirrors the oxidation process, but occurs in the opposite scan direction, resulting in a cathodic peak (i_{pc}) at the cathodic peak potential (E_{pc}) (f). Ideally, the anodic and cathodic peak currents should have equal magnitudes but opposite signs, assuming the process is reversible (and if the cathodic peak is measured relative to the baseline after the anodic peak) see Figure 4.5 .

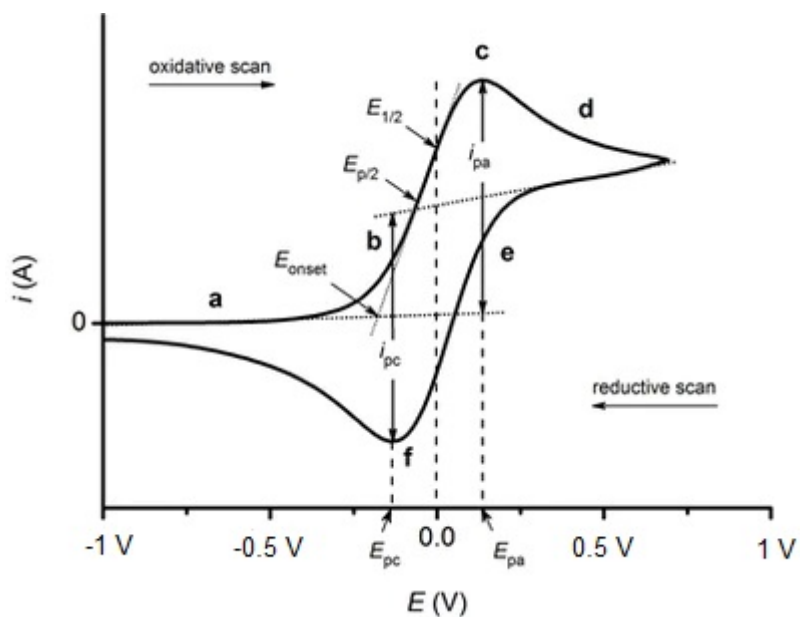
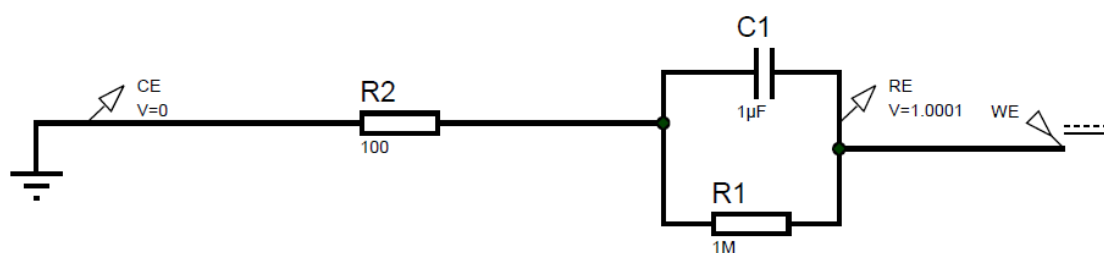


Figure 4.5: a cyclic voltammogram for an electrochemically reversible one-electron redox process.

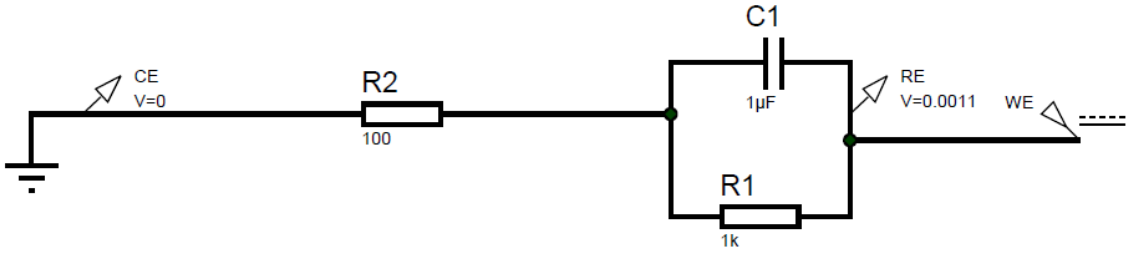
4.6 Electrode modulation

Some Experiment :

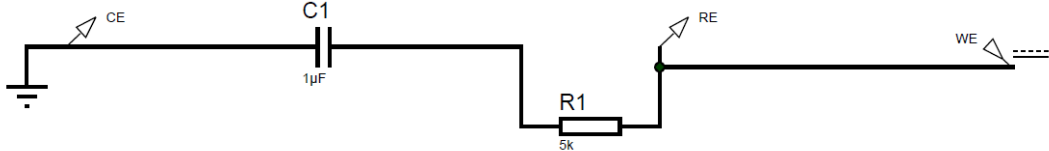
Experiment a:



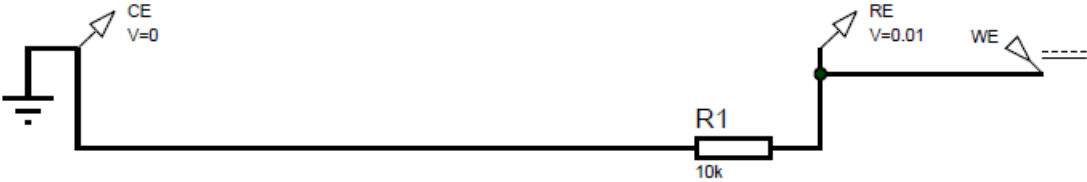
Experiment b :



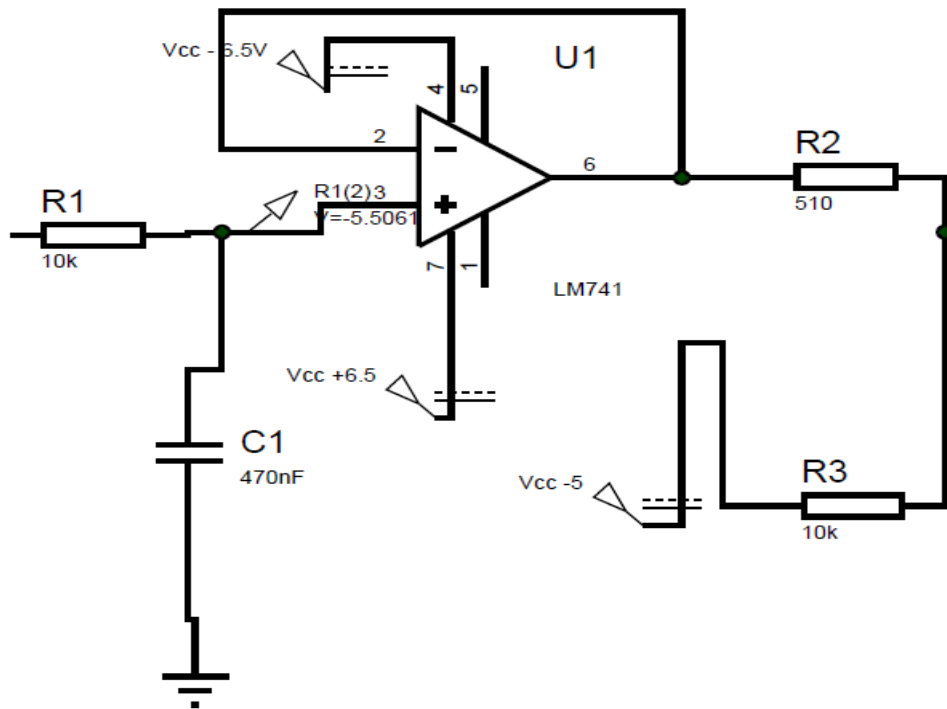
Experiment c :



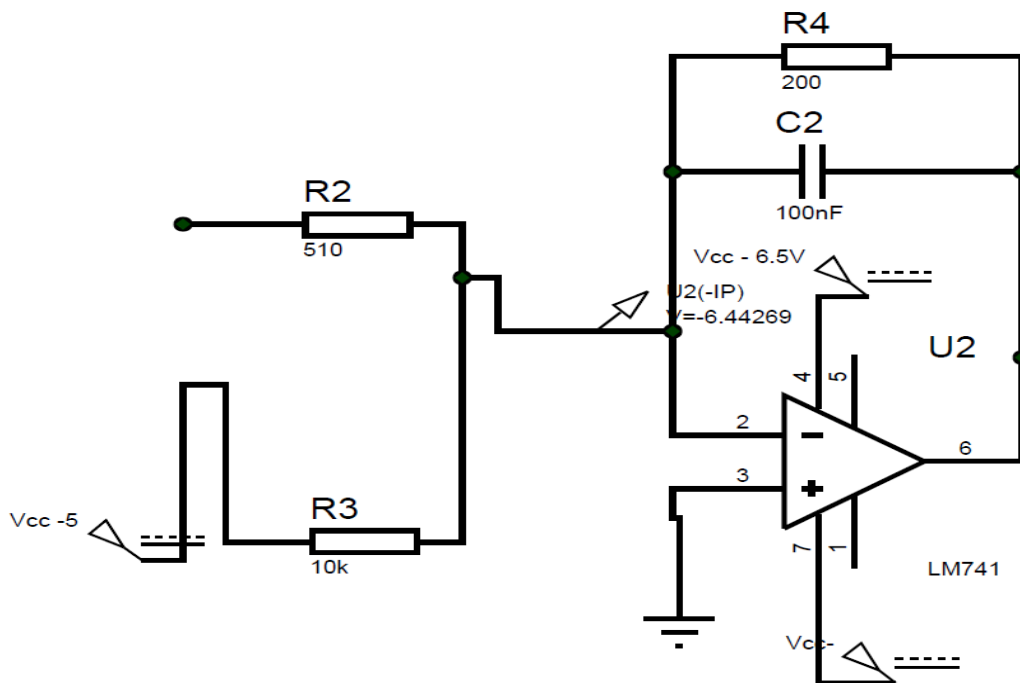
Experiment d :



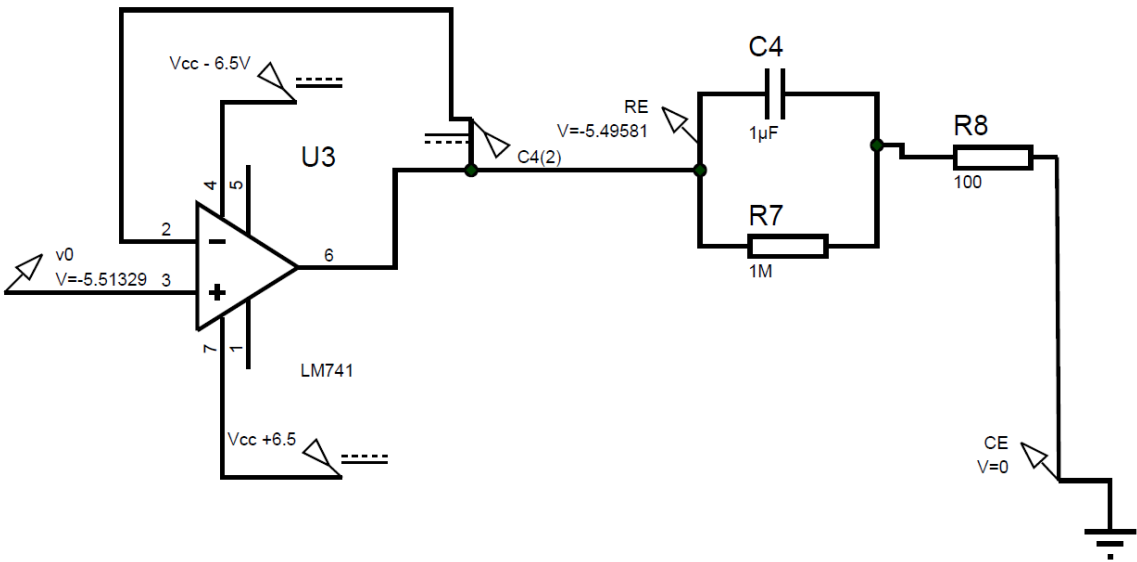
AOP assembly 1 :



AOP assembly 2 :



AOP assembly 3 :



General Conclusion

A simple potentiostat capable of detecting currents at the microampere level (μA) can be constructed using only a few easily accessible electronic components. This straightforward design enables students with basic knowledge of electronics to comprehend the functionality of a potentiostat, identify equipment limitations, and recognize sources of error.

The proposed device is suitable for collaborative educational experiments involving electrochemistry, electronics, and programming. Although its capabilities are somewhat limited in comparison to commercial equipment, its affordability, with a total material cost of less than \$80.00 (including the Arduino Uno board), makes it a viable alternative, particularly in settings where electrochemistry experiments are typically conducted using computer software or web-based simulators.

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