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**Study of Direct Current Electrocatalytic Hydrogen Evolution on Bismuth
(111) Electrode In Diluted Acidic Solutions**

Bachelor's Thesis (12 ECTS)

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Abstract

This thesis investigates the Hydrogen Evolution Reaction (HER) on Bismuth (111) single crystal electrodes in dilute acidic solutions (pH 2.0 to 3.5) to validate a robust chronopotentiometric model that characterizes the transition from proton reduction to water reduction and identifies the specific moment of near-electrode alkalization. Using cyclic voltammetry (CV) for surface characterization and chronopotentiometry to monitor potential transients under constant current, the study demonstrates that HER on Bi(111) is a diffusion-controlled process that is highly sensitive to proton availability. Experimental data analysis revealed that the unified diffusion coefficient (D) decreases with increasing bulk pH, a trend consistent with the Grotthuss mechanism, while the cathodic charge transfer coefficient (α_c) increases from approximately 0.74 at pH 2.0 to 0.9 at pH 3.0, suggesting improved electron transfer kinetics in less acidic environments. Ultimately, the research confirms that while Bismuth (111) is an ineffective HER catalyst compared to noble metals due to its weak hydrogen binding and slow Volmer adsorption steps, the proposed mathematical model accurately determines critical kinetic parameters and benchmarks catalytic activity by identifying the exact point of surface pH shifts.

Keywords:

Bismuth (111)

Hydrogen Evolution Reaction (HER)

Chronopotentiometry

Cyclic Voltammetry

Dilute Acidic Solution

Unified Diffusion Coefficient

Charge Transfer Coefficient

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Uuring elektrolüütilise vesiniku eraldumise kohta vismuti (111) elektroodil lahjendatud happelistes lahustes

Lühikokkuvõte

See väitekirj uurib vesiniku eraldumise reaktsiooni (HER) vismut(111) monokristallelektroodidel lahjendatud happelistes lahustes (pH 2,0 kuni 3,5), et valideerida töökindlat kronopentiomeetrilist mudelit, mis iseloomustab üleminekut prootoni redutseerimisest vee redutseerimisele ja tuvastab elektroodilähedase leeliselisuse hetke. Kasutades tsüklilist voltammeetriat (CV) pinna iseloomustamiseks ja kronopentiomeetriat potentsiaali siirete jälgimiseks konstantse voolutugevuse juures, näitab uuring, et HER Bi(111)-l on difusiooniga kontrollitud protsess, mis on prootonite kättesaadavuse suhtes väga tundlik. Eksperimentaalsete andmete analüüs näitas, et ühtne difusioonikoefitsient (D) väheneb pH suurenemisega, mis on kooskõlas Grotthussi mehhanismiga, samas kui katoodse laenguülekande koefitsient (αc) suureneb ligikaudu 0,74-lt pH 2,0 juures 0,9-ni pH 3,0 juures, mis viitab elektronülekande kineetika paranemisele vähem happelises keskkonnas. Lõppkokkuvõttes kinnitab uuring, et kuigi vismut (111) on oma nõrga vesiniku adsorptsiooni ja aeglase Volmeri adsorptsioonietappide tõttu võrreldes väärismetallidega ebaefektiivne HER-katalüsaator, määrab pakutud matemaatiline mudel täpselt kriitilised kineetilised parameetrid ja hindab katalüütilist aktiivsust, tuvastades pinnalähedase pH muutuse täpse punkti.

Võtmesõnad:

Vismut (111)

Vesiniku eraldumise reaktsioon (HER)

Kronopentiomeetria

Tsükliline voltammeetria

Lahjendatud happeline lahus

Ühendatud difusioonikoefitsient

Laenguülekande koefitsient

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TERMS, ABBREVIATIONS AND NOTATIONS

Table 1. List of symbols, brief explanation and units of physical quantities used in the text

Symbol	Definition	Unit
pH_∞	bulk pH value	
α_c	(cathodic) charge transfer coefficient	
$c^\ominus$	standard concentration	mol dm^{-3}
E_{ref}	the potential of the used Ag AgCl KCl reference electrode	$E_{\text{ref}} = 0.21 \text{ V vs. SHE}$
D_s	diffusion coefficient of the species S	m^2/s
η	overpotential	V
j	current density	$\mu\text{A cm}^{-2}$
j_{ex}	exchange current density	$\mu\text{A cm}^{-2}$
[S]	molar concentration of the species S	M
A	electrode area	cm^2
c	H^+ ions concentration	M
C	capacitance	F
D	Unified diffusion coefficient of OH^- and H^+ ions	cm^2/s
E	electrode potential (vs. the standard hydrogen electrode, SHE, unless otherwise noted)	V
F	Faraday constant	$F = 96485.3 \text{ C mol}^{-1}$
k	reaction rate coefficient	$k = 10^{-5} \text{ m s}^{-1}$
n	number of electrons	

R	gas constant	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
t	time	s
T	temperature	$T = 298.15 \text{ K}$
x	distance between the electrode surface	cm
v	scan rate	mV/s

1. Introduction

The experimental and theoretical study of the hydrogen evolution reaction (HER) has significantly influenced the course of electrochemistry. Tafel [1], Erdey-Gruz and Volmer [2] and Butler [3] pioneered this field, leading to significant findings. Over the last century, significant progress has been made in understanding the kinetic properties of HER and unraveling its complicated processes across various electrode materials, including Au and Pt, as well as other metallic substrates. The interest in electrolytic hydrogen evolution remains strong, largely due to hydrogen's recognition as a high-gravimetric, energy-dense, and environmentally friendly fuel—an embodiment of renewable, clean energy.

Electrochemical water splitting stands out as a clean and efficient route to produce high-purity hydrogen, which serves as a crucial reactant or raw material in numerous non-electrochemical processes, such as ammonia synthesis and the Fischer–Tropsch process. Furthermore, hydrogen evolution captures attention as an inevitable side reaction in other significant electrode processes, such as CO₂ electroreduction and the galvanic deposition of various non-precious metals, including Zn, Co, Fe, and Ni. This leads to near-surface alkalination, which can profoundly influence the primary process rate. Typically, at high negative potentials, hydrogen evolution can proceed not only through the reduction of H⁺ ions but also through the direct reduction of H₂O molecules, unless the electrolyte solution is strongly acidic. Thus, it is essential to understand the kinetics of hydrogen evolution as it emerges in slightly acidic solutions under high overpotential

2. Literature Review

2.1. Fundamental Concepts and Mechanisms of Electrochemical Hydrogen Evolution Reaction (HER)

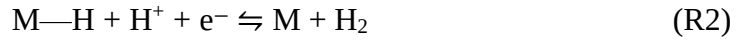
The Hydrogen Evolution Reaction (HER) is a fundamental electrochemical process that reduces protons or water molecules to produce hydrogen gas (H₂), with its mechanism depending on electrolyte pH [4] [5].

Under an acidic medium, HER proceeds through the following mechanism: Volmer step i.e., the initial electrochemical adsorption of a proton (H⁺) from the solution onto an active site on the electrode surface. As shown in the equation below



M represents an adsorption site on the catalyst surface, and H* denotes the adsorbed hydrogen atom.

Subsequently, the Heyrovsky step involves the electrochemical desorption of the adsorbed hydrogen atom from the electrode surface. In this step, the adsorbed hydrogen atom reacts with another proton from the solution and an electron (e^-) to form a hydrogen molecule (H_2). The reaction is represented as:

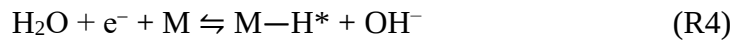


Or the Tafel step, where two adsorbed hydrogen atoms combine on the surface to form a hydrogen molecule, freeing up two active sites



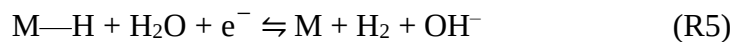
M—H denotes a site where a hydrogen atom has been adsorbed.

In an alkaline medium, HER proceeds via the reduction of water molecules rather than protons, due to the low H^+ concentration [6]. The Volmer step involves the dissociation of a water molecule at the electrode surface, resulting in the adsorption of a hydrogen atom and the release of a hydroxide ion (OH^-) into solution. It can be represented as:



The adsorbed hydrogen atom proceeds to hydrogen production through either one of the following steps:

- **Heyrovsky Step**, where adsorbed hydrogen atoms react with another water molecule and an electron, desorbing as a hydrogen molecule, releasing a hydroxide ion, and regenerating the active site



- **Tafel Step**, where two adsorbed hydrogen atoms combine on the electrode surface to form a hydrogen molecule, freeing two active sites



The rate-determining step among these determines the overall reaction kinetics. The system is restricted by proton discharge whenever the Volmer step operates slowly [7]. System performance depends on the desorption rate and recombination speed, as these steps control Tafel or Heyrovsky reactions. Each material shows its preference for reaction steps with different rates. [8]

Platinum uses Volmer-Tafel kinetics as its primary mechanism due to its strong hydrogen adsorption, which leads to this pathway [9]. Understanding the full reaction mechanism of bismuth (Bi) (111) is crucial because its high overpotential leads to weak hydrogen binding, making it an ineffective catalyst for the hydrogen evolution reaction (HER). Additionally, the slow Volmer adsorption steps influence how we interpret performance variations in the system. [10]

2.2. Kinetics- and Electrocatalytic Activity of Metals in HER

The kinetics and thermodynamics of the Hydrogen Evolution Reaction (HER) are governed by electrochemical rate laws, primarily the Butler-Volmer and Tafel equations, which relate current density to the overpotential required to drive the reaction. [11]

The Butler-Volmer equation is:

$$j = j_0 \left[-\exp\left(-\frac{\alpha_c F \eta}{RT}\right) + \exp\left(\frac{(1-\alpha_c) n F \eta}{RT}\right) \right] \quad (1)$$

where j is the current density, j_0 is the exchange current density, α_c is the cathodic charge transfer coefficient, η is the overpotential, F is the Faraday constant, R is the gas constant, and T is the temperature. At sufficiently high cathodic overpotentials, the anodic contribution becomes negligible, and the Butler-Volmer equation simplifies to the Tafel equation:

$$\eta = a + b \log(i) \quad (2)$$

where b is the Tafel slope. The Tafel slope provides insight into the rate-determining step of HER: values of approximately 120 mV dec^{-1} correspond to the Volmer step (proton adsorption),

$\sim 40 \text{ mV dec}^{-1}$ to the Heyrovsky step (electrochemical desorption), and $\sim 30 \text{ mV dec}^{-1}$ to the Tafel step (chemical recombination) under standard conditions.

Thermodynamically, HER requires an electrode potential below 0 V vs. SHE, with overpotential overcoming kinetic barriers. Optimal catalysts exhibit low overpotential and high exchange current density, which reflects fast kinetics and low activation energy

According to the Sabatier principle, optimal HER catalysts exhibit a hydrogen adsorption free energy near zero, enabling efficient adsorption and desorption, as exemplified by platinum, which peaks on the volcano plot [12]. In contrast, metals such as gold (with weak hydrogen binding) and tungsten (with overly strong binding) exhibit reduced HER efficiency.

2.3. Bismuth as an Electrocatalyst for HER

Bismuth (Bi) is a metal of interest as an electrocatalyst for HER due to its distinctive physical and chemical properties, though it has certain inherent limitations. It has a semi-metallic nature and a relatively low carrier density, which refers to the number of mobile charge carriers per unit volume, resulting in fewer electrons participating in conduction compared to most transition metals. However, studies indicate that the density of states at the bismuth surface is higher than in its bulk, which could facilitate the charge transfer processes required for HER. The Bi (111) surface exhibits a rhombohedral crystal structure. The interatomic distances within the same atomic layer are approximately $3.10 \text{ \AA}$, whereas the spacing between adjacent layers is about $3.47 \text{ \AA}$. Notably, this interlayer spacing is shorter than the van der Waals radius of bismuth ($4.8 \text{ \AA}$), indicating that robust covalent bonding within layers coexists with weaker van der Waals interactions between layers. The double-layered rhombohedral structure of Bi (111) single crystals makes their surfaces highly amenable to reproducible electrochemical polishing — each polishing cycle reliably restores the nominal surface orientation. This guarantee of structural consistency is not merely a practical convenience; it is a prerequisite for meaningful kinetic measurements, as it ensures that observed electrochemical responses reflect the intrinsic properties of the Bi(111) facet rather than preparation-induced surface artefacts. The surface of bismuth is characterized by a suboptimal adsorption free energy, which is a crucial factor in the kinetics of HER. Modifications, such as Bi (111) facet engineering or bismuth oxide layer formation, enhance its HER activity in acidic media, though its performance remains inferior to platinum, warranting further investigation for dilute acidic solutions. [13]

2.3.1. Role of Bismuth Oxide (Bi_2O_3) in Electrochemical HER

Bismuth electrodes inherently exhibit low efficiency toward HER; however, introducing a bismuth oxide layer on their surface can moderately enhance their activity. This improvement mainly comes from the generation of oxygen vacancies, especially in alkaline environments, even though bulk Bi_2O_3 itself is generally regarded as catalytically inactive due to its suboptimal hydrogen adsorption energy [14].

Research has demonstrated that plasma-treated Bi_2O_3 nanosheets with controlled oxygen vacancy concentrations exhibit significantly improved HER performance. However, it's crucial to optimize the vacancy concentration, as excessive vacancies can lead to overly stable hydrogen adsorption, thereby diminishing HER efficiency. Studies have confirmed that synthesized bismuth nanohexagons, comprising both polycrystalline bismuth and bismuth oxide, exhibit effective hydrogen-ion storage and evolution properties [15]. Additionally, the formation of Bi_2O_3 -containing oxide films on bismuth electrode surfaces during electrochemical processes has been observed, indicating that bismuth oxide forms readily and likely contribute significantly to the HER mechanism. While these studies demonstrate that forming composites, engineering oxygen vacancies, or operating in alkaline media can enhance the HER performance of bismuth-based electrodes, they inherently mask the intrinsic catalytic behavior of the pure metal. The heavy focus in current literature on these modified systems and alkaline environments highlights a significant gap: a fundamental understanding of how pure, unmodified bismuth operates. Therefore, to establish a true baseline for bismuth's electrocatalytic capabilities, it is critical to investigate well-defined single-crystal surfaces, such as pure Bi(111), specifically within dilute acidic solutions. This approach allows the direct reduction of protons to be isolated and studied without the compounding effects of engineered oxide layers, structural defects, or alkaline water-reduction pathways.

2.4. Effect of Crystal Structure on Hydrogen Evolution Reaction

2.4.1. Polycrystalline Bismuth

Polycrystalline bismuth electrodes are attracting attention for their hydrogen evolution reaction (HER) activity across a range of pH values. Research on bismuth nanohexagons, composed of polycrystalline bismuth and bismuth oxide, highlights their effective hydrogen-ion storage and gas-evolution capabilities. While some studies emphasize bismuth's role in carbon dioxide reduction, they often note that hydrogen evolution competes with this process, showcasing

polycrystalline bismuth's catalytic potential for HER [16]. A notable study demonstrated a bismuth tungstate composite anchored to the conductive polymer PEDOT: PSS, which exhibited enhanced HER activity in alkaline conditions, achieving a Tafel slope of 106 mV/dec. This suggests that the reaction may follow a Volmer-Heyrovsky mechanism, where water dissociation and hydrogen adsorption are rate-limiting steps. Additionally, a composite of graphene oxide and a mononuclear bismuth metal complex showed excellent HER performance in 1 M KOH, with a low Tafel slope of 44 mV/dec, indicating improved reaction kinetics [17]. Surface morphology plays a critical role in HER performance. Porous polycrystalline bismuth often has higher hydrogen evolution overpotentials compared to smoother surfaces, suggesting that increased porosity may not lead to better activity due to limited access to active sites and unfavorable electronic conditions [18]. Nonetheless, forming composites with materials like conducting polymers or graphene oxide shows promise for enhancing HER performance, as demonstrated by the improved Tafel slopes and lower overpotentials in these systems. While investigations into polycrystalline bismuth and its composites highlight the material's potential to drive HER—especially when coupled with conductive matrices or in alkaline environments—the inherent complexity of these surfaces presents a significant analytical challenge. Polycrystalline materials consist of a mixture of different crystallographic orientations and grain boundaries. Furthermore, variations in surface morphology, such as increased porosity, can limit access to active sites and create unfavorable electronic conditions. Because these structural variables make it difficult to isolate specific active sites or determine fundamental reaction kinetics, it is imperative to study a well-defined, uniform surface. This necessitates transitioning to single-crystal electrodes, such as pure Bi(111), which provide a platform free of grain boundaries to accurately investigate and benchmark bismuth's intrinsic catalytic activity.

2.4.2. Monocrystalline Bismuth

Bismuth single crystals are available for fundamental research, including electrochemical studies, due to their ordered structure, which enables investigation of anisotropic properties. Surface crystallography plays a crucial role in determining the electrochemical reactivity of electrode surfaces. Direct studies of the HER activity of various facets of pure bismuth single crystals are relatively limited; we fill this gap with our work. Single crystals, characterized by well-defined surface orientations and the absence of grain boundaries, provide a more uniform platform for studying intrinsic catalytic activity compared to polycrystalline materials, which consist of a mixture of different crystallographic orientations. The anisotropic thermoelectric

effects and variations in specific resistance observed in bismuth single crystals, depending on growth conditions, further highlight the importance of controlled crystalline structure in determining the material's fundamental properties, which, in turn, can influence its electrochemical performance. Future research focusing on the HER activity of specific bismuth single crystal facets deepens understanding of the structure-activity relationships in this system.

2.5 Influence of pH, Electrolyte Composition of Bismuth Electrodes in HER

The HER performance of bismuth electrodes is strongly pH-dependent, with catalytic activity varying by electrolyte conditions. In acidic media, bismuth supports HER with certain limitations, though its effectiveness is nuanced and tied to electrode composition. In neutral pH, bismuth may suppress HER, acting as an inhibitor. Conversely, alkaline environments yield the highest HER efficiency for tailored bismuth-based catalysts. This pH sensitivity arises from bismuth's surface chemistry, with distinct oxide and hydroxide species forming at different pH levels, influencing catalytic behavior. The HER mechanism also shifts between acidic (proton-driven) and alkaline (water-driven) conditions, altering bismuth surface interactions and reaction pathways. The superior performance in alkaline media suggests more favorable reaction kinetics and stable catalytic sites, highlighting bismuth's potential when optimized [19]

3. Aims and Objectives

- Evaluate a mathematical model for fitting chronopotentiometry data on Bi(111) to isolate intrinsic kinetic parameters, confirming the model's robustness by demonstrating the pH-independence of the fundamental reaction rate coefficient.
- Systematically investigate the effect of electrolyte pH on the chronopotentiometric response of the Bi(111) electrode, quantifying the resulting variations in current behaviour to determine model parameters.

4. Experimental Part

4.1. Electrochemical Methods

Electrochemical techniques, such as chronopotentiometry and cyclic voltammetry, are used to investigate electron-transfer processes. They offer crucial information about reaction pathways,

the characteristics of materials, and the performance of electrochemical systems in practical applications [20].

4.1.1. Cyclic Voltammetry

Cyclic voltammetry is one of the simplest and most widely used electrochemical techniques for characterizing materials and processes that occur at electrochemical interfaces. This technique provides valuable information and reveals two critical aspects: the condition of the electrode surface (e.g., single-crystal structure such as single crystal characterization and the presence or absence of impurities in the studied system).

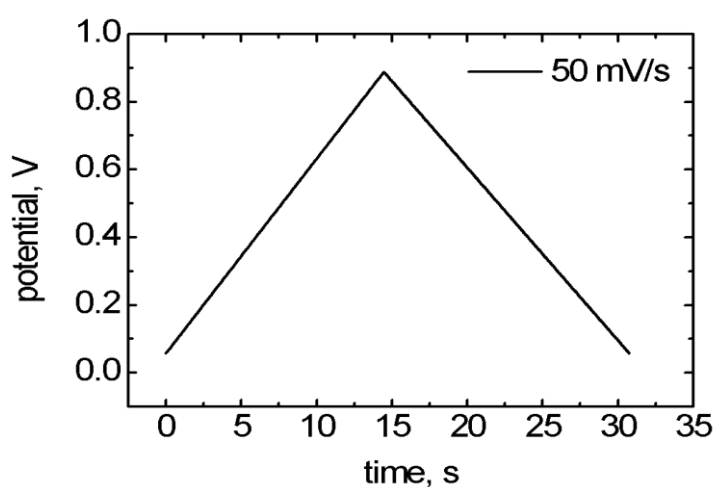


Figure 1. Triangular signal applied in cyclic voltammetry

The process involves recording the current that flows through the working and counter electrodes while applying a potential sweep at a constant rate. This linear potential sweep is

achieved using a triangular signal, with the slope (in absolute value) representing the scanning rate, v , figure 1

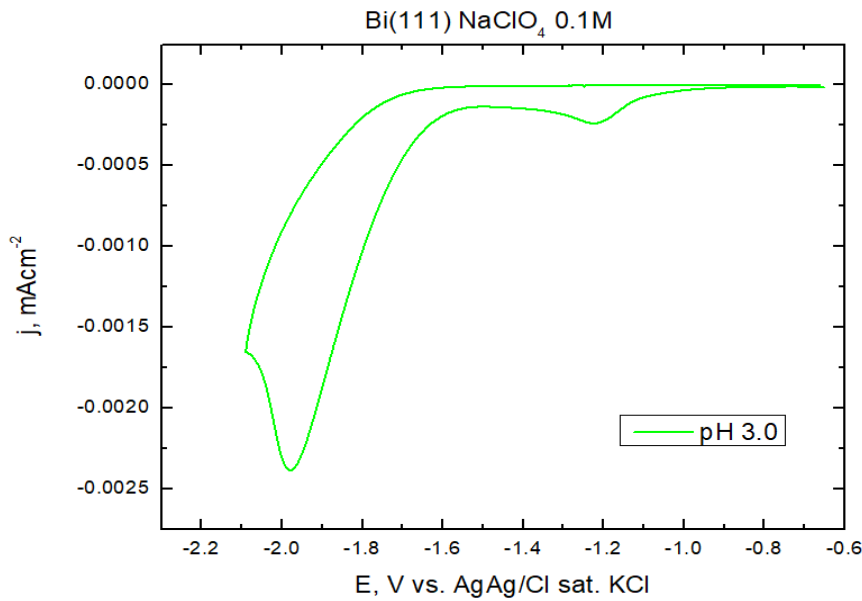


Figure 2. Cyclic voltammogram for Bi (111) electrode measured in 0.1 M NaClO₄ + HClO₄ aqueous electrolyte at $v = 50 \text{ mV}\cdot\text{s}^{-1}$.

The current density, j , plotted against the potential, E , is referred to as a voltammogram (see Figure 2.). Typically, different electrochemical processes at the electrode are characterized by the appearance of oxidation or reduction peaks (or waves in the case of irreversible processes with complex mechanisms) in the current versus potential plot. The current peak generally corresponds to the process occurring at the electrode, and the voltammetric waveform (or peak) provides insight into the nature and kinetics of the process initiated by the potential scan [8]. In Figure 2, this behavior is illustrated: the small cathodic peak observed around -1.2 V is attributed to the reduction of protons present in the electrolyte. As the potential becomes more negative, a much larger increase in cathodic current occurs near -1.9 V , indicating the onset of water splitting, which dominates once the available protons are depleted.

Electrode processes can be classified into two major categories: adsorption-controlled and diffusion-controlled. The current peak is proportional to the applied sweep rate for adsorption-controlled processes. Additionally, the charge circulated during the sweeps gives information about the surface coverage of the adsorbed species. In contrast, for diffusion-controlled processes, the peak current is directly proportional to the square root of the potential sweep rate

[21]. This distinction helps differentiate these processes from adsorption-controlled ones. Furthermore, the shape of the waveform is influenced by the kinetics of the redox reaction.

4.1.2. Chronopotentiometry

Chronopotentiometry is a technique that involves applying a fixed current to an electrochemical cell and monitoring the resulting changes in potential over time. This controlled current drives the electrochemical reaction, and the resulting potential-time curve, known as the chronopotentiogram, provides valuable information about the formal potential, diffusion coefficient, and the number of electrons transferred [22]. Critically, directly yields the time–potential transients needed to fit the proposed mathematical model. In this work, chronopotentiometry was essential for examining how stable and efficient the Bi (111) electrode operates when a constant current is applied for hydrogen evolution; a key parameter in this process is the transition time. Analyzing this transition using the Sand equation makes it possible to determine species concentrations and diffusion coefficients; it provides an estimate for the transition time (t_{char}), it is only an approximation because it assumes a constant Faradaic current, whereas in real experiments, a portion of the current is used for double-layer charging. This makes chronopotentiometry a powerful tool for investigating electrochemical kinetics and various analytical applications, including concentration determination, electrode kinetic studies, mixture analysis, and adsorption investigations. However, there are some limitations to be mindful of, including sensitivity to the electrode surface, mass-transport limitations, and difficulties arising from irreversible reactions or interfering substances. These factors necessitate careful consideration to ensure reliable analysis. [23] [24]

The obtained time–potential profiles provided information on how the Bi (111) electrode activated, evolved over time, and performed in terms of hydrogen evolution. These chronopotentiometric transients formed the primary dataset upon which all subsequent modelling and analysis in this study were based. Chronopotentiometry enabled the measurement of electrode stability and the identification of changes in performance or mechanisms during the electrolysis process.

4.2. Electrode preparation

The working electrode, a bismuth (111) electrode with a diameter of 3.68 mm, was electrochemically polished to ensure a clean and uniform surface. The geometric surface area of the electrode was calculated from the diameter as 0.106 cm^2 and used to normalize all

surface-area-dependent quantities, such as current densities and specific capacitance. After brief mechanical polishing, the electrode was immersed in an ultrasonic bath containing Millipore water to remove any residual polishing materials. After this, the surface of the working electrode was electrochemically polished in a saturated aqueous KI and HCl solution by controlled anodic dissolution. As soon as the electrode had been polished, it was immediately rinsed with ultrapure water (18.2 M Ω cm; Milli-Q purification system by Millipore). A small droplet of ultrapure water protected the surface from airborne contaminants during transfer into the electrochemical cell. The electrode was immersed in the electrolyte at open circuit potential, and later, the chronopotentiometry program was started.

4.3. Electrochemical cell and setup:

Electrochemical measurements were performed in a three-electrode glass cell using ultrapure water and analytical-grade reagents. The auxiliary electrode was a platinum wire, and the reference electrode was a double-junction Metrohm Ag/AgCl electrode in saturated KCl. The electrolyte solutions were prepared with varying concentrations of perchloric acid (HClO₄, Merck Suprapure, 70%) and sodium perchlorate (NaClO₄, Sigma-Aldrich, 99.9%, trace metals basis) to achieve pH values of 2.0, 2.5, 3.0, and 3.5 while maintaining a constant ionic strength of 0.1 mol dm⁻³. The pH of each solution was measured using a calibrated pH meter (Metrohm 913). Prior to the measurements, the electrolyte solutions were saturated with argon (Ar) for 15 minutes, followed by additional saturation to remove hydrogen gas (H₂) produced during the experiments and hydrogen bubbles from the electrode surface. Voltammetric and chronopotentiometric measurements were performed using an Autolab PGSTAT302N potentiostat controlled by Nova v2.1 software; open-circuit voltage and recorded transients were additionally inspected/measured using the digital oscilloscope Rigol DHO 814.

To systematically evaluate the electrochemical behavior of the Bi(111) electrode, both Cyclic Voltammetry (CV) and Chronopotentiometry (CP) were performed. Prior to the transient measurements, cyclic voltammograms were recorded at a constant scan rate of 50 mV s⁻¹ to assess the initial surface state and confirm the absence of impurities in the system. Following this, chronopotentiometric measurements were executed by applying constant cathodic current densities. To properly capture the potential transients and account for the varying availability of protons across the different electrolytes, the applied current densities were scaled according to the bulk pH. Specifically, the applied current densities (*j*) ranged from approximately -40 μ A cm⁻² in the least acidic solution (pH 3.5) up to roughly -7000 μ A cm⁻² in the most acidic solution

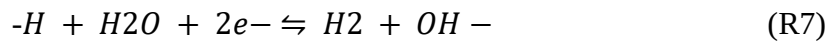
(pH 2.0). The resulting potential-time curves were then recorded to identify the characteristic transition time (t_{char}) for near-surface alkalization.

5. Model Fit and Data Analysis

The data analysis in this thesis is based on a robust mathematical model designed to characterize the electrochemical performance of the Bi (111) electrode during the hydrogen evolution reaction. This model simulates how the electrode's potential changes over time when a constant current is applied in a convection-free, mildly acidic environment [23]. Instead of modeling multiple complex steps, it simplifies the process to a single charge-transfer reaction in which H^+ is consumed and OH^- ions are produced. By adjusting three variable parameters—the unified diffusion coefficient (D), the reaction rate coefficient (k), and the charge transfer coefficient (α)—the model accurately fits experimental data to identify the exact moment the solution near the electrode surface turns from acidic to alkaline. Ultimately, fitting this model allows for the calculation of a pH-dependent exchange current density, which provides a standardized score to benchmark bismuth's catalytic activity against other materials like platinum or gold.

5.1. Fundamentals of Model Fit

In the actual fit the mathematical model used to characterize the electrode's electrochemical performance during the Hydrogen Evolution Reaction (HER) under constant-current conditions in a convection-free, mildly acidic environment [23]. Rather than modeling multiple complex intermediate steps, the model simplifies the process into a single charge transfer reaction where protons are consumed, and hydroxide ions are produced:



The kinetics of this reaction are governed by the Erdey-Grúz–Volmer equation, which relates the Faradaic current density to the electrode potential (E) and the near-surface proton concentration

$$j_F = -2FkK_w^{\frac{\alpha_c}{2}} \left(e^{-\alpha_c \frac{FE}{RT}} [\text{H}^+]_0 - \frac{e^{(2-\alpha_c) \frac{FE}{RT}}}{[\text{H}^+]_0} \right) \quad (3)$$

The model is based on several physically justified simplifying assumptions. First, the fugacity of hydrogen gas is assumed to be unity, implying that the region near the electrode is saturated with hydrogen gas at standard pressure. Secondly, water autoprotolysis is considered to be in

instantaneous equilibrium throughout the system, enforcing the condition that the product of the concentrations of protons and hydroxide ions remains constant at all times and positions, independent of spatial or temporal variations.

$$[H^+][OH^-] = K_w(c^\ominus)^2 \quad (4)$$

Lastly, the diffusion coefficients of protons and hydroxide ions are assumed equal, allowing a simplified treatment of mass transport in the electrolyte by assuming equidiffusivity of these ions.

$$D = D_{H^+} \approx D_{OH^-} \quad (5)$$

To calculate the electrode potential E at any given time, the near-surface proton concentration must be determined by solving the governing equations for ion transport. By introducing the differential acidity (ξ), defined as $\xi = [H^+] - [OH^-]$, the separate diffusion equations for H^+ and OH^- , they are combined into a single expression:

$$\frac{\partial \xi}{\partial t} = \left(\frac{\partial^2 \xi}{\partial x^2} \right) \quad (6)$$

Assuming the system starts at a constant bulk differential acidity, this equation can be integrated to express the time-dependent near-surface differential acidity

$$\xi_0(t) = \xi_\infty + \frac{M(t)}{F\sqrt{D}} \quad (7)$$

In this expression, $M(t)$ is the semi-integral (Riemann–Liouville of order 1/2) of the Faradaic current density, which tracks the history of the current that has passed through the electrode up to time t . Once (t) is calculated, it is converted back into the near-surface proton concentration ($[H^+]$) using the autoprotolysis equilibrium constraint:

$$[H^+] = \frac{1}{2}(\xi - \sqrt{4K_w(c^\ominus)^2 + \xi^2}) \quad (8)$$

In actual galvanostatic experiments, the applied current density (j) is held constant, but it is not entirely Faradaic. A portion of the total current is required for charging the electrical double layer, characterized by the double-layer capacitance (C_d). Thus, the total current density is defined as:

$$j = j_F + C_{dl} \frac{dE}{dt} \quad (9)$$

This model predicts that a sharp potential drop occurs at a characteristic transition time (t_{char}), at which the near-surface concentration of H^+ ions approaches zero and the solution becomes alkaline. On planar electrodes with low double-layer capacitance, this transition is approximately described by the Sand equation, represented as:

$$t_{char} = \frac{F^2 \pi D \xi_{\infty}^2}{4 j_F^2} \quad (10)$$

which shows that t_{char} is directly proportional to the diffusion coefficient and the square of the bulk proton concentration. By fitting this mathematical framework to experimental chronopotentiograms, we can extract critical kinetic parameters, including the diffusion coefficient (D), the reaction rate coefficient (k), and the charge transfer coefficient

6. Results and Discussion

6.1. Cyclic Voltammetry and Surface Characterization

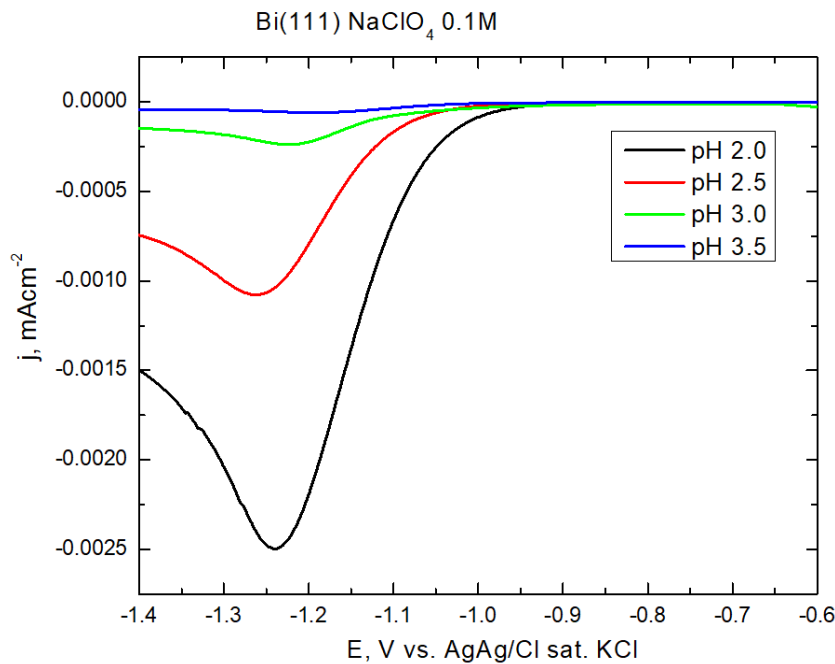


Figure 3. Cyclic voltammogram for Bi (111) electrode measured in 0.1 M NaClO₄ + HClO₄ aqueous electrolyte at $v = 50$ mV/s.

The cyclic voltammetry (CV) curves recorded for the Bi (111) electrode in 0.1 M NaClO₄ across pH levels 2.0 to 3.5 demonstrate a significant dependence of electrochemical behavior on the acidity of the electrolyte. At lower pH levels (2.0 and 2.5), the voltammograms exhibit a prominent cathodic current with a distinct reduction peak appearing around -1.25 V versus

Ag/AgCl, which corresponds directly to proton reduction or the Hydrogen Evolution Reaction (HER). As the pH increases to 3.5, this current response is nearly suppressed across the entire potential range, indicating that the HER on the Bi (111) surface is extremely sensitive to proton availability. The appearance of a peak rather than a plateau in this stationary setup is consistent with a diffusion-controlled process, where the peak current follows a linear relationship with proton concentration. This relationship is accurately described by a modified Randles-Sevcik equation, which accounts for the inherently sluggish kinetics of the bismuth electrode

$$I_m = 0.443 nFAc \sqrt{\frac{nFvD}{RT}} \quad (11)$$

Assuming n , F , A , v , D constant, the equation simplifies to

$$I_m = k' [H^+] \quad (12)$$

6.2 Chronopotentiometric Transients

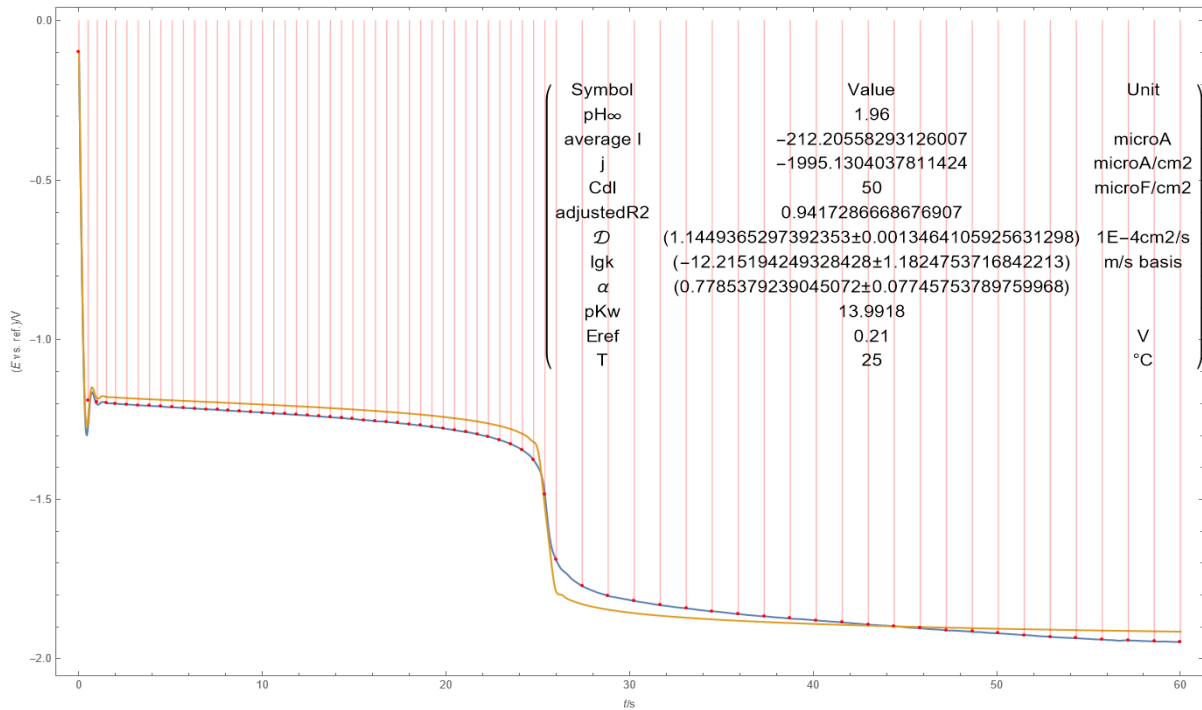


Figure 4. Chronopotentiogram measured on Bi (111) electrode, in solution of bulk pH = 1.96; line – measured response; dots – the model fit.

An imposed cathodic constant current causes a series of interfacial processes, which are reflected in the chronopotentiogram recorded on the Bi(111) electrode (Figures 4, A1 and A2

and Tables A2.1-A2.4). The transition from open-circuit conditions to galvanostatic control, where the applied current is initially used to charge the electrical double layer at the electrode/electrolyte interface, is what causes the abrupt initial potential drop at $t = 0$. Proton reduction takes over in the next region ($\approx 0-5$ s), but the diffusion of H^+ ions from the bulk solution cannot quickly enough replenish the interfacial region due to the relatively high current density. Consequently, the proton concentration at the electrode surface gradually drops and gets closer to depletion in about 6 seconds. Between approximately 6 and 10 s, once H^+ ions are nearly exhausted at the interface, water reduction becomes the prevailing cathodic reaction, generating OH^- ions and leading to the formation of a localized alkaline layer adjacent to the electrode surface. The establishment of this alkaline region increases the required overpotential to sustain the imposed current, producing the additional drop in potential observed in the chronopotentiogram.

6.3 Kinetic Parameters Derived from Model Fitting:

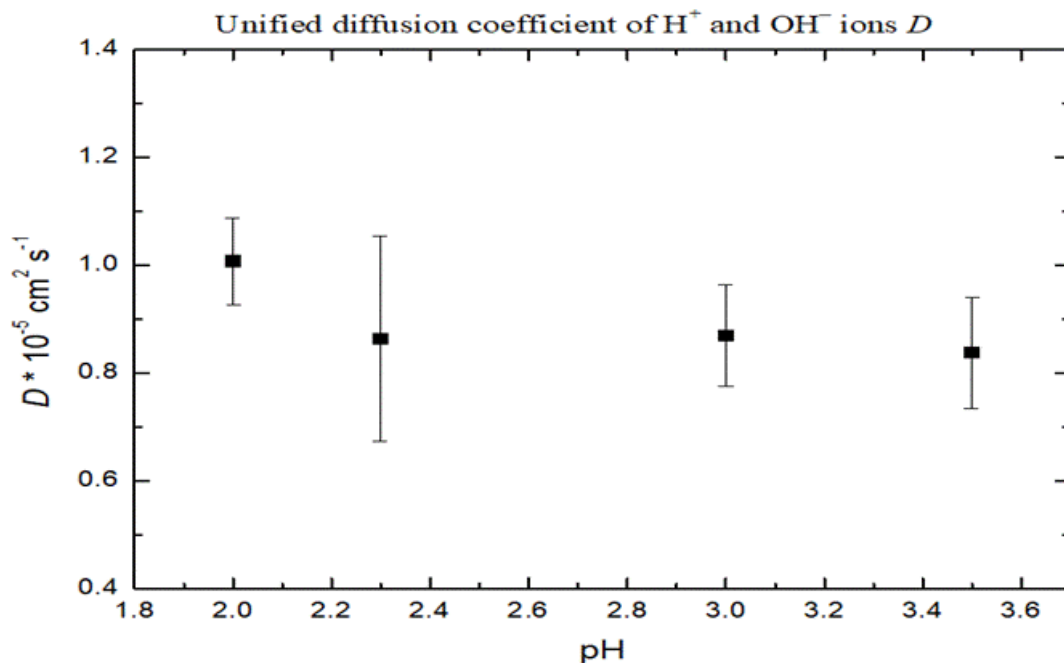


Figure 5. represents the variation of the unified diffusion coefficient (D) for the hydrogen evolution reaction (HER) recorded on the Bi (111) electrode as a function of pH.

Figure 5 illustrates the behavior of the unified diffusion coefficient (D) for H^+ and OH^- as a function of the bulk solution pH. As a transport parameter, D serves as a critical measure of the

movement of these ions through the electrolyte toward the catalyst surface. The data indicates that at pH 2.0, D is relatively high due to the dominant proton activity. As the bulk pH increases toward 3.5, the diffusion coefficient decreases because protons become less available and are partially replaced by hydroxide ions, which diffuse much more slowly than protons. This relationship is fundamentally characterized by the Grotthuss mechanism [25], which describes the rapid movement of protons; when their concentration decreases in less acidic conditions, the overall diffusion rate of the system declines correspondingly. Understanding this pH dependence is crucial for determining the precise moment of near surface alkalination, as D determines the rate at which reactants reach the catalyst surface.

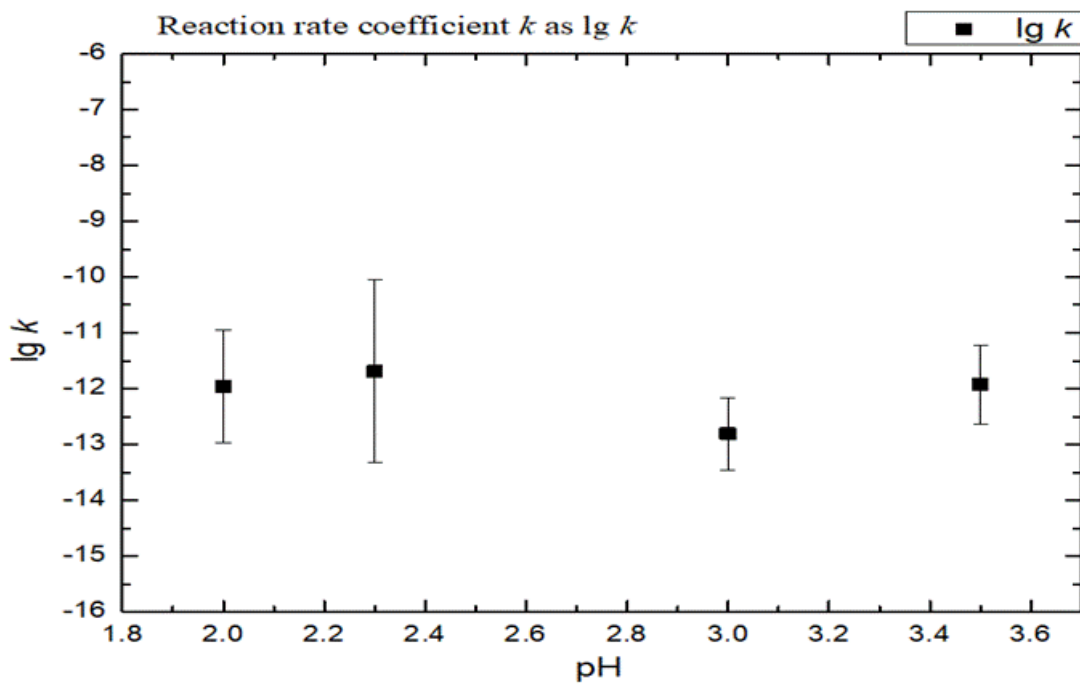


Figure 6. represents the variation of the reaction rate coefficient (k) as a logarithmic function for the hydrogen evolution reaction (HER) recorded on the Bi (111) electrode as a function of pH.

The reaction rate coefficient (k) is an inherent kinetic characteristic that defines the charge-transfer process; it depends on the chemical properties of the electrode material rather than on the electrolyte's acidity. Figure 6 shows that the Bi (111) electrode examination indicates that k remains invariant and exhibits no significant pH dependence over the measured range of 2.0 to 3.5. The observed independence is a crucial finding, as it directly indicates the robustness of the Erdey-Grúz-Volmer equation used in the model; it verifies that the mathematical framework effectively isolates the intrinsic catalytic properties of the bismuth surface from the influence of the bulk proton concentration. Although k remains constant with pH, it is used to denote the exchange current density (j_{ex}), which shows pH dependence when the cathodic charge transfer

coefficient (α_c) deviates from unity. As a result, the exchange current density, not the reaction rate coefficient, quantitatively captures any pH-dependent changes in bismuth's catalytic performance. The reaction rate coefficient remains constant as a standard for the material's particular activity.

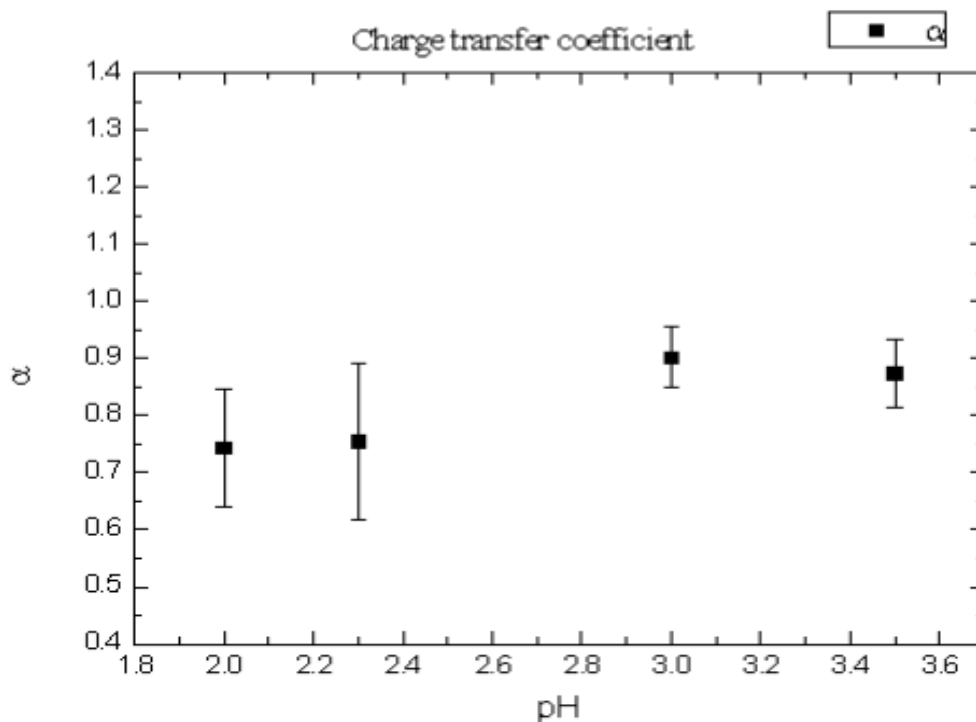


Figure 7. represents the variation of the charge transfer coefficient (α_c) as a logarithmic function for the hydrogen evolution reaction (HER) recorded on the Bi (111) electrode as a function of pH.

While the experimental data exhibits some variance, as indicated by the error bars, the overall upward trend points toward a modest improvement in electron transfer kinetics as the electrolyte becomes less acidic. At higher pH values, fewer protons are available, which necessitates a smaller absolute applied current to sustain the reaction; this in turn reduces the absolute applied potential and, consequently, weakens the interfacial electric field. We therefore hypothesize that the observed improvement in electron transfer kinetics may partly reflect this reduction in field strength, though it remains unclear without further experimental evidence. The possible contribution of specific surface states inherent to the Bi (111) crystal structure cannot be excluded, but in the absence of direct supporting citations for this system, this too should be regarded as a hypothesis rather than an established explanation. Furthermore, the consistently high α_c values observed across the studied pH range indicate that the rate-determining step involves a significant electron transfer component. This aligns with the characterization of

bismuth as a relatively ineffective HER catalyst, where weak hydrogen binding and a sluggish Volmer adsorption step collectively limit overall performance

7. Summary

This thesis investigates the Hydrogen Evolution Reaction (HER) using Bismuth (111) electrodes in dilute acidic environments (pH 2.0–3.5). The primary objective of research is to validate a robust chronopotentiometric model that characterizes the transition from proton reduction to water reduction, particularly at the moment of near-electrode alkalination. Bismuth is considered an ineffective HER catalyst compared to platinum due to its weak hydrogen binding and slow Volmer adsorption. The reaction on Bi(111) is extremely sensitive to proton availability and proceeds diffusion-controlled. Analysis shows that the unified diffusion coefficient (D) for ions decreases with increasing bulk pH, consistent with the Grotthuss mechanism. Conversely, the charge transfer coefficient (α_c) increases slightly with rising pH (from 0.74 to 0.9), indicating a modest improvement in electron transfer kinetics as the electrolyte becomes less acidic. The research uses cyclic voltammetry (CV) to characterize the electrode surface and chronopotentiometry to monitor potential transients over time at a constant current. These methods provide essential data on transition times and species concentration, which are fitted to the mathematical model to determine catalytic activity.

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ANNEX

1. Chronopotentiograms

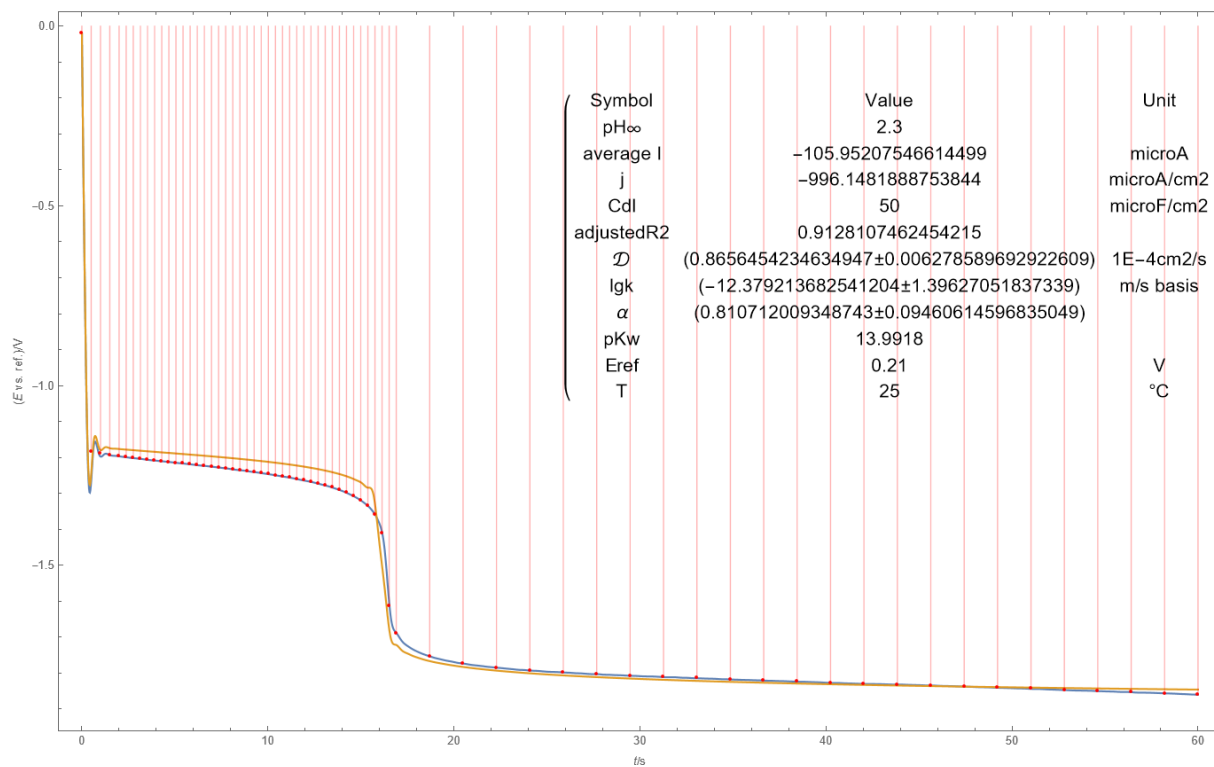


Figure A1. Chronopotentiogram measured on Bi (111) electrode, in solution of bulk pH = 2.3; line – measured response; dots – the model fit.

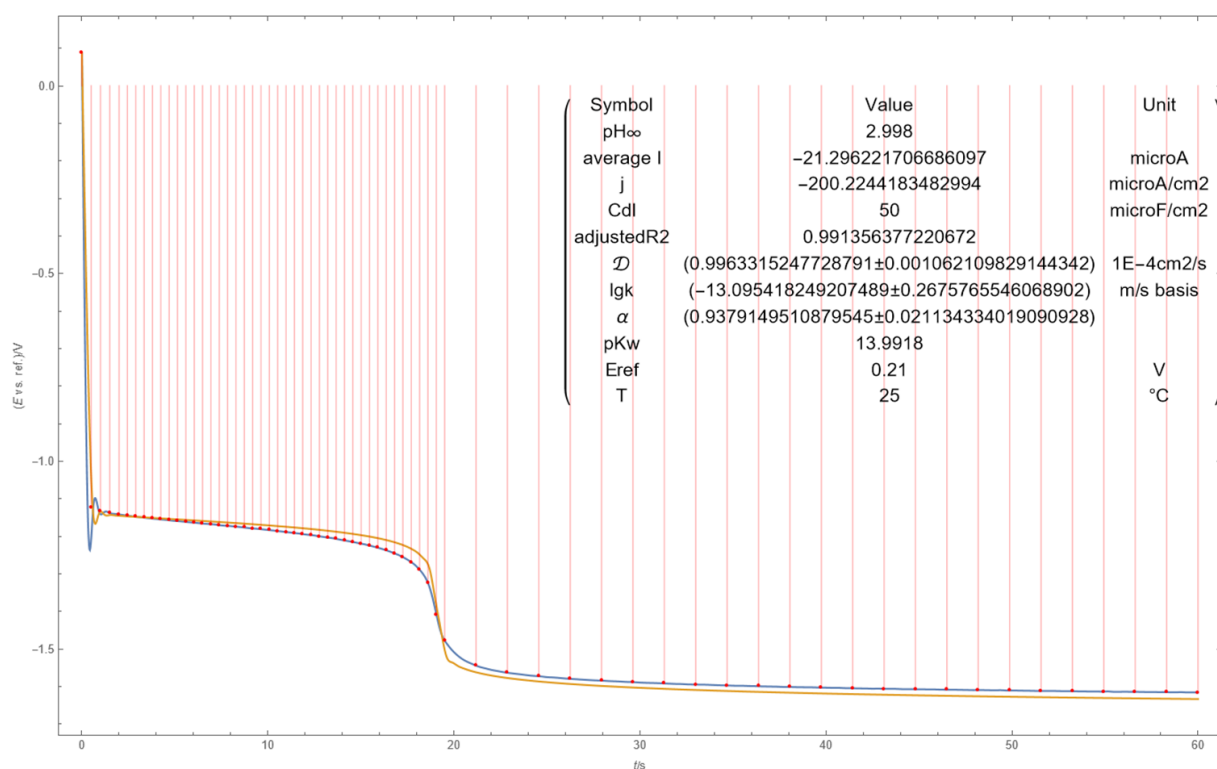


Figure A2. Chronopotentiogram measured on Bi (111) electrode, in solution of bulk pH = 2.998; line – measured response; dots – the model fit.

2. Chronopotentiometric Data Recorded in Different pH

pH	T (°C)	Eref (V)	pKw	R2	D (1E-4cm2/s)	lg k	a (μA/cm2)	j (μA/cm2)	Avg I (μA)
3.5	25	0.21	13.991	0.713	0.741	-12.790	0.941	-89.618	-9.532
3.5	25	0.21	13.991	0.739	0.753	-11.334	0.803	-84.764	-9.016
3.5	25	0.21	13.991	0.724	0.767	-11.581	0.825	-79.751	-8.482
3.5	25	0.21	13.991	0.777	0.783	-11.636	0.836	-69.711	-7.415
3.5	25	0.21	13.991	0.721	0.778	-11.598	0.835	-64.691	-6.881
3.5	25	0.21	13.991	0.672	0.786	-11.543	0.841	-59.677	-6.347
3.5	25	0.21	13.991	0.790	0.806	-11.644	0.851	-54.822	-5.831
3.5	25	0.21	13.991	0.744	0.828	-12.740	0.966	-49.799	-5.297
3.5	25	0.21	13.991	0.647	0.878	-12.686	0.968	-45.092	-4.796
3.5	25	0.21	13.991	0.623	0.967	-10.795	0.801	-40.077	-4.263
Avg.				0.715	0.809	-11.835	0.867	-63.800	-6.786
Std Dev.				0.054	0.068	0.672	0.065	17.005	1.809

Table A2.1 Chronopotentiometric data recorded on Bi (111) electrode in pH of bulk solution = 3.5

pH	T (°C)	Eref (V)	pKw	R2	D (1E-4cm2/s)	lg k	a (μA/cm2)	j (μA/cm2)	Avg I (μA)
2.998	25	0.21	13.991	0.726	0.776	-12.128	0.839	-497.411	-52.906
2.998	25	0.21	13.991	0.991	0.996	-13.095	0.938	-200.224	-21.296
2.998	25	0.21	13.991	0.996	0.882	-13.573	0.953	-300.480	-31.960
2.998	25	0.21	13.991	0.759	0.825	-12.438	0.877	-400.768	-42.626
2.998	25	0.21	13.991	0.845	0.090	-2.152	0.350	-696.574	-74.089
2.998	25	0.21	13.991	0.705	0.495	-4.147	0.423	-796.912	-84.761
Avg				0.837	0.870	-12.809	0.902	-349.721	-37.197
Std Dev				0.130	0.095	0.650	0.053	128.052	13.620

Table A2.2 Chronopotentiometric data recorded on Bi (111) electrode in pH of bulk solution = 2.998

pH	T (°C)	Eref (V)	pKw	R2	D (1E-4cm2/s)	lg k	a (μA/cm2)	j (μA/cm2)	Avg I (μA)
2.3	25	0.21	13.991	0.911	0.841	-12.503	0.826	-946.018	-100.620
2.3	25	0.21	13.991	0.913	0.866	-12.379	0.811	-996.148	-105.952
2.3	25	0.21	13.991	0.922	0.846	-10.714	0.634	-1495.743	-159.090
2.3	25	0.21	13.991	0.874	0.785	-11.147	0.667	-1994.237	-212.111
2.3	25	0.21	13.991	0.905	0.802	-10.758	0.634	-2494.195	-265.287
2.3	25	0.21	13.991	0.749	0.821	-7.889	0.490	-2992.930	-318.333
2.3	25	0.21	13.991	0.807	1.368	-13.520	0.926	-596.802	-63.477
2.3	25	0.21	13.991	0.899	0.912	-12.697	0.853	-697.020	-74.136
2.3	25	0.21	13.991	0.909	0.739	-12.605	0.848	-797.250	-84.797
2.3	25	0.21	13.991	0.900	0.661	-12.648	0.854	-895.824	-95.281
Avg				0.879	0.864	-11.686	0.754	-1390.617	-121.887
Std Dev				0.056	0.190	1.627	0.138	831.471	32.328

Table A2.3 Chronopotentiometric data recorded on Bi (111) electrode in pH of bulk solution = 2.3

pH	T	Eref	pKw	R2	D (1E-4cm2/s)	lg k	a μA/cm2	j (μA/cm2)	Avg I μA
1.96	25	0.21	13.991	0.932	1.093	-12.931	0.892	-1995.368	-212.231
1.96	25	0.21	13.991	0.942	1.145	-12.215	0.779	-1995.130	-212.206
1.96	25	0.21	13.991	0.922	1.007	-12.892	0.848	-2993.865	-318.433
1.96	25	0.21	13.991	0.884	0.949	-9.987	0.591	-6988.652	-743.325
1.96	25	0.21	13.991	0.902	0.947	-12.259	0.704	-5990.486	-637.159
1.96	25	0.21	13.991	0.888	0.969	-11.724	0.708	-3992.085	-424.605
Avg.				0.912	1.018	-12.001	0.754	-3992.598	-424.660
Std Dev.				0.024	0.083	1.087	0.109	2094.954	222.823

Table A2.4 Chronopotentiometric data recorded on Bi (111) electrode in pH of bulk solution = 1.96

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