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Using Cyclic Voltammetry for Studying Corrosion Mechanisms

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ABSTRACT

Corrosion is a significant challenge across various industries, resulting in economic losses and safety concerns. Traditional methods for assessing corrosion often yield limited mechanistic insights, which can impede the development of effective mitigation strategies. Cyclic voltammetry (CV), a well-established electrochemical technique, holds promise for providing a detailed understanding of corrosion mechanisms, although its full potential in this area is not yet fully realized. CV involves the sweeping of an electrode's potential within a specified range, enabling the observation of current responses that reveal oxidation and reduction processes on metal surfaces. This paper reviews the existing literature on the use of cyclic voltammetry (CV) in corrosion studies, with a focus on the theoretical basis of the technique and its relevance to corrosion science. Additionally, this paper presents experimental investigations on the effect of various parameters on CV outcomes. These experimental findings provide a comprehensive understanding of how different factors influence the CV technique and its application in corrosion studies.

Keywords: Cyclic Voltammetry (CV), Corrosion Mechanisms, Electrochemical Techniques, Corrosion Inhibition, Electrochemical Parameters.

INTRODUCTION

Corrosion degrades metals through electrochemical reactions causing significant material loss and eventual failure. It can lead to massive economic problems across various industries, in including oil and gas production, infrastructure integrity, and manufacturing. The global cost of corrosion was calculated to cost trillions of dollars each year, with huge resources allocated for prevention and mitigation.[1] Corrosion can compromise safety and shorten the life of key equipment, requiring thorough monitoring and protective measures.[2]

Corrosion is an electrochemical phenomenon caused by reactions at the metal-environment interface. As corrosion involves electrochemical processes like oxidation and reduction, it's essential to use electrochemical techniques to study and understand these reactions.[3] Several methods, including potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry, are key tools for investigating corrosion behavior and mechanisms.[4] In most relevant systems, the primary electrochemical reactions that cause corrosion involve iron oxidation, H^+ reduction, and oxygen reduction. H^+ reduction, in acidic settings, accelerates the rate of corrosion. Oxygen reduction mainly occurs in systems exposed to the atmosphere, having a critical effect on corrosion. Since steel is a very common material for construction, iron oxidation leads to infrastructure degradation. In order to fully understand corrosion phenomena, the mechanisms and kinetics of these reactions need to be understood. This is essential to predict the rate of corrosion and employ effective corrosion mitigation strategies. These reactions play a key role in cathodic and anodic protection systems. Cathodic protection aims to drive reduction reactions, like H^+ or oxygen reduction, to stop metal from oxidizing. Anodic protection utilizes controlled oxidation to create a passive layer that protects the metal from further degradation.

Cyclic voltammetry is an important electrochemical technique that offers insights into corrosion mechanisms. It enables monitoring of redox reactions and their reaction intermediates as they form. Although its application is not as widespread as other methods in corrosion studies, it enables an understanding of the mechanisms that lead to corrosion.[3] An example of practical applications can be alternating current (AC) corrosion, which is one of the major issues faced by buried structures, e.g., pipelines & storage tanks, in environments containing alternating electrical fields. CV can be used to reveal the corrosion mechanisms, which can help predict the corrosion rates. Such mechanistic understanding can aid in predicting corrosion rates at other areas of the buried structure, facilitating targeted mitigation strategies. This study aims to demonstrate practical usage of cyclic voltammetry, and to elucidate its experimental application to understand corrosion and develop effective mitigation strategies.[2]

THEORETICAL BACKGROUND OF CYCLIC VOLTAMMETRY

Cyclic voltammetry (CV) sweeps the potential of a working electrode within a set range while measuring the resulting current. The potential scans in a cyclic way, first reaching the specified peak potential and then back to the original potential value. A CV plot typically has the applied potential on the x-axis and the measured current on the y-axis.[3] CV plots resemble mountains and valleys, with anodic (oxidation- typically mountains) and cathodic (reduction- typically valleys) peaks/troughs matching redox reactions at the electrode surface. These features help identify electrochemical processes such as metal oxidation or the reduction of oxygen or H^+ ions. The position and sizes of the peaks in the plot provide insights into reaction speeds and reversibility of the redox processes.[5]

The main factors in cyclic voltammetry, such as scan rate potential range and electrode materials, have a big impact on the resulting cyclic voltammetry plots. The scan rate, which determines the speed of potential changes, has an influence on the current response and gives key insights into the rate of electrochemical reactions.[3] The potential ranges need to capture the important oxidation and reduction processes, in limits without degrading the electrode or capturing side reactions. Each factor impacts the plot and can hinder the key underlying electrochemical processes. These experiments are typically performed on three electrode setups: the working electrode, reference electrode, and counter electrode. To understand this technique, it is essential to establish the effect of each factor on features of cyclic voltammetry results. Understanding the effect of these factors on key electrochemical corrosion reactions, like iron oxidation, oxygen reduction or H^+ reduction, would provide valuable insights into corrosion mechanisms.[5] The ability to spot reversible redox reactions or evaluate surface properties provides critical insights for cathodic protection applications. For instance, reversible redox processes can help identify potential windows over which active corrosion or passivation occurs and thus serve to further inform a successfully designed cathodic protection (CP) approach.

Table 1 below illustrates a comparison of different electrochemical techniques often used to study corrosion. Each technique has key parameters that define it such as the type of potential applied (e.g., sweep or fixed), the kind of current measured (DC or AC), the experimental setup (a 3-electrode system), and the type of data it captures. Linear sweep voltammetry (LSV) and potentiodynamic polarization help understand mechanisms and determine corrosion rates. LSV gives current vs. potential curves, while potentiodynamic polarization produces Tafel plots. Cyclic potentiodynamic polarization (CPP) focuses on examining pitting corrosion and passivation breakdown, which shows up as hysteresis loops in its plots. Cyclic voltammetry (CV) excels at spotting reversible redox reactions and kinetic behavior. Other methods such as electrochemical impedance spectroscopy (EIS) apply AC potential to understand surface properties, which show up in Nyquist plots. Techniques such as Tafel extrapolation and ;linear polarization resistance (LPR) prove useful to figure out corrosion rates and polarization behavior. This table serves as a guide to choose the right technique based on the aspect of corrosion that needs to be studied. Typical scan rates for these CV studies, see Table 1, vary from 1 to 100 mV/s depending on the resolution required to analyze the redox peaks. For cathodic protection practitioners, these rates provide a benchmark for understanding diffusion-limited versus kinetically controlled reactions, which are central to CPP.

Table 1. Key Electrochemical Techniques for Corrosion Studies

Technique	Potential	Current	Experimental Configuration	Type of Information	Typical Plot
Linear Sweep Voltammetry (LSV)	Overpotential; Potential sweep (one direction); Scan rate (e.g., 1-100 mV/s)	DC	3-electrode setup, metal working electrode, electrolyte varies (e.g., acidic, neutral)	Mechanistic insights, reaction kinetics, corrosion rates	Current vs. Potential (I-V curve)
Potentiodynamic Polarization (PDP)	Potential sweep from OCP to anodic/cathodic; Variable scan rates; Single direction Scan rate (e.g., 0.1-1 mV/s)	DC	3-electrode setup; typically in corrosive environments	Corrosion rates, Tafel slopes, passivation behavior	Current vs. Potential (Tafel plot)
Cyclic Potentiodynamic Polarization (CPP)	Potential swept forward and backward; Overpotential; Range determined by passivation/pitting potential; Scan rates 1-100 mV/s	DC	Same as PDP, but with cycling potentials	Pitting corrosion, passivation breakdown, hysteresis loop	Current vs. Potential with hysteresis loop

Cyclic Voltammetry (CV)	Cyclic potential sweep; Scan rate (1-100 mV/s); Reversible redox reactions identified by peak potential	DC	3-electrode setup; Inert electrodes often used (e.g., Pt, glassy carbon), variety of electrolytes	Redox reactions, kinetics, passivation behavior, adsorption	Current vs. Potential (cyclic loop with peaks)
Electrochemical Impedance Spectroscopy (EIS)	AC potential; Wide frequency range (mHz to kHz); No potential sweep	AC	Same 3-electrode setup; Metal surface area, electrolyte specific to study	Surface properties, charge transfer resistance, film integrity	Nyquist plot (Impedance vs. Frequency)
Tafel Extrapolation	Fixed potential sweep near OCP; No cycling; Slow scan rate for accuracy	DC	3-electrode setup, often in corrosive or neutral electrolytes	Corrosion rates, polarization behavior, kinetic data	Log(Current) vs. Potential
Linear Polarization Resistance (LPR)	Small potential sweep around OCP; Low scan rates for accuracy	DC	3-electrode setup with inert counter electrode	Corrosion rate, polarization resistance	Current vs. Potential (near-linear)
Zero Resistance Ammeter (ZRA)	No potential applied; Measures current only (natural potential difference)	DC	2-electrode setup; galvanic couples between two dissimilar metals	Galvanic corrosion, current flow without applied potential	Current vs. Time
Chronoamperometry (CA)	Fixed potential applied; Time-dependent measurement of current	DC	3-electrode setup	Reaction kinetics, diffusion rates	Current vs. Time
Chronopotentiometry (CP)	Fixed current applied; Time-dependent potential measurement	DC	3-electrode setup	Reaction kinetics, passivation, film formation dynamics	Potential vs. Time

APPLICATION OF CYCLIC VOLTAMMETRY IN CORROSION MECHANISMS

Cyclic Voltammetry in Iron Oxidation Studies

Some studies have employed cyclic voltammetry (CV) to examine iron oxidation at different conditions. Li, *et al.*, used CV to study iron dissolution and formation of a passive layer in acetonitrile (CH_3CN) and water. With more acetonitrile content, iron demonstrated a greater tendency to form a path of passive layer formation[6]. With greater amounts of acetonitrile, the peaks on the anodic scans diminished, indicating a slowing active dissolution and flat current regions[6]. Vela, *et al.*, utilized CV on iron electrodes to demonstrate a two-layer passive formation, with an inner Fe_3O_4 layer and an outer hydrous $Fe(OH)_3$ layer during passivation[7]. Together, these studies demonstrate that CV can elucidate the mechanisms of iron oxidation and intermediates during passivation.

Cyclic Voltammetry in Oxygen Reduction Studies

Cyclic voltammetry (CV) has been used to study the oxygen reduction reaction (ORR) in fuel cell applications. Awad, *et al.*, used CV to investigate oxygen reduction on copper nanoparticlemodified gold electrodes in alkaline solutions. Their work demonstrated better catalytic activity because of the direct four-electron reduction pathway for ORR which was characteristic of the single prominent cathodic peak in the CV curve[8]. Similarly, Bakir, *et al*., demonstrated shifting of the oxygen reduction peak to more positive potentials on introduction of copper modified gold electrodes, indicating a more efficient reduction process associated with the four-electron pathway[9]. These studies illustrate the ability of CV to elucidate the kinetics and mechanisms of ORR giving key insights to improve corrosion protection and on electrocatalytic processes.

Cyclic Voltammetry in Hydrogen Ion (H^+) Reduction Studies

Cyclic voltammetry (CV) used to study H^+ reduction provides insights into the electron transfer process and formation of H_2. Bentley, *et al.*, used CV to demonstrate that the nature of anions in the electrolyte affected the H^+/H_2 process. They noted for weak acids that H^+ reduction proceeded through a dissociation-controlled pathway, demonstrated by a lack of secondary peaks on the cyclic voltammetry plots[10]. Their study emphasized a need to understand the effect of different parameters on the H^+ reduction process. These parameters, such as scan rate, potential range, and electrolyte composition, need to be thoroughly investigated for better corrosion prediction and efficient mitigation strategies.

Table 2. Summary of Key Electrochemical Reactions Studied Using Cyclic Voltammetry

Reaction	Key Insights from CV Studies	Relevant Parameters	Challenges in Understanding
Iron Oxidation[6,7]	Identified critical potentials for dissolution. Observed formation of passive layers at higher potentials.	Scan rate, Potential range, Electrolyte composition	Influence of water content and surface preparation. Complex dissolution/passivation transitions.
Oxygen Reduction[8,9]	Enhanced electrocatalytic reduction with metal nanoparticles. Identification of ORR pathways and current shifts.	Scan rate, Electrode material, Electrolyte type	Complexity in multi-electron transfer reactions. Sensitivity to surface conditions.
H^+ Reduction[10]	Effects of ionic liquid anion composition on H^+ reduction. Proton-coupled electron transfer mechanisms.	Scan rate, Electrolyte composition, Electrode material	Limited data on parameter effects. Complex reaction kinetics.

As Table 2 demonstrates, H^+ reduction plays a vital role in many scenarios, such as in oil and gas pipelines, concrete rebar degradation, and marine structure integrity. Almost all types of corrosion involve H^+, and their reduction has a big impact on the rate of corrosion. To understand cyclic voltammetry better and how it can be used to study corrosion, the effects of difference parameters on H^+ reduction needs to be investigated. These factors include scan rate, potential range, scan cycles and electrolyte composition. An insight into these effects will clarify the behavior of H^+ reduction and support protection strategies, helping to improve corrosion mitigation in industrial contexts. Critical potentials identified for iron dissolution and passivation (Table 2) have direct implications for cathodic protection. These are potential references for the protection criteria, ensuring that operating conditions remain within ranges where active/pitting corrosion can be mitigated and passive film formation can be promoted.

INFLUENCE OF EXPERIMENTAL PARAMETERS ON CV IN CORROSION STUDIES

Experimental Set up

The experiments were carried out in a 2-liter glass cell. The glass cell was equipped with all the necessary components required for electrochemical corrosion studies, viz a RDE working electrode, reference probe, Luggin capillary, counter electrode, RCE (rotating cylinder electrode), thermocouple, hotplate stirrer, and a pH probe. Rotating disk electrodes (RDE) and rotating cylinder electrodes (RCE) allow us the simulation of hydrodynamic conditions in electrochemical studies, similar to the actual fluid flow that affect corrosion processes.

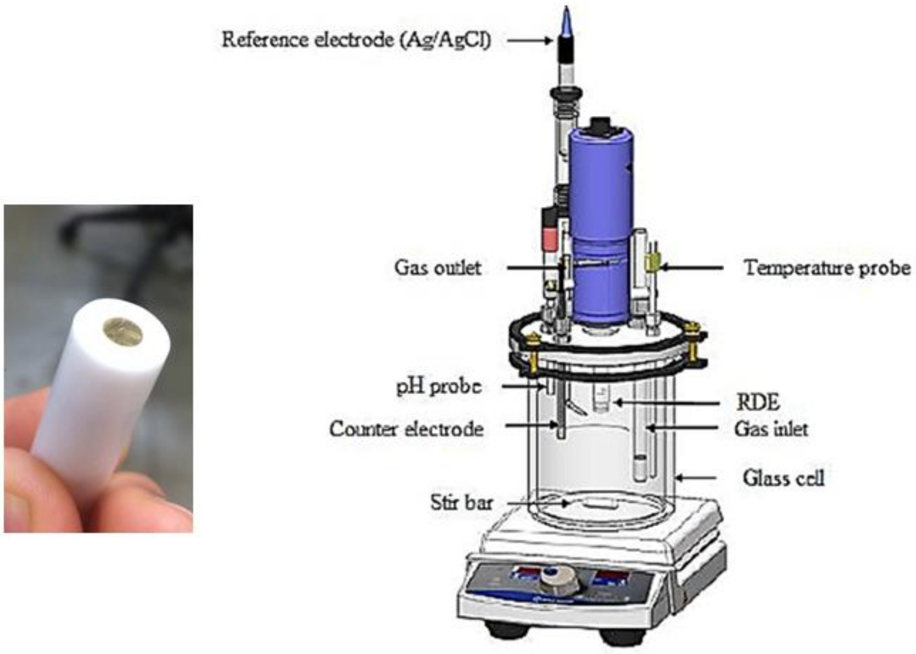

Figure 1. Left) gold RDE electrode, right) A 2-electrode glass cell setup used for electrochemical measurements.

Testing Parameters

Gold was chosen as the substrate materials for the RDE as it enables for detection of distinct charge transfer on mass transfer kinetics for the H^+ reduction reaction.

Table 3. List of experimental test conditions

Parameters	Conditions
Temperature	30 ^{o}C
pH	3.0, 3.5, 3.8, 4.0, 7.0
Total Pressure	1 bar

Gas Phase Components	N_2
$[O_2]_{aq}$	0 ppm
Electrolyte	1 wt.% NaCl
RDE Speed	100 rpm-2000rpm
Specimen	Gold
Scan rate	1, 10, 50, 100, 200, 500, 800, 1000, 2000, 5000 mV/s
Electrochemical Tests	Potentiodynamic sweeps, linear sweep voltammetry, cyclic voltammetry

Experimental Results and Discussion

Effect of scan rate on potentiodynamic sweeps and LSV sweeps

Potential dynamic sweeps were performed at changing scan rates ranging from 0.1 millivolt per second to 1000 millivolts per second as seen in Figure 2. At the slowest scan rates the limiting current was relatively straight with no evidence of visual peaks. However, at higher scan rates formation of peaks were observed as seen in Figure 2. These peaks are formed because at faster scan rates the H^+ ions at the surface are consumed at a quicker rate leading to higher currents peaks.

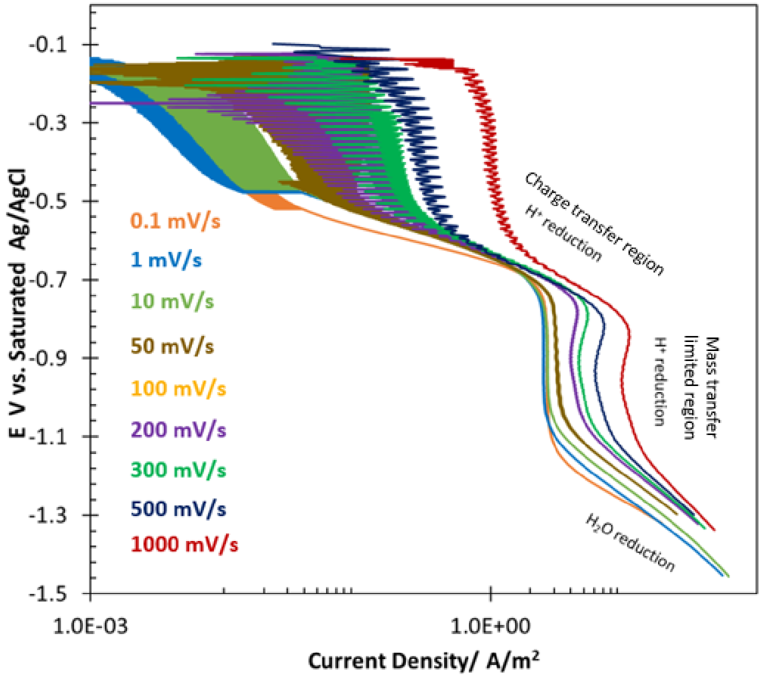

Figure 2. Comparison of potentiodynamic experiments performed at different scan rates (pH 3.5, 0ppm $[O_2]_{aq}$, 30 ^{o}C, 1 wt.% NaCl, gold, 100rpm RDE, 1 bar N_2 system)

Distinct charge transfer and mass transfer characteristics, such as those marked in Figure 2, highlight the dominance of electrochemical reactions at specific potentials. These characteristics can assist the CP practitioners in locating active corrosion areas and refining protection strategies. Sweeps performed at relatively faster scan rates are referred to as linear sweep voltammetry. Linear sweep voltammetry sweeps are typically plot on a different axes scale, where the current density is plotted on the y-axis without a log scale and the potentials are plotted on the x-axis without any log scale. Figure 2 is plotted again on the linear sweep voltammetry scale as seen in Figure 3.

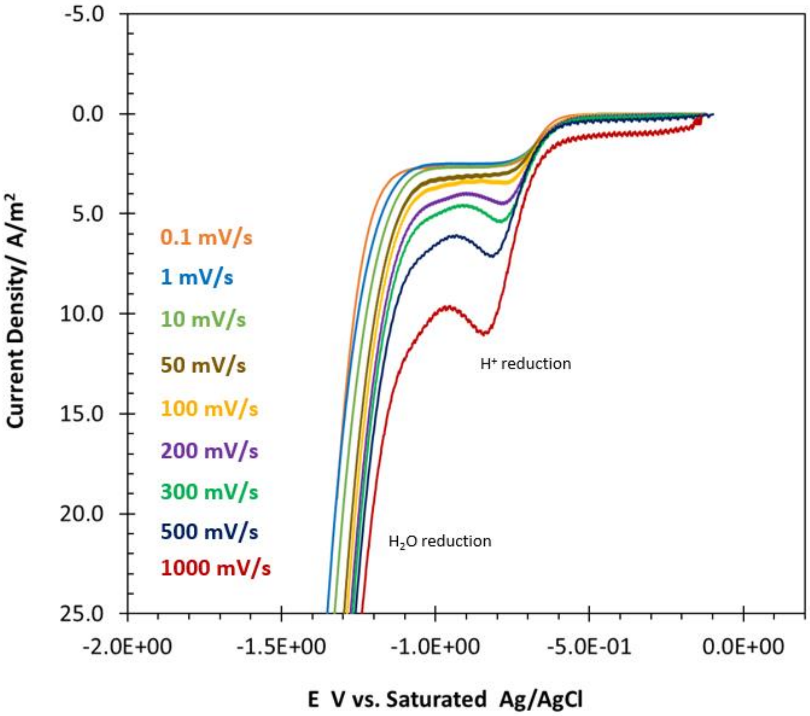

Figure 3. Comparison of linear sweep voltammetry experiments performed at different scan rates (pH 3.5, 0ppm $[O_2]_{aq}$, 30 ºC, 1 wt.% NaCl, gold, 100rpm RDE, 1 bar N_2 system).

Effects of scan rate on cyclic voltammetry experiments

Cycling voltammetry experiments were performed at changing scan rates as seen in Figure 4. The cyclical voltammetry experiment was performed by cycling the potential from OCP to a set negative overpotential and then back to the OCP. The set negative overpotential was chosen based on preliminary experiments to ensure the initiation of the hydrogen evolution reaction without interference from secondary reactions, such as water reduction. For this condition shown in Figure 4, in the forward scan peaks were observed for the H^+ plus reduction and water reduction. The forward scan demonstrated peaks correspond to the reduction reactions. On the reverse scan, with increasing potentials a peak is observed for H_2 oxidation. At lower scan rates the peaks were shorter and narrower whereas at higher scan rate they were taller and wider. A sufficiently slow scan rate, such as 100 mV/s, was selected to allow for diffusion-controlled reactions to dominate. On the other hand, faster scan rates, above 500 mV/s, were employed to investigate kinetically controlled processes and their dependence on potential.

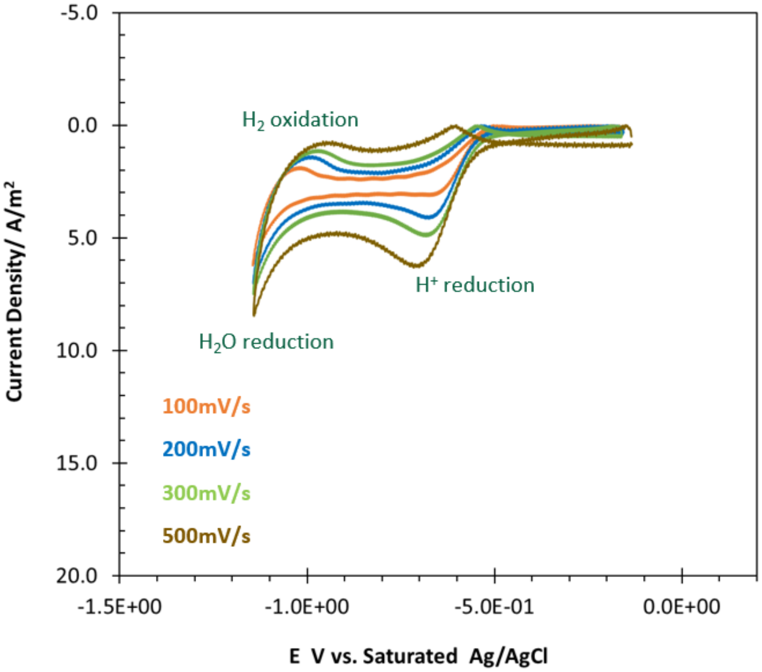

Figure 4. Comparison of cyclic voltammetry experiments performed at different scan rates (pH 3.5, 0ppm $[O_2]_{aq}$, 30 ºC, 1 wt.% NaCl, gold, 100rpm RDE, 1 bar N_2 system).

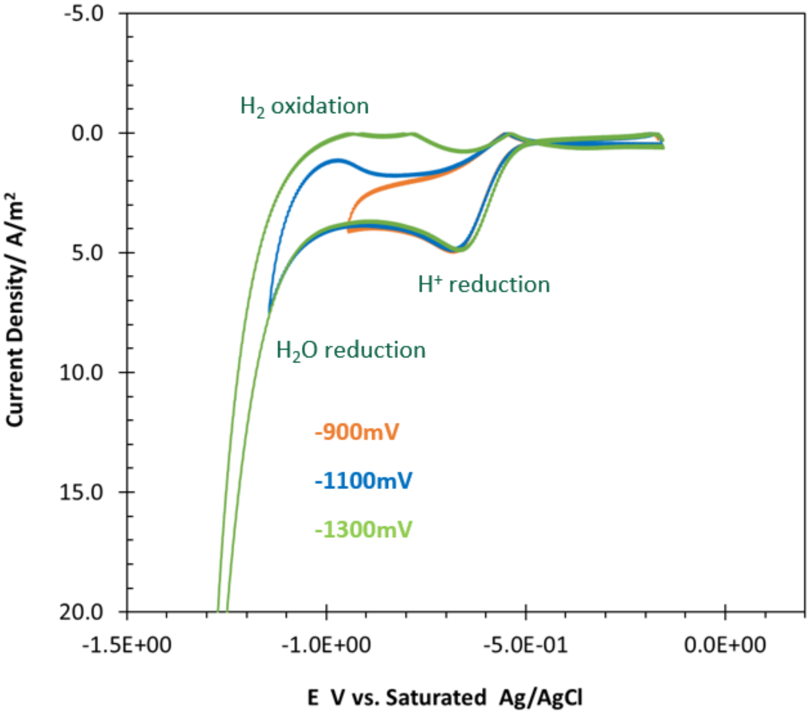

Figure 5. Comparison of cyclic voltammetry experiments performed at peak potentials (pH 3.5, 0ppm $[O_2]_{aq}$, 30 ºC, 1 wt.% NaCl, gold, 100rpm RDE, 1 bar N_2 system, 300mV/s).

Effects of peak potential on cyclic voltammetry experiments

The nature of the changing peak potentials was studied for the cyclic voltammetry experiments. As seen in Figure 5, three different peak potentials were tested for the given condition. As discussed previously, the downward peaks correspond to reduction reactions, namely H^+ reduction and water reduction. The upward peaks correspond to the oxidation reaction, in this case H_2 oxidation. Lower the peak potential (higher the magnitude) leads to a higher water reduction peak, which in turn leads to a higher H_2 oxidation peak because H_2 is a product of the water production reaction. Changing the peak potentials influences the resolution and clarity of the hydrogen oxidation peak as demonstrated in Figure 5, does emphasising the need to select optimum big potential for the best resolved peaks.

$$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \qquad (1)$$

Effects of scan cycle on cyclic voltammetry experiments

Cyclic voltammetry experiments are usually performed in continuous successive potential scan cycles. As seen in Figure 6, successive scans were performed for the given condition between the open circuit potential and the peak potential. The first scan depicted slight inconsistency, however, reaching up to the fifth scan very good consistency was observed.

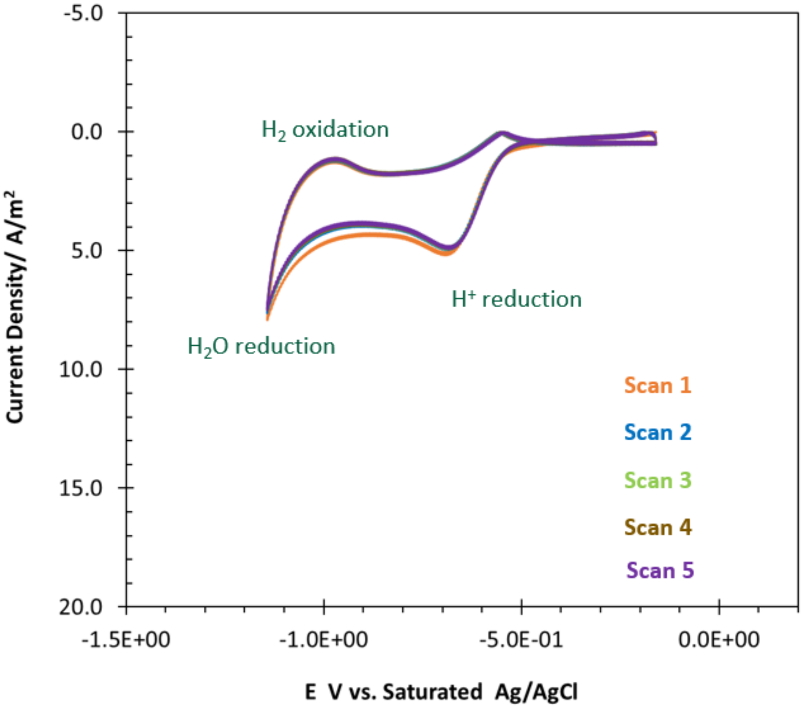

Figure 6. Comparison of successive scans of a cyclic voltammetry experiment (pH 3.5, 0ppm $[O_2]_{aq}$, 30 °C, 1 wt.% NaCl, gold, 100rpm RDE, 1 bar N_2 system, 300mV/s).

CONCLUSIONS AND IMPLICATIONS

This study examined how cyclic voltammetry (CV) parameters affect the H^+ reduction reaction. The following conclusions and practical implications are drawn:

- Effect of scan rate on potentiodynamic polarization and linear sweep voltammetry (LSV): at lower scan rates flat limiting currents were seen however at faster scan rates peaks were observed because of faster consumption of species at the electrode surface.
- Effect of scan rate on cyclic voltammetry: The study found that increased scan rates yield broader and taller peaks and impact the shape of the CV curves. Faster scan rates avoid any diffusion effects to dominate, resulting in detection of any species like H_2 which otherwise would've diffused to the bulk.
- Effect of peak potential (switching potential) on CV: The switching potential significantly impacted the formation of oxidation peaks, offering a broader resolution of the oxidation peak.
- Effect of scan cycle on CV experiments: Multiple scan cycles revealed the stability and reproducibility of the reactions.

Implications for Industry

- Anodic and cathodic protection:
    - In cathodic protection, understanding H^+ reduction mechanisms and kinetics aid in optimizing the conditions under which metals are protected from corrosion. The findings from this study, such as the role of scan rate and peak potentials, provide a foundation for optimizing current densities in cathodic protection systems.
    - In anodic protection, understanding the switching potential and how it affects passive layer growth is key for the safety of metals controlling the anodic reactions.
- Practical implications for corrosion mitigation:
    - This study demonstrates the need to control scan rates and potential ranges to accurately model real-world corrosion behavior in pipelines, industrial equipment, and marine environments.

Cyclic voltammetry proves useful to study corrosion as it provides deep insights into anodic and cathodic reactions. This method has a big impact on the understanding of corrosion processes and helps create better mitigation strategies. This technique is sensitive to the reaction kinetics, passivation behavior and surface properties which makes it unique to study corrosion mechanisms and design effective protection strategies.

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