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Electropolymerization of Pyrrole on Mild Steel for Corrosion Protection

BY

Mohammed S. Ba-Shammakh

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

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This thesis, written by

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under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

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24/4/2002

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(Dean of Graduate Studies)

Dedicated to

My loving parents & my wife

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Praise and gratitude be to God " who taught (the use of) the pen. Taught the man that he knew not." It is a great pleasure to any human being to accomplish the work he devoted to. Yet, it is a pride to the human being to remember, in those moments of pleasure, those who contributed to get the work completed.

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ABSTRACT

Name:	MOHAMMED BA-SHAMMAKH
Title:	ELECTROPOLYMERIZATION OF PYRROLE ON MILD STEEL FOR CORROSION PROTECTION
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Polypyrrole (PPy) can be synthesized by either chemical or electrochemical methods. Electrochemical methods (electropolymerization) usually give higher PPy conductivity than the chemical methods. However, the electropolymerization of pyrrole on oxidizable metals such as mild steel is difficult because the metallic electrode undergoes strong dissolution before oxidation potential of the monomer (pyrrole) is reached. Recently, a few electrochemical methods have been proposed to polymerize pyrrole on various steel substrate successfully. In this work, these methods are evaluated to select the best one, from the corrosion protection point of view. Subsequently, a parametric study was undertaken on the selected method to study the effect of electropolymerization parameters namely; applied current density, electrolyte pH and temperature.

Among the tested methods, a method that uses oxalic acid as electrolyte showed the most adherent deposition of polypyrrole on mild steel. The parametric study on this method shows that increasing the current density can enhance the deposition but the surface becomes rough. The time needed for passivating the steel surface (induction time) decreases with increased applied current density while the electropolymerization potential increases with current density.

The induction time increases as the pH increases up to 7.0 while it is minimum at pH 8.5. The electropolymerization potential for the neutral or alkaline solution is much higher than that for acidic solution. The temperature has negative effects on the deposition in both acidic and neutral medium. On the other hand, it has positive effects on the deposition for the alkaline solution. The induction time does not change much as the temperature elevates except at neutral solution in which the induction time is increasing with temperature.

Oscillation in potential were observed at temperature higher than 25 °C in acidic media. Occurance and nature of the oscillation depend on current density, pH and temperature. This phenomenon is explained by two reactions cometing each other, namely, corrosion reaction and the oxidation reaction for formation of polypyrrole. Apparently, corrosion reaction dominates at high temperature for acidic and neutral solution while the deposition reaction is favored as the temperature increases for alkaline solution.

Master of Science Degree

King Fahd University of Petroleum & Minerals

Dhahran, Saudi Arabia

ملخص الرسالة

الإسم: محمد صالح محمد باشماخ
العنوان: البلمرة الكهربائية للبايرول على الحديد لحمايته من الصدأ
الدرجة: مـــاجســتير
التخصص: هندسة كيميائية
التاريخ: أبريل ٢٠٠٢ م

البولي بايرول يتم تصنيعه إما بواسطة الطريقة الكيميائية أو الطريقة الكهروكيميائية (البلمرة الكهربائية) التي تعطي بالعادة موصلية للتيار أكثر من ذلك المصنع بالطريقة الكيميائية. البلمرة الكهربائية للبايرول على المعادن القابلة للأكسدة مثل الحديد هي عملية صعبة لأن المعدن يمر بإنحلال شديد قبل الوصول إلى جهد التأكسد اللازم للبايرول ليتكون على سطح الحديد. بعض الطرق الكهروكيميائية عرضت لبلمرة البايرول على الحديد في الوقت الحالي. تلك الطرق قيمت في هذه الرسالة لاختيار الطريقة الأفضل في ضوء حماية الحديد من الصدأ. دراسة تقييمية تمت على الطريقة المختارة لدراسة أثر العناصر المؤثرة على عملية البلمرة وهي: كثافة التيار، ودرجة الحموضة ودرجة الحرارة.

هناك طريقة من ضمن الطرق المقيمة تستخدم حامض الأوكساليك كمحلول كهربائي التي أعطت ترسب للبولي بايرول شديد الالتصاق على الحديد. الدراسة التقييمية لهذه الطريقة أوضحت أن زيادة كثافة التيار يؤدي إلى ترسب أفضل لكن مع خشونة للسطح. الوقت اللازم للتمهيد للترسيب (وقت التمهيد) يقل بزيادة كثافة التيار في حين أن جهد البلمرة يزيد بزيادة كثافة التيار.

وقت التمهيد يزيد بزيادة درجة الحموضة إلى ٧،٠ في حين أنه الأقل في درجة الحموضة ٨،٥. جهد البلمرة الكهربائية للمحلول المتعادل أو القلوي في العادة هو ذو قيمة أكبر بكثير من ذلك في المحلول الحمضي. درجة الحرارة لها تأثير إيجابي على عملية الترسيب في الوسط القلوي. وقت التمهيد لايتأثر بدرجة الحرارة إلا في الوسط المتعادل الذي يزيد فيه وقت التمهيد بزيادة درجة الحرارة.

لوحظ تذبذب على شكل موجات في الجهد الكهربائي عند درجة الحرارة أكثر من ٢٥° م في الوسط الحمضي. حدوث وشكل الذبذبة يعتمد على كثافة التيار ودرجة الحموضة ودرجة الحرارة. هذه الظاهرة يمكن أن تشرح في ضوء أن هناك تفاعلين يتنافسان فيما بينهما وهما كما يبدو: التفاعل المؤدي للصدأ أو تآكل المعدن والتفاعل المؤدي لعملية الترسيب. التفاعل المؤدي للصدأ يطغى في حالة درجة الحرارة العالية للوسط الحمضي والمتعادل في حين أن التفاعل المؤدي لعملية الترسيب يطغى إذا زادت درجة الحرارة للوسط القاعدي.

درجة الماجستير في العلوم الهندسية

جامعة الملك فهد للبترول و المعادن

CHAPTER 1

INTRODUCTION

Conductive polymers can be defined as polymers that are capable of transmitting and holding charge due to their conjugating double bond. Polyacetylene, polypyrrole and polyaniline are typical examples of these conducting polymers. Since the discovery of the conducting polymers about twenty-five years ago, these materials are finding an increasing use in various branches of technology. Conducting polymers have been extensively studied due to their exclusive physical properties. Compared with metals, conducting polymers are lightweight, flexible and have tremendous potential for future scientific and technological development in electronic applications. Among the many conjugated polymers that have been studied, polypyrrole (C_4H_5N) has emerged as one of the most attracted conducting polymer due to its high electrical conductivity, good environmental stability and the ease of synthesis by chemical or electrochemical methods. Among myriad of applications, polypyrrole have been studied for corrosion protection of steels. The conducting polypyrrole stores electrical charge that raises the potential of metal in the passive range reducing the corrosion rate. This application requires that polypyrrole films are very adherent and have good electronic conductivity.

Polypyrrole can be synthesized from monomer by both electrochemical and chemical methods in either aqueous or nonaqueous media. The electropolymerization of pyrrole on oxidizable metals (e.g. Fe, Zn, Pb etc.) is associated with a number of inherent problems. One of them is to obtain adherent polypyrrole films in aqueous solutions. Since the dissolution potentials are much lower than the oxidation potential of pyrrole, dissolution of metal dominates and polymerization does not take place at all or very loosely adherent film is formed in some cases.

The problem, in principle, can be solved by selecting appropriate supporting electrolyte, pretreating the metal surface, and/or varying polymerization parameters, e.g., concentration of monomer, concentration of electrolyte, pH of the electrolyte and current density. However, these changes will be associated with change in the conductivity and morphology of the film. A number of experimental studies have been reported in the literature utilizing these approaches. For iron and mild steel several ways of overcoming this difficulty have been investigated by several researchers forming adherent polypyrrole film by slowing the dissolution rate without stopping the electropolymerization process. It has been shown that chemical pretreatment of the metal surface and the choice of the electrolyte solution play important roles.

1.1 Research Objectives

This work has following two objectives:

(A). To electropolymerize pyrrole on mild steel substrate using four different methods to identify the best method which could be used for corrosion protection applications.

(B). To carry out a parametric study to find out the effect of several parameters on the electrochemical synthesis of polypyrrole coatings for the selected method. The parameters studied are applied current density, pH of the solution and temperature.

CHAPTER 2

LITERATURE REVIEW

2.1. Conductive Polymers:

Conducting polymers have been intensively studied in the last decade with attention to synthesis methods, structure and morphological characterizations, electrical and mechanical properties. Recently, strong interest in the synthesis of conducting polymers, such as polypyrrole has manifested in literature, motivated fundamentally, by the excellent conducting properties of these polymers, which make them preferential candidates for many modern applications. The possibility of synthesizing materials capable of simultaneously presenting the properties of organic polymers and of semiconductors, has attracted the interest and efforts of both academic and industrial researchers.

The conductivity of these polymers is explained by interchain hopping of electrons. However, the electronic properties of the polymers can be controlled by a doping process, in which electrons donating or accepting molecules (or ions) are incorporated into a polymer matrix. This may increase the polymer conductivity by as much as 18 orders of magnitudes. Polypyrrole was chosen for study because it is easy to prepare by standard electrochemical techniques and its surface charge characteristics can easily be modified by changing the dopant anion that is incorporated into the material during synthesis. [1, 2]

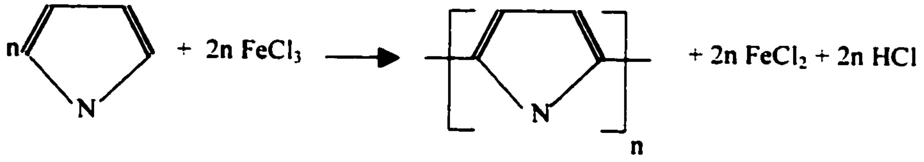
2.2. Synthesis of Polypyrrole

The polypyrrole can be synthesized by chemical methods from monomer solutions or by electrochemical polymerization from an electrolyte containing monomer. The major advantage of chemical synthesis is its flexibility for introducing certain active chemical groups onto the polymer backbones. These groups can make the polymers soluble in non-aqueous or aqueous solutions depending on their properties [3].

Electrochemical polymerization has played an important role in the preparation of polypyrrole films. In order to obtain highly conductive and flexible polypyrrole films, many efforts have been exerted on the studies of the electropolymerization mechanism and the optimization of the electropolymerization conditions. The advantage of using this method is improved control of the initiating species concentration and relatively lesser reaction rate. It is found that when a monomer (**R**) is electrooxidized to its radical cation ($\mathbf{R}^{+}$) at the electrode surface, the transfer of electron is much faster than the diffusion of **R** from the bulk solution to the electrode surface [3].

2.2.1. Chemical Synthesis of Polypyrrole

Pyrrole was first chemically polymerized in 1916 by the oxidation of pyrrole with hydrogen peroxide (H_2O_2) to give an amorphous powdery product known as pyrrole black, which was found to be insoluble in organic solvents. However, polypyrrole (PPy) prepared from acid or peroxide initiators has low conductivity associated with the high degree of saturation of the pyrrole rings in the polymer either by oxygen incorporation or by hydrogen saturation. From a synthetic point of view, one of the advantages of PPy is the low oxidation potential of the pyrrole monomer [3]. Pyrrole is one of the most easily oxidized monomers and hence a variety of oxidizing agents are available for preparing PPy. A list of the oxidizing agents is given in Table 2.1. In addition, polypyrroles are obtained directly in a conducting state because the polymer oxidation occurs with oxidant salts acting as doping agents. Oxidative transition metal ions are the most used oxidizing agents for pyrrole polymerization. Different metallic salts have been reported to polymerize pyrrole with a variety of conductivity but ferric salts are the most commonly used oxidants for the chemical synthesis of highly conductive PPy [4]. In the case of $FeCl_3$, which is one of the most used initiators, the polymerization process is described as :



(1)

In general, polymer conductivity is a function of the monomer and oxidant agent concentrations, solvent, time of reaction and temperature of synthesis. The optimum reactant (Fe(III)/monomer) molar ratio for the polymerization of pyrrole by $FeCl_3$ has been suggested to be about 2.4. Low temperatures (0-5 °C) are the most appropriate for obtaining the best conductivities in aqueous solutions of ferric salts. This seems that lowering the reaction rate results in an increasing conductivity of the polymer.

Table 2.1. Different oxidizing agents used for pyrrole polymerization [3].

Oxidizing Agent	Solvent	Conductivity(S/cm)
$FeCl_3$	Water	>200
$FeCl_3$	MeOH	190
$FeCl_3$	C_6H_6	20
$Fe(BF_4)_3$	water	90
$Fe(NO_3)_3$	water	36
$FeBr_3$	water	44
I_2	water	8
I_2	CH_3CN	2
Br_2	CH_3CN	5
Cl_2	CH_3CN	0.5
$CuBr_2$	water	45

Moreover, a drop in the polypyrrole conductivity may occur as a result of a slight increase in the ferric salt concentration. This could be related to the coplymerization of some secondary products, having an oxidation potential of the same order as that of pyrrole.

2.2.2 Electrochemical Synthesis of Polypyrrole

Electrochemical Deposition of Polypyrrole on Inert Metals

Most of the work done in this field devoted to conducting polymers has been carried out with inert metal electrodes such as platinum or gold. The electrochemical polymerization of pyrrole is a fast process: a few seconds after the beginning of the anodic current flow, the electrode is coated with a polymeric film. Growth of polypyrrole on a gold electrode was investigated by Chung et al. [5]. They used Electrochemical Quarts Crystal Microbalance (EQCM) when the polymer was synthesized by applying a constant potential (potetiostatic mode). The electrolytes used for the synthesis were sodium perchlorate ($NaClO_4$), lithium perchlorate ($LiClO_4$), and potassium perchlorate ($KClO_4$). The concentration of electrolyte was 0.1M. Myrick et al. [6] studied growth morphology of underpotential electropolymerization of pyrrole on graphite. However, Stankovic et al. [7] deposited polypyrrole under galvanostatic conditions on platinum anodes in a solution of N-methylpyridinium perchlorate in propylene carbonate. The influence of current density and amount of water in the reaction mixture on the conductivity and morphology of the prepared polypyrrole films was studied. It was shown that the electrochemical activity of thick polypyrrole films in a solution of 0.1 M $LiClO_4$ in propylene carbonate was satisfactory.

Electrochemical Deposition of Polypyrrole on Oxidizable Metals

The electrochemical synthesis method, which is also known as electropolymerization is useful to obtain polypyrrole with high conductivity. However, the deposition of polypyrrole on common metals requires maintinance of certain conditions. The supporting electrolyte must be carefully chosen to avoid anodic dissolution of the substrate and allow the formation of the polymer film. This is because the metal undergoes strong dissolution before the oxidation potential of pyrrole is reached.

A few studies on electropolymerization of pyrrole on oxidizable metals such as iron and aluminum have recently been reported. Polypyrrole has been synthesized electrochemically from various aqueous solutions. Troch-Nagels et al. [8] studied the possibility of passivating mild steel using polypyrrole and other conductive polymers. Polypyrrole prepared in Na_2SO_4 solution was reported to function better than the other candidates. It demonstrated good corrosion resistance but exhibited poor adhesion and films were brittle. Schirmesien and Beck [9] drew similar conclusion using KNO_3 solution instead of Na_2SO_4.

Beck et al. [10] deposited polypyrrole on iron from aqueous solutions of pyrrole and oxalic acid which yielded strongly adherent, smooth polymer layers. The influence of current density, pyrrole concentration and KNO_3 addition on the electrodeposition process and electrochemical and physical properties of the layers was studied.

De bruyne et al. [11] electropolymerized pyrrole on galvanized steel substrates. Pretreatment of the galvanized steels was performed prior to electropolymerization with a solution of 0.1M sodium sulfide for 18 hours and at room temperature. Without this pretreatment, no film could be formed.

The adherence of polypyrrole film was greatly enhanced by Ferreira et al. [12] through electropolymerization of pyrrole on pretreated iron and mild steel. Several chemical pretreatments of the metal surfaces were compared. The results showed that a treatment by 10% aqueous nitric acid inhibits the metal dissolution without preventing the pyrrole oxidation. Different adherent polypyrrole films were obtained in various aqueous media containing Na_2SO_4, $K_2C_2O_4$ or KNO_3. They found that the best of these was the pretreatment of mild steel with 10% aqueous nitric acid (HNO_3) followed by electropolymerization from KNO_3 solution. From their study, oxidation potential of an iron electrode in a 0.1M Na_2SO_4 + 0.1M pyrrole aqueous medium, after pretreatments by 10% HNO_3 for 4 min was +0.7 V vs SCE. It was a negative value in the case of pretreatment by 30% HCl for 10 min, 10% H_2SO_4 for 10 min or by 10% H_3PO_4 for 10 min. The results are summarized in Table 2.2.

Su and Iroh [13] formed polypyrrole coatings on stainless steel using aqueous benzene sulfonate solution as electrolyte. They studied the effect of various parameters on electropolymerization. It was found that amount of polypyrrole formed during electropolymerization increased with current density and monomer concentration, but was unaffected by increased electrolyte concentration. Krstajic et al. [14] formed polypyrrole coatings on mild steel from oxalic acid solution and studied resulting

Table 2.2: Oxidation Potential of an Iron Electrode in a 0.1M Na_2SO_4 + 0.1M Pyrrole Aqueous Medium, After Various Surface Pretreatments [12].

Pretratment	**Oxidation Potential (V)**	**Film**
Industrial cleaning	-0.6	No
4 min in 10% HNO_3	+0.7	Yes
10 min in 30% HCl	-0.5	No
10 min in 10% H_2SO_4	-0.5	No
10 min in 10% H_3PO_4	-0.5	No

corrosion protection in acid sulfate solutions. They observed the change in open circuit potential with respect to time for various thickness of polypyrrole coating. Idla et al. [15] electropolymerized pyrrole on mild steel from sodium p-toluenesulphonate (ToS) water-ethanol solution and studied the characteristics of polypyrrole film.

Polypyrrole can be deposited from aqueous solution at a wide range of pH. Recently, it is shown that a good choice of the electrolyte medium can reduce the dissolution rate of the metal without impeding monomer oxidation and give adherent polypyrrole films on iron or steel [16]. Ferreira et al. [16] showed that modified polypyrrole films could be electrosynthesized on oxidizable metals like mild steel and zincated steel. This modified polypyrrole film was obtained by oxidation of a mixture of pyrrole, N-methylpyrrole-2-carboxilic acid and N- methyl-2[(2-ethylamino)] pyrrole at a total concentration of 0.1M. Good adherence of the film was achieved only after pretreatment of the electrode.

The effect of surface treatments such as polishing and immersion in acid on the corrosion behavior of polypyrrole coated mild steel was investigated by Reut et al. [17]. Polypyrrole films were synthesized electrochemically from the aqueous solution of pyrrole and sodium p-toluenesulphonate (Py/ToS) at a constant current density of 2 mA/cm^2. It was found that mechanical and chemical treatments of the electrode surface could create a significant positive shift of corrosion potential. The greatest shift of the corrosion potential values to the positive direction was observed for the PPy/ToS coatings on the chemically treated steel.

A one step electrosynthesis of polypyrrole films on zinc substrates was done by Aeiyach et al. [18]. This was achieved by electro-oxidation of pyrrole in aqueous oxalate solution containing small amounts of sulfide ion at pH 5 in either the galvanostatic or potentiodynamic modes. The process is easier since there is no pretreatment step.

The corrosion behavior of aluminum alloys coated with intrinsically conducting polymers has been determined by Shah et al. [19]. Conducting polymer coatings were deposited on aluminum substrate using oxalic acid as electrolyte. The corrosion resistance of the coated aluminum was found to be strongly dependent on the applied current density and deposition time.

Su and Iroh [20] investigated effects of electrochemical process parameters such as pH of the reaction media, applied current density and initial monomer (pyrrole) and electrolyte (oxalic acid) concentrations on the formation process of polypyrrole coatings.

Rajagopalan and Iroh [21] studied recently polyaniline-polypyrrole composite coatings formed on low carbon steel using oxalic acid as electrolyte by a potentiostatic method under aqueous conditions. A passive layer of iron (II) oxalate is deposited on the steel surface prior to the formation of composite coatings. The electrochemical process shows three distinct regimes: formation of passive layer, dissolution of passive layer and formation of polymeric composite coatings.

A summary of the some techniques used for deposition of polypyrrole on metals for corrosion protection purpose is given in Table 2.3.

Table 2.3: Summary of techniques reported in the literature for electropolymerization of pyrrole.

Author/ Ref	Year	Substrate Metal	Pretreatment	Electrolyte	Method
Troch-Nagels [8]	1992	Mild steel	No	Na_2SO_4	Potentiostatic & galvanostatic
Beck et al [10]	1994	Iron	Mechanical	Aqueous Oxalic acid	Galvanostatic
Ferreira et al [12]	1996	Iron/ steel	10% nitric acid for 4 min	Aqueous Na_2SO_4 $K_2C_2O_4$ Or KNO_3	Galvanostatic
Su and Iroh [13]	1997	Stainless steel	Mechanical	Benzene sulfonate	Galvanostatic
Idla et al [15]	1997	Mild steel	Mechanical	Aqueous sodium toluene sulphonate	Galvanostatic
Krstajic,et al [14]	1997	Mild steel	Mechanical	Aqueous oxalic acid	Galvanostatic
Su and Iroh [20]	1998	steel	Mechanical	Oxalic acid	Galvanostatic
Ferreira et al [16]	1999	Mild steel Zn steel	Nitric acid Na_2S	Modefied pyrrole Modefied pyrrole	Galvanostatic Galvanostatic
Aeiyach et al [18]	1999	zinc	No	Oxalate +small amount sulfide at pH 5	Galvanostatic
Shah et al [19]	2001	Aluminum	Mechanical	Oxalic acid	Potentiostatic & galvanostatic

Petitjean et al. [22] observed, during the electropolymerization of pyrrole on an iron electrode in aqueous acetonitrile containing tetrabutylammonium hexafluorophosphate, well defined periodic current oscillations. The periodicity, amplitude and shape of the oscillations depend on the concentrations of the electrolyte species.

2.3. Conductive Polymers For Corrosion Protection

It is well known that corrosion is largely an electrochemical reaction occurring on the surface of the metals. One of the approaches to protect metals against corrosion is the application of polymeric coatings that are capable of inhibiting the oxidation of metals. However, in the traditional coating techniques, the hazardous and environmentally unsafe chromate rinse process is generally required. Electrpolymerization is an alternative process which can provide polymeric coatings without involving toxic chemicals. Conducting polymers have recently been reported to be used for corrosion protection of some active metals and alloys. The rate of corrosion can be reduced by manipulating the electrode potential by some external means. A technique that makes the electrodes potential negative enough such as to reach the immunity range is known as cathodic protection. On the other hand, the technique in which electrode potential is increased so that it is in the passive range, is called anodic protection. In anodic protection, although the metal is not thermodynamically stable, the corrosion rate is very low due to the presence of a passive film.

The electrode potential can be manipulated in order to get anodic protection through galvanic contact with a charged conducting polymer. A substrate metal coated with a charged conducting polymer will poise the electrode potential in the passive range in the absence of any redox reaction. However, in the presence of a redox reaction, which is inevitable even in the passive regime, the conducting polymer film will discharge. Consequently, the potential will drift towards negative values. The length of time during which the potential is maintained in passive regime depends on the total charge stored in the polymer and rate of the reaction. Therefore for sustained protection, the polymer film must be charged continuously. This is done by cathodic reduction of oxygen on the polymer.

The principle can be illustrated with help of schematic in Figure 2.1. In the passive ranges, corrosion of metal takes place (although at very small rate):

$$M \longrightarrow M^{n+} + ne^- \qquad (2)$$

The generated electron discharge the polymer:

$$(poly)^{n+} + ne^- \longrightarrow (poly)^0 \qquad (3)$$

The polymer is recharged by reduction of oxygen on the polymer surface:

$$(poly)^0 + \tfrac{n}{4}\,O_2 + nH^+ \longrightarrow (poly)^{n+} + \tfrac{n}{2}\,H_2O \qquad (4)$$

Therefore the overall reaction (1 + 2 + 3) is

$$M + \tfrac{n}{4}\,O_2 + nH^+ \longrightarrow \tfrac{n}{2}\,H_2O + M^{n+} \qquad (5)$$

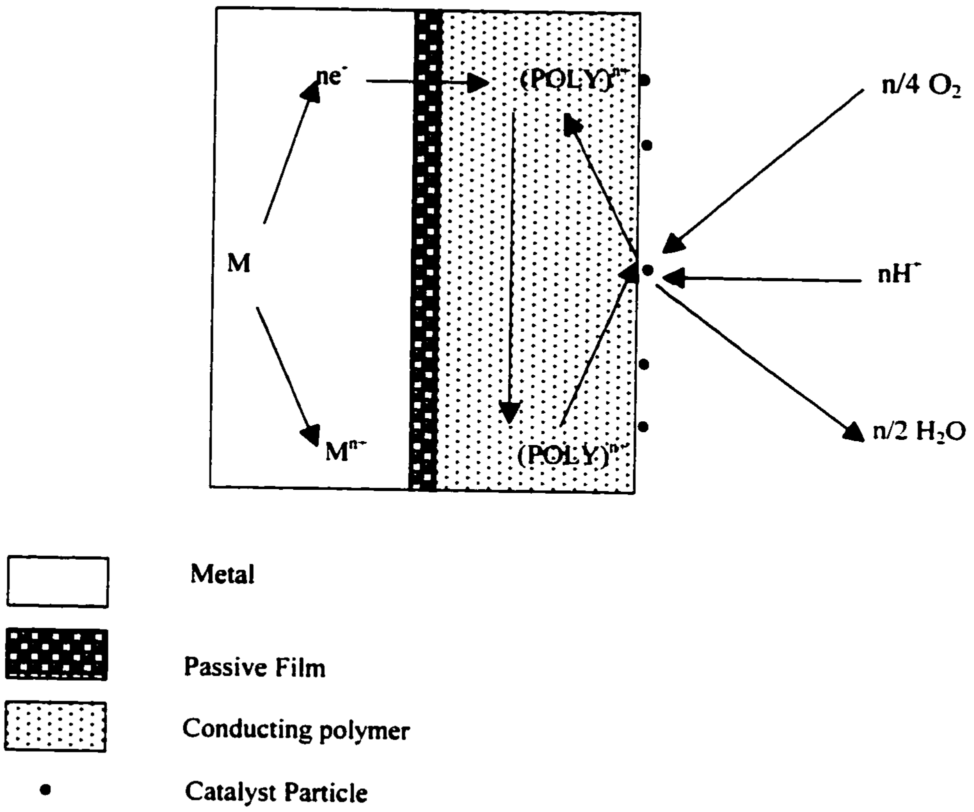


Figure 2.1 Principle of corrosion protection by conducting polymer

Several researchers studied deposition of various conducting polymers for corrosion protection purpose. Deberry [23] electrochemically synthesized polyaniline in perchloric acid solution using cyclic voltametery. Type 410 and 430 stainless steels were used as substrate metals. A passive metal oxide film was generated in first few scans before deposition of polyaniline. The coated samples remained passive for longer period of time in acid solutions in which they are normally active and subject to corrosion.

Deng et al. [24] demonstrated the use of poly (3-methyl thiophene) (P3MT) coating on Ti–TiO_2 surface to hold the corrosion potential of Ti metal in the passive regime. It was shown to be necessary to use oxygen reduction on the film to keep the film from discharging and thus poising the potential in desired range. It was found that oxygen reduction kinetics was dramatically improved by incorporating Pt particles on P3MT film. The oxygen reduction with the catalytic surface was fast enough to balance the passivation current.

Ren and Barkey [25] deposited P3MT film on Pt and SS430 in organic electrolyte galvanostatically. Adherence of the film was better on phosphated SS430 samples. The coating was stable in 1.0 N H_2SO_4 for long periods of time.

Hasse and Beck [26] used electropolymerization to deposit polypyrrole, P3MT, poly (Bisthiophene) and polyaniline on iron and platinum, in various aqueous and non-aqueous electrolytes. Their use as corrosion inhibiting polymer layers has also been demonstrated.

Ahmed and MacDiarmid [27] utilized electrochemically synthesized polyaniline for corrosion protection of iron and steel. For enhancing adhesion of polyaniline, several pre-treatments were tried. The best of these were phosphoric acid, polyphosphoric acid, metal chelating agents, alizarin sulfonate and chromotropic acid. It was emphasized that while poising the potential of steel in passive region, polyaniline (in the form of emeraldine salt) reversibly reduces to leucoemeraldine. The later is quickly oxidized by ambient oxygen to reproduce emeraldine. In this fashion, the discharged polymer is continuously charged resulting in stabilized open circuit voltage (OCV) in passive range.

Kinlen et al. [28] studied polyaniline coating on carbon steels with an epoxy top coat. They concluded that corrosion protection is not solely due to formation of a 'passive' iron oxide, rather interfacial redox reactions occur at the interface to form Fe-polyaniline complex.

Although some studies on the electrodeposition of conductive polymers on metals like nickel and stainless steel have been reported, the use of iron or mild steel as substrate have been less well investigated in spite of their technological importance. However, the electrodeposition of polypyrrole on oxidizable metals such as iron is not easy, since the metal will dissolve before the electrpolymerization potential of the monomer (pyrrole) is reached. The oxidation potential of the metal is much more negative than that of the monomer and dissolution of the metal will occur and stabilize the potential of the electrode at a negative value preventing monomer oxidation [29]. Thus, to achieve the deposition of the polypyrrole on iron or other oxidizable metals it is necessary to find electrochemical conditions that lead to a partial passivation of the metal and decrease its dissolution rate without preventing electropolymerization .

2.4. Characterization of Polypyrrole

Several studies were done to characterize polypyrrole synthesized chemically or electrochemically. Nishio et al. [4] investigated characteristics of chemically synthesized polypyrrole by various oxidizing agents. They concluded that polypyrrole with a smaller particle size and a larger specific surface area showed better discharge performance than that with a larger particle size and a smaller specific surface area. They found that the polypyrrole synthesized by $FeCl_3$ or $Fe(ClO_4)_3$ had high specific surface area and small particle size.

The characteristics of electrochemically deposited polypyrrole film has been the subject of much recent discussions. Idla et al. [15] characterized electrically deposited polypyrrole films on mild steel with atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The polypyrrole films were polymerized electrochemically from sodium p-toluene sulphonate (ToS) water-ethanol solution. A strong variation of the chemical composition at the interfacial layers was observed. A sulphur-rich layer was formed at the interface, indicating that the counter-anions (ToS) were accumulated on the surface of the metal. Nitrate counter-anion containing polypyrrole films were also studied in some cases for comparison. They concluded that the mean surface roughness in case of PPy/NO_3 was small and the distribution of surface heights was much wider in the case of PPy/NO_3 film.

The variations in the parameters used during polypyrrole deposition such as electrolyte type and concentration can greatly affect the morphology of the resultant polymer. Different techniques like X-ray diffraction (XRD) and scanning electrode microscopy (SEM) have been used to study the composition and morphology of the surface. Lemon and Haigh [30] studied the surface morphology and structure of electrochemically deposited polypyrrole films by electron probe microanalysis, crossed polar optical microscopy and X-ray diffraction (XRD).

Su and Iroh [31] investigated morphology and structure of the passive interphase formed during aqueous electrodeposition of polypyrrole coatings on steel by SEM and XRD. They electrodeposited an iron oxalate dihydrate on steel from aqueous oxalate solutions prior to the electropolymerization of pyrrole. It was concluded that the size of the crystals, formed in the passive interphase, was dependent on the experimental conditions. In another study [32], they compared polypyrrole and poly(N-methylpyrrole) coatings electrodeposited on steel from aqueous oxalate solution and investigated the process by SEM and XRD techniques. They found that polypyrrole coatings exhibited better adhesion and corrosion performance than poly(N-methylpyrrole) coatings .

CHAPTER 3

EXPERIMENTAL SETUP & PROCEDURE

3.1 Experimental Setup

A sketch of the experimental setup is shown in Figure 3.1. The electropolymerization is done in an electrochemical cell. A flag shape mild steel coupon, on which pyrrole is intended to polymerize, functioned as working electrode. A stainless steel bar and saturated calomel electrode (SCE) worked as counter and reference electrodes respectively. These three electrodes were connected to a potentiostat (EG&G PARC model 273 A) via an electrometer. The potentiostat was controlled through an electrochemical software (M270, EG&G PARC) from an IBM compatible microcomputer.

The cell has jacketed body to allow circulation of hot/cold water so that a desired temperature is maintained during the electropolymerization. Figure 3.2 shows a photograph of the cell. The temperature was recorded using a thermometer of 0.1°C least count. The pH of the electrolyte was measured by a calibrated pH meter. Analytical grade chemicals were used as received. Pyrrole was purified by silica gel bed. The solutions were made in deionized water.

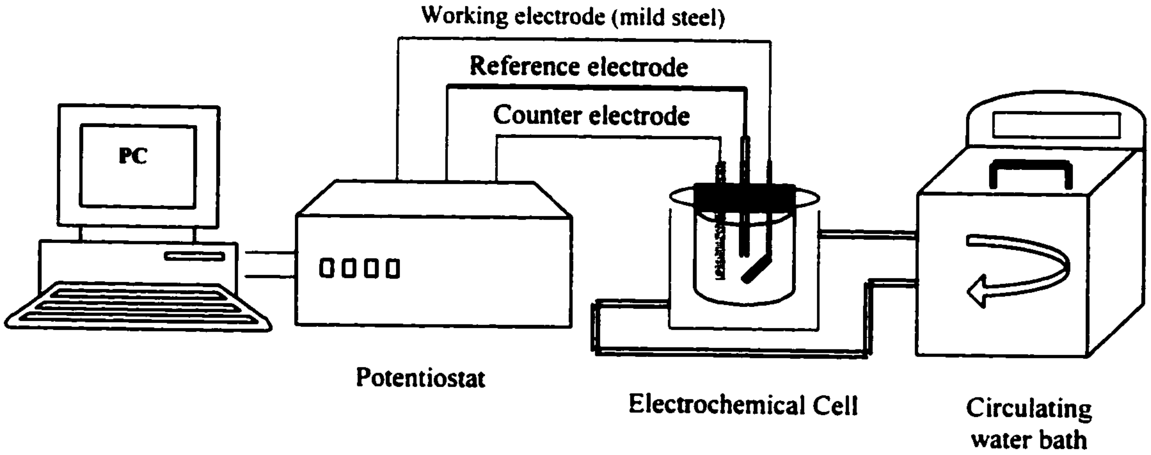


Figure 3.1. Experimental setup

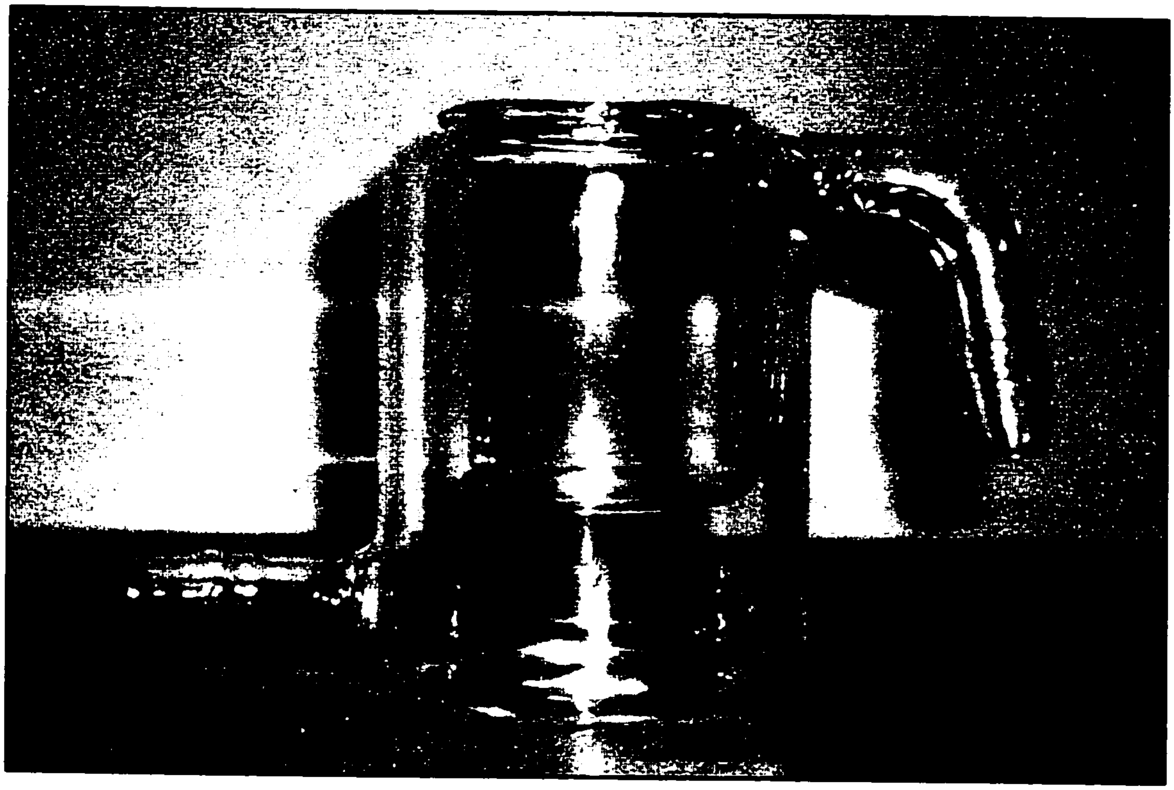


Figure 3.2 Photograph of the cell

3.2 Preparation of Mild Steel Coupons

Mild steel coupons of predetermined size in flag shape were machined from a mild steel sheet of 1 mm thickness. The composition of the mild steel is given in Table 3.1. These coupons were used as working electrode (anode of the electrochemical cell). A sketch of the mild steel coupon with the dimension is given in Figure 3.3. The coupons were first cleaned mechanically with increasing grades of emery papers with grit size 100, 400, 600 and 1500. Subsequently a wash with acetone removed any oil or grease. The stem of the coupon was insulated with an insulation paint such as to expose the desired deposition area.

3.3 Experimental Procedure

The electropolymerization was done in the cell which was described in the previous section. Fifty milliliters of the prepared solution were used in one experiment. All three electrodes were placed vertically in the cell. The temperature and the pH were measured. The deposition was done galvanostatically. Chronopotentiametry, one of the predesigned experiment in the software M270, was used. Parameters chosen to run this experiment are tabulated in Table 3.2

3.4 Experimental Design

There are two main aspects of this research. The first part focuses on screening several available methods of electropolymerizationin of pyrrole on mild steel in the

Table 3.1 Composition of mild steel.

Substance	Composition (%)
Iron (Fe)	99.47
Manganese (Mn)	0.34
Carbon (C)	0.089
Chromium (Cr)	0.037
Nickel (Ni)	0.022
Phosphorus (P)	0.01
Molybdenum (Mo)	0.007
Copper (Cu)	0.005
Vanadium (V)	0.005

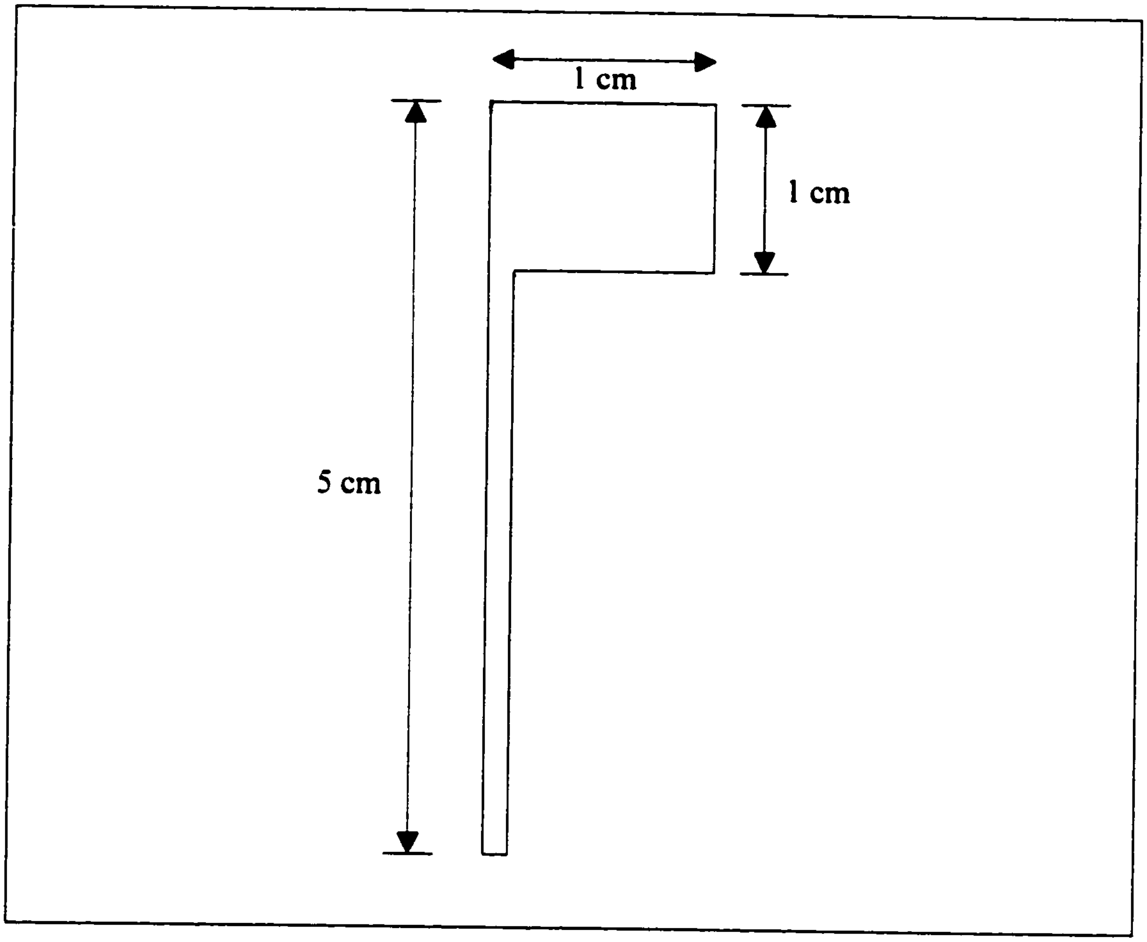


Figure 3.3 Sketch of the coupon

Table 3.2 Parameters used in running the software (M270).

Parameter	Symbol	Value
Purge Time (s)	PT	0.0
Cond. Time (s)	CT	0.0
Cond. Pot. (V)	CP	0.0
Dept. Time (s)	DT	0.0
Dept. Pot. (V)	DP	0.0
Equil. Time (s)	ET	0.0
Time/Pt. (s)	TP	1.816
No. of Points	NP	1001
Stop On	S0	0.0
Rise Time	RT	High stability
Working Elec.	WE	Solid
Ref. Elec. (V)	RE	SCE (241.5E-3)
Aux A/D	AU	No
Elec. Area (cm^2)	AR	2.00
Curr. Step (A)	I1	Applied current
Time Step (s)	T1	1800

literature. Four different methods were reported for deposition of polypyrrole. These methods are summarized as follows:

1. A method by Troch-Nagels et al. [8] showing that polypyrrole was deposited on mild steel substrate from aqueous solution of Na_2SO_4 without pretreating the electrode surface. The applied current density was 5 mA/cm^2 for a period of five minutes.

2. A method by Ferreira et al. [12] for electropolymerization of polypyrrole on mild steel was studied. The method investigated the deposition of polypyrrole on iron and mild steel treated with 10% nitric acid for 4 min and using KNO_3 as electrolyte solution. The applied current density was 4 mA/cm^2 for five minutes.

3. A method by Beck et al. [10] in which electrochemical deposition of polypyrrole was performed on iron substrate from aqueous solution of pyrrole and oxalic acid. The electrode was pretreated mechanically with increasing grades of emery papers. The electrochemical process proceeded at constant current density of 2 mA/cm^2 for a period of five minutes.

4. A method by Aeiyach et al. [18] which used aqueous oxalate solution at pH 5. The experiment was performed in galvanostatic mode for current density of 4 mA/cm^2 for ten minutes.

Electropolymerization of pyrrole on mild steel coupon was carried out with the given parametric values according to these four methods. The deposited polypyrrole film was tested for adherence and surface uniformity morphology. Surface adherence was tested qualitatively by scratching with stainless steel spatula. The surface uniformity and morphology were determined by obtaining Scanning Electron Microscopy (SEM).

In the second part of this work, a parametric study on the best method was undertaken to find out optimum parameters and to elucidate the effect of various parameters. The considered parameters are, applied current density, pH and temperature of the reaction medium. The applied current density was varied from 0.5 mA/cm^2 to 6 mA/cm^2. The electrochemical reaction was carried out in media of four different pH; namely, 2.0, 4.0, 7.0 and 8.5. The pH of the solution containing the monomer (pyrrole) and the electrolyte (oxalic acid) was adjusted by sodium bicarbonate $NaHCO_3$. The experiments were done for five different temperatures varying from 25 °C to 65 °C using the circulating water bath. The electropolymerization time, monomer concentration and electrolyte concentration were fixed. Table 3.3 shows values of different parameters in the experiment. After each experiment, the coated steel sample was rinsed with water and dried in a vacuum oven at 50 °C to obtain constant weight.

Table 3.3: Values of various parameters in the experiments.

Parameters	**Value**
Pyrrole concentration (M)	0.1
Electrolyte concentration (M)	0.1
Time of deposition (sec)	1800
Temperature (°C)	25, 35, 45, 55 & 65
Current density (mA/cm^2)	0.5, 2.0, 4.0 & 6.0
pH	2.0, 4.0, 7.0 & 8.5

CHAPTER 4

RESULTS & DISCUSSION

4.1 Introduction

This chapter essentially has two main parts. The first one concerns about screening of four different methods available in the literature for electropolymerization of polypyrrole on various steel substrate. The second part is a parametric study on the best method.

4.2 Screening of Electropolymerization Methods

Electropolymerization of pyrrole on mild steel was first performed using four different methods available in the literature in order to identify the best method from corrosion point of view. The methods were described previously in Chapter 3 and shown in Table 4.1. Method (A) by Troch-Nagels et al. [8] used Na_2SO_4 as electrolyte without pretreating the surface. The applied current density was 5 mA/cm^2 for a period of five minutes. Method (B) by Ferreira et al. [12] investigated the deposition of polypyrrole on iron and mild steel treated with 10% nitric acid for 4 min and using KNO_3 as electrolyte solution. The applied current density was 4 mA/cm^2 for five minutes also. Method (C) by Beck et al. [10] in which deposition of polypyrrole was performed on iron substrate from aqueous solution of pyrrole and oxalic acid. The electrode was pretreated with increasing grades of emery papers. The applied current

Table 4.1. Synthesis methods considered in this study.

Method	Author/ Ref (year)	Substrate Metal	Pretreatment	Electrolyte	Method & Parameters
A	Troch-Nagels [8] (1992)	Mild steel	No	(0.08 M Na_2SO_4 +0.5 pyrrole)	Galvanostatic i=4 mA/cm^2 (5 min) T=25 °C
B	Ferreira et al [12] (1996)	Iron/steel	10% nitric acid for 4 min	(0.1 M KNO_3+ 0.1 M pyrrole)	Galvanostatic i=4 mA/cm^2 (5 min) T=25 °C
C	Beck et al [10] (1994)	Iron	Mechanical Emery papers	(0.1 M oxalic acid+ 0.1 M pyrrole)	Galvanostatic i=2 mA/cm^2 (5 min) T=25 °C
D	Aeiyach et al [18] (1999)	Zinc	No	Oxalate - pH 5 (0.1 M sodium oxalate + 0.1 M pyrrole)	Galvanostatic i=4 mA/cm^2 (10 min) T=25 °C

density was 2 mA/cm^2 for five minutes. Method (D) by Aeiyach et al. [18] used aqueous oxalate solution at pH 5. The experiment was performed with current density of 4 mA/cm^2 for ten minutes. However, all four methods were performed in galvanostatic mode at room temperature. The morphology of the coating from these methods was examined by visual inspection and Scanning Electron Microscopyy (SEM). Method (A) which did not involve any pretreatment of the surface gave very poor adherent deposition of polypyrrole on the steel surface. The formed polypyrrole film could be scratched or removed easily. Figure 4.1 shows the SEM for this method that show large grains. The grain size was between 5 to 8 µm. It also shows that the polypyrrole deposition was not distributed uniformly on the steel surface. Method (B) is a two steps process involving chemical pretreatment of the steel surface. It showed a good adherent surface of polypyrrole coating. The surface was also smooth and the deposition could not be scratched easily. The grains were larger than those from method (A) as shown from the SEM in Figure 4.2. The average grain diameter was about 10 µm. In addition, the deposition was not distributed uniformly on the surface. The deposition from method (C), which is a one step process was adherent, shiny and it cannot be removed easily. Uniform, smooth and well covered surface were noticed in this method. The SEM micrograph in Figure 4.3 for this method shows much better distribution of the polypyrrole coatings on the steel samples. The grains were small as shown in SEM. They were less than 2 µm in size resulting into a uniform polypyrrole film. However, rough surface was observed in method (D). The SEM analysis fortified visual inspection as shown in Figure 4.4.

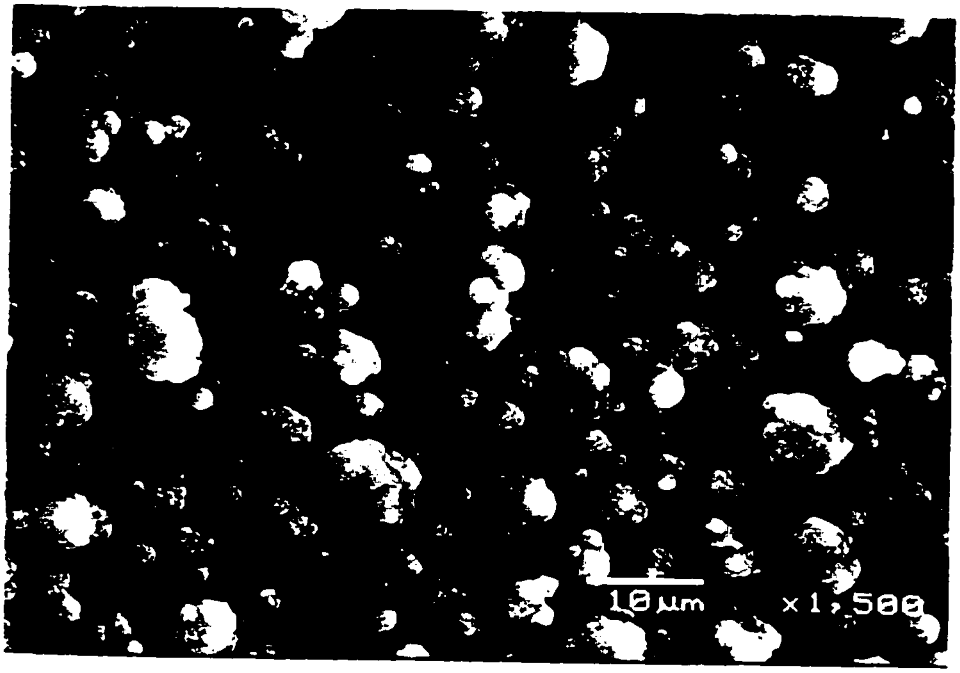


Figure 4.1 SEM for Troch-Nagels's method

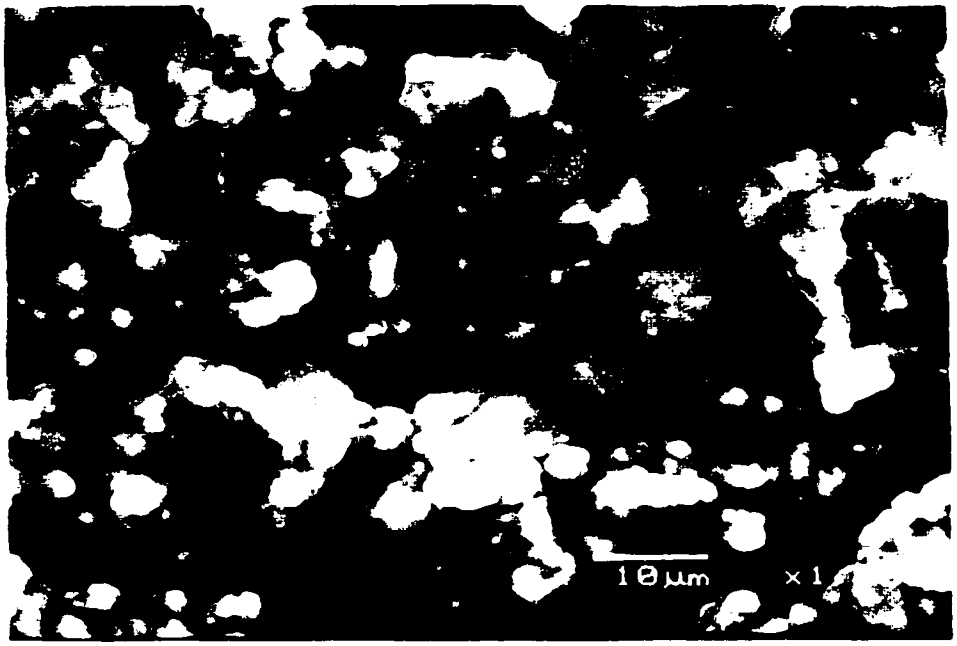


Figure 4.2 SEM for Ferreira's method

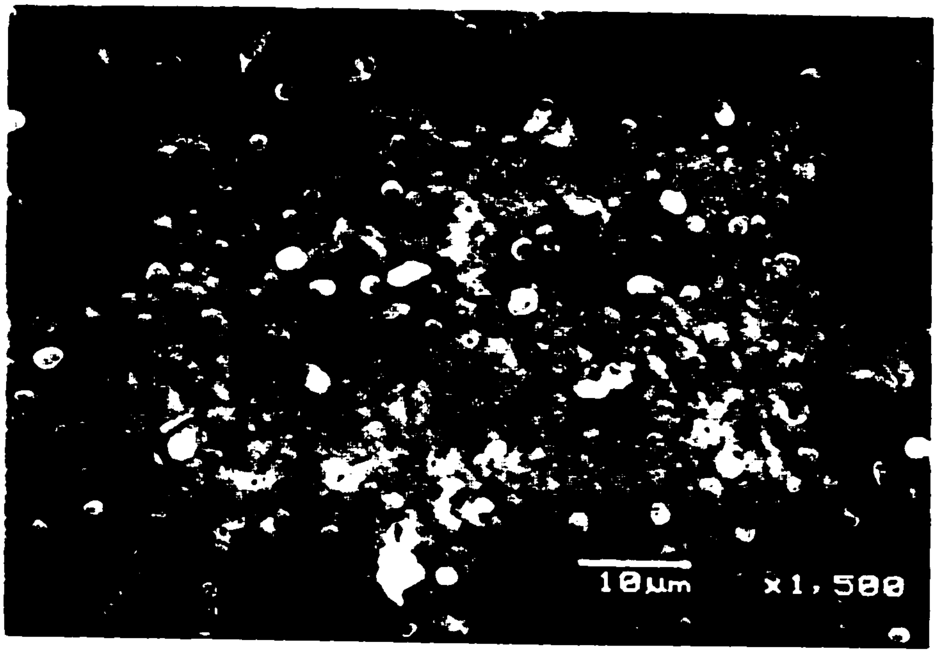


Figure 4.3 SEM for Beck's method

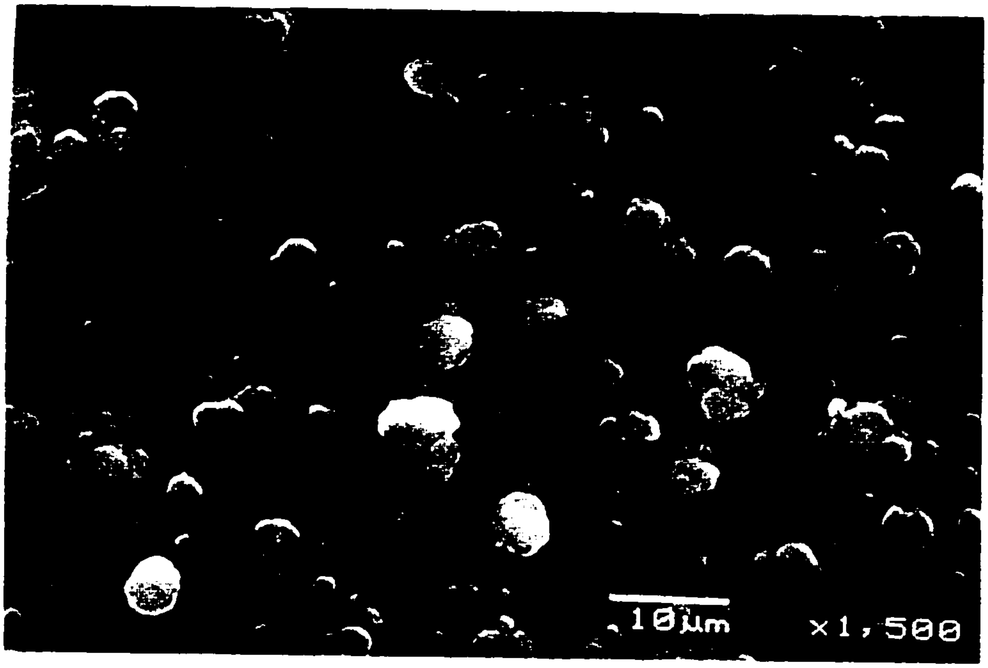


Figure 4.4 SEM for Aeiyach's method

The grains size was about 5 μm which is smaller than the grains obtained from both method (A) and (B). The deposition was not uniform and exhibited many pinholes. A typical pinhole is in SEM in Figure 4.5.

Comparing the SEM analysis and visual inspection for the four methods showed that method (C) (Beck's method) gives the best adherent and uniform film of polypyrrole on mild steel. The deposition was free from defects like pinholes. In addition, this method is a one step method. Because of these reasons this method is selected for further parametric study.

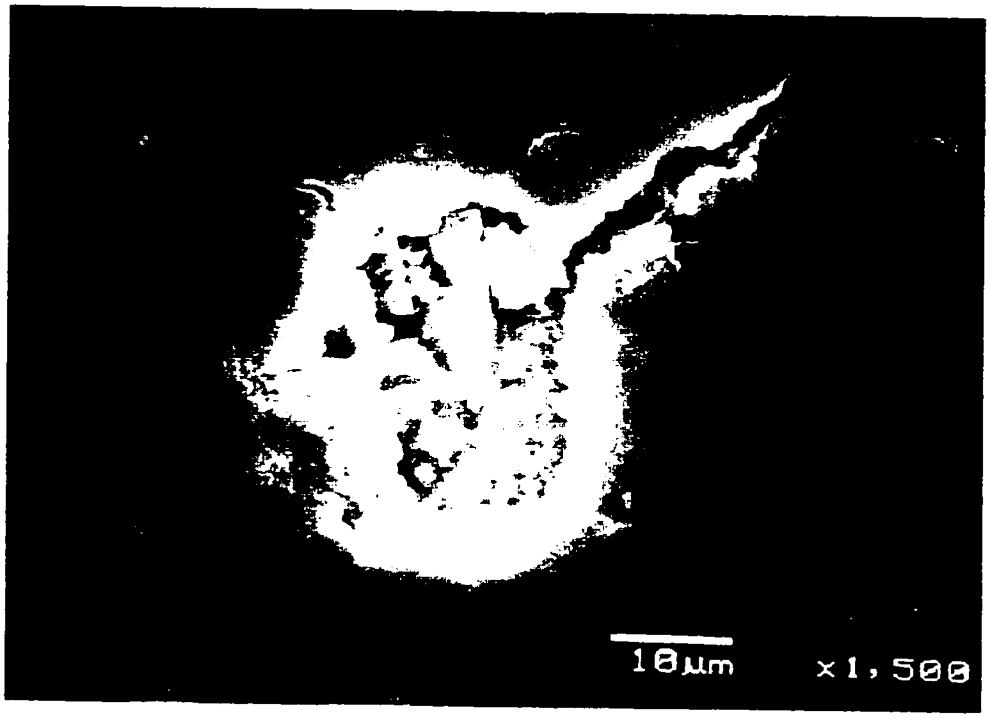


Figure 4.5 Pinholes on the steel surface (Aeiyach's method)

4.3 Parametric Study

The electropolymerization method by Beck et al. [10] was chosen for further investigation as described in previous section. The method is explained earlier in chapter 3. A typical galvanostatic electropolymerization gives chronopotentiometric curve as shown in Figure 4.6. The process evidently has two distinct stages. In the first stage the electrode potential remained constant and negative. (e.g. approximately –500 mV SCE at pH 2.0 and 25 °C). The potential corresponds to the acidic dissolution of iron. This stage is termed as induction and the duration as induction time. During this stage acidic dissolution of iron takes place till sufficient corrosion products have been formed needed for surface passivation. The iron dissolution slows down and eventually stops as the oxidation of pyrrole starts as soon as the surface is passive. This stage could be termed as pyrrole oxidation stage. It manifests itself as a sharp peak at the end of induction period. Both of these stages have been affected by various process parameters, namely,

- Monomer (pyrrole) concentration
- Electrolyte (oxalic acid) concentration
- Time of deposition
- Current density in galanostatic mode
- Applied potential in potentiostatic mode
- Surface pretreatment

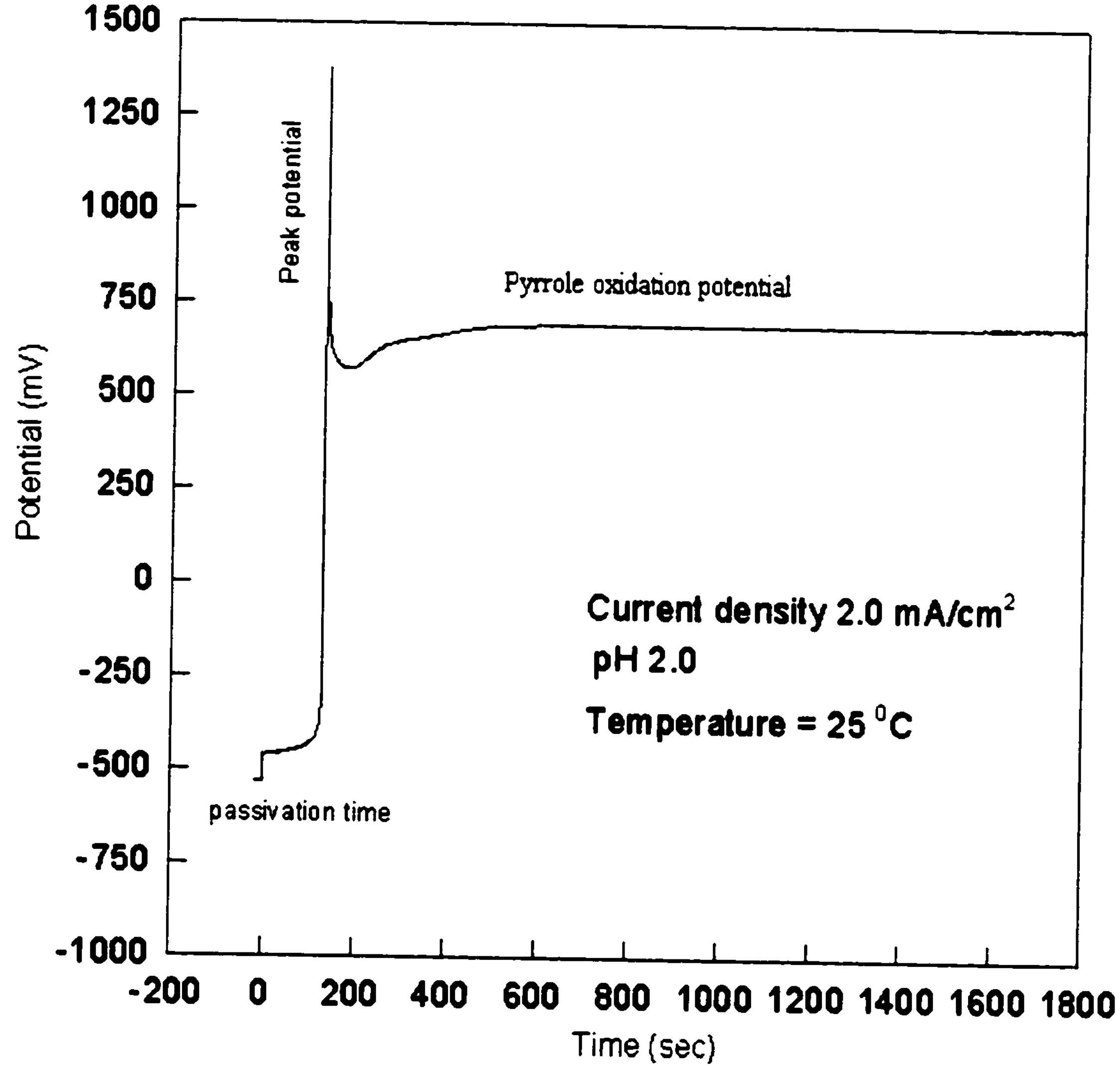


Figure 4.6. A typical potential-time curve

- pH of the solution

Su and Iroh [20] have studied the effects of current density, monomer concentration, electrolyte concentration and solution pH. It was shown that the induction time, oxidation potential, morphology and adherence depend on these parameters. The studied pH values were 1.4, 2.4, 4.1 and 6.0. Electropolymerization at neutral and alkaline pH was not investigated in detail.

As observed earlier, the electropolymerization of pyrrole on iron involves two chemical reactions, namely, dissolution of iron and oxidation of pyrrole. Since the rate of chemical reactions strongly depends on reaction temperature, the process is expected to be greatly influenced by temperature. Studying temperature as an additional parameter will give clearer insight of the process. In the present study, temperature, pH (including acidic, neutral and alkaline ranges) and current density were varied. The monomer (pyrrole) concentration, electrolyte (oxalic acid) concentration and reaction time were held constant at 0.1 M, 0.1 M and 1800 seconds respectively. Values of parameters are tabulated in Table 4.2. The solution pH was adjusted by adding sodium bicarbonate.

Table 4.2: Set of experiments done in this study.

Expt.	pH	Current density (mA/cm^2)	Temperature (° C)
1	2.0	0.5	25
2	2.0	2.0	25
3	2.0	4.0	25
4	2.0	6.0	25
5	4.0	0.5	25
6	4.0	2.0	25
7	4.0	4.0	25
8	4.0	6.0	25
9	7.0	0.5	25
10	7.0	2.0	25
11	7.0	4.0	25
12	7.0	6.0	25
13	8.5	0.5	25
14	8.5	2.0	25
15	8.5	4.0	25
16	8.5	6.0	25
17	2.0	0.5	35
18	2.0	2.0	35
19	2.0	4.0	35
20	2.0	6.0	35
21	4.0	0.5	35
22	4.0	2.0	35
23	4.0	4.0	35
24	4.0	6.0	35
25	7.0	0.5	35
26	7.0	2.0	35
27	7.0	4.0	35
28	7.0	6.0	35
29	8.5	0.5	35
30	8.5	2.0	35
31	8.5	4.0	35
32	8.5	6.0	35
33	2.0	0.5	45
34	2.0	2.0	45
35	2.0	4.0	45
36	2.0	6.0	45
37	4.0	0.5	45
38	4.0	2.0	45
39	4.0	4.0	45
40	4.0	6.0	45
41	7.0	0.5	45
42	7.0	2.0	45
43	7.0	4.0	45
44	7.0	6.0	45
45	8.5	0.5	45
46	8.5	2.0	45
47	8.5	4.0	45
48	8.5	6.0	45
49	2.0	0.5	55
50	2.0	2.0	55
51	2.0	4.0	55
52	2.0	6.0	55
53	4.0	0.5	55
54	4.0	2.0	55
55	4.0	4.0	55
56	4.0	6.0	55
57	7.0	0.5	55
58	7.0	2.0	55
59	7.0	4.0	55
60	7.0	6.0	55
61	8.5	0.5	55
62	8.5	2.0	55
63	8.5	4.0	55
64	8.5	6.0	55
65	2.0	0.5	65
66	2.0	2.0	65
67	2.0	4.0	65
68	2.0	6.0	65
69	4.0	0.5	65
70	4.0	2.0	65
71	4.0	4.0	65
72	4.0	6.0	65
73	7.0	0.5	65
74	7.0	2.0	65
75	7.0	4.0	65
76	7.0	6.0	65
77	8.5	0.5	65
78	8.5	2.0	65
79	8.5	4.0	65
80	8.5	6.0	65

4.3.1 Effect of Temperature and Current Density in Acidic Media

A. Effect at 25 °C.

Chronopotentiometric plots of polypyrrole deposition at 2.0 pH and 25 °C are shown in Figure 4.7. When the applied current density was 0.5 mA/cm^2, the polymer film was very thin and it was difficult to determine whether it was due to corrosion product or polypyrrole. Since an expected plot was observed, it was inferred that it was a thin polypyrrole film. At 2.0 mA/cm^2 current density a perceptible black film was observed and the film surface was smooth. Increasing current density resulted into even smoother, compact and more adherent film. However, at 6.0 mA/cm^2, the surface became rough but film was adherent. Some pinholes were also observed. The roughness of surface at higher current density was also observed by Su and Iroh [20] . They suggested that the roughness is due to some side reactions. The reactions were not mentioned. Nevertheless, the increased surface roughness with higher current density could be because of higher polymerization rate. As the rate of polymerization increases, orderliness decreases which is observed as increased roughness. Photos of steel samples with polypyrrole films are shown in Figure A1 through A4.

The oxidation potential increases with increased current density as expected in any kinetics controlled electrochemical reactions. However, the induction time decreased sharply with current density. The induction time (τ) was 358 seconds at 0.5 mA/cm^2 while it was only 27.2 seconds at 6.0 mA/cm^2 for the same temperature and pH. The values are plotted in Figure 4.8. A linear regression of these data at pH 2.0 results

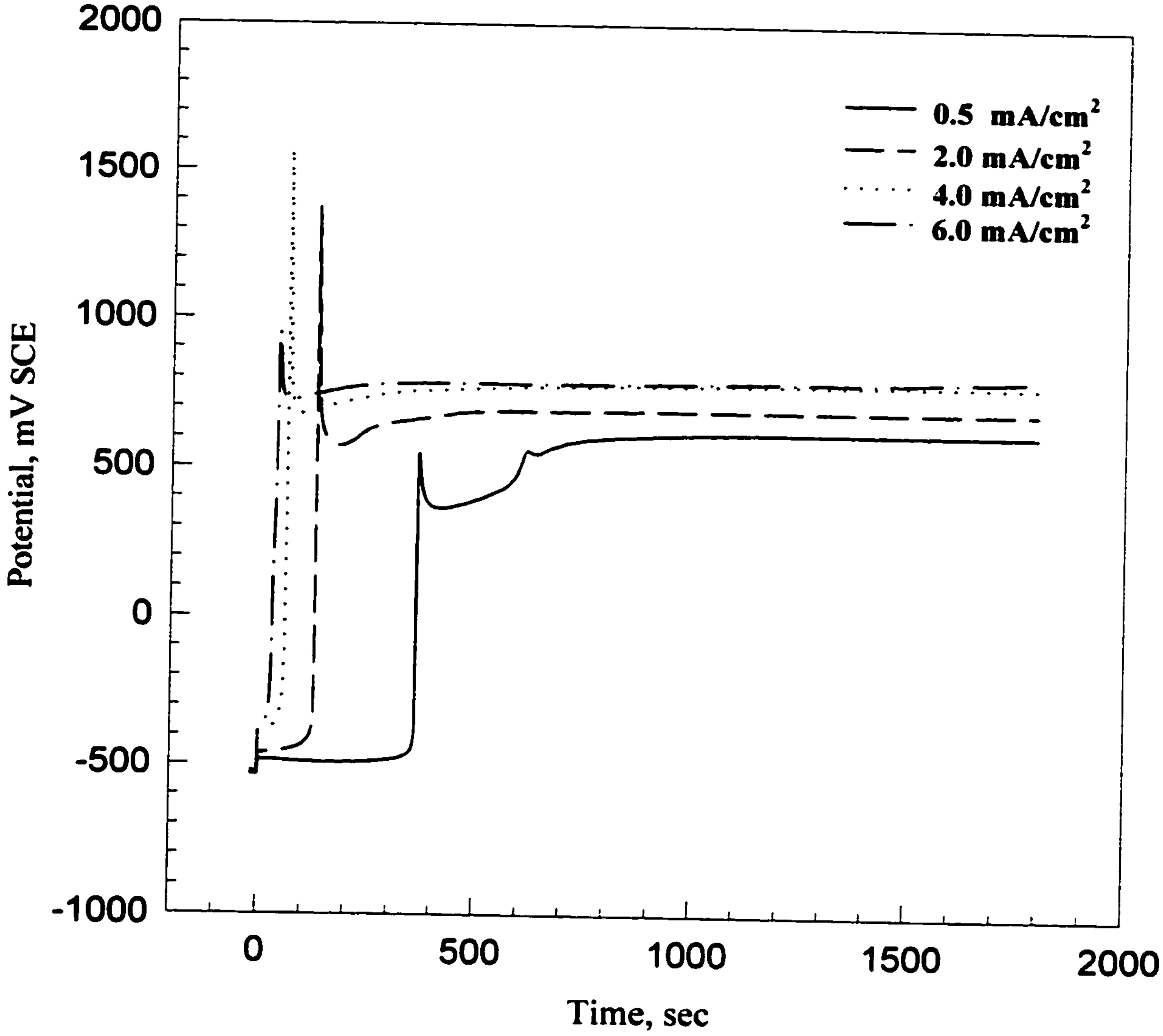


Figure 4.7 Potential vs time at pH 2.0 and T= 25 °C

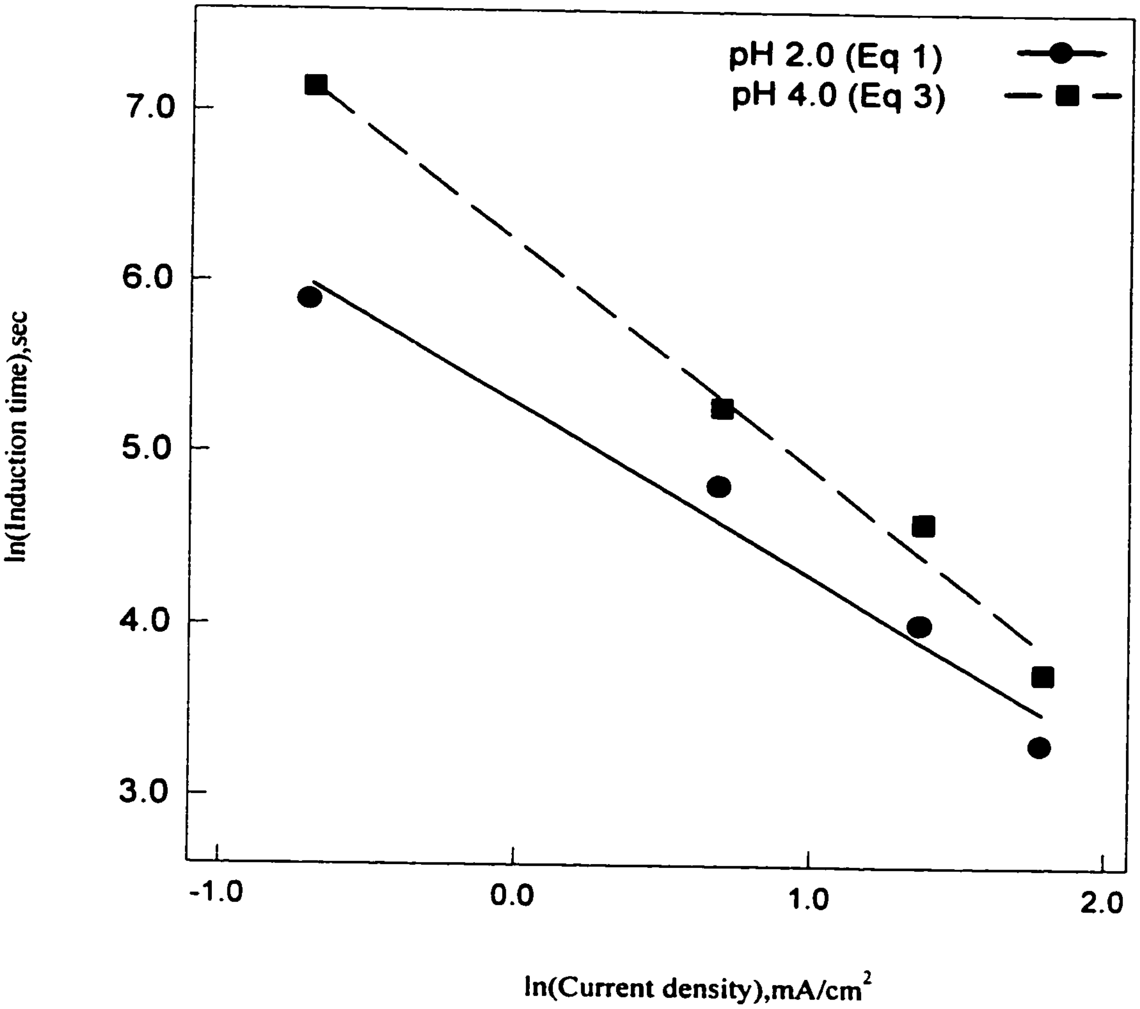


Figure 4.8 Dependence of induction time on the applied current density in acidic medium (T=25 °C)

into:

$$\ln\tau = 5.29 - 1.0 \ln i \quad (1)$$

Where τ is induction time (sec) and i is current density (mA/cm^2).

This equation is comparable with an equation by Su and Iroh [20] with pyrrole concentration of 0.25 M at pH 2.4.

$$\ln\tau = 5.22 - 1.16 \ln i \quad (2)$$

It seems that a certain amount of corrosion products are needed to achieve sufficient passivation needed for successful deposition of pyrrole on iron. It takes longer to obtain the required degree of passivation at lower current densities. However, it does not mean that a certain amount of charge is needed at constant pH. The passivation charge decreased with increasing current density as shown in Figure 4.9. It suggests that the required degree of passivation is also a function of current density.

Chronopotentiometric plots of polypyrrole deposition at pH 4.0 and 25 °C are shown in Figure 4.10. The polymer film was very thin, at 0.5 mA/cm^2 like the one obtained at 2.0 pH. At higher current density, adherent, black films were observed. The film surfaces were relatively smoother than those obtained at 2.0 pH using same current densities. Apparently, at higher pH, the rate of pyrrole oxidation is lesser which provides orderliness in the process of polymerization.

The induction time at pH 4.0 is generally higher than those at pH 2.0. It is known that the rate of iron dissolution in acidic media becomes less as pH is increased.

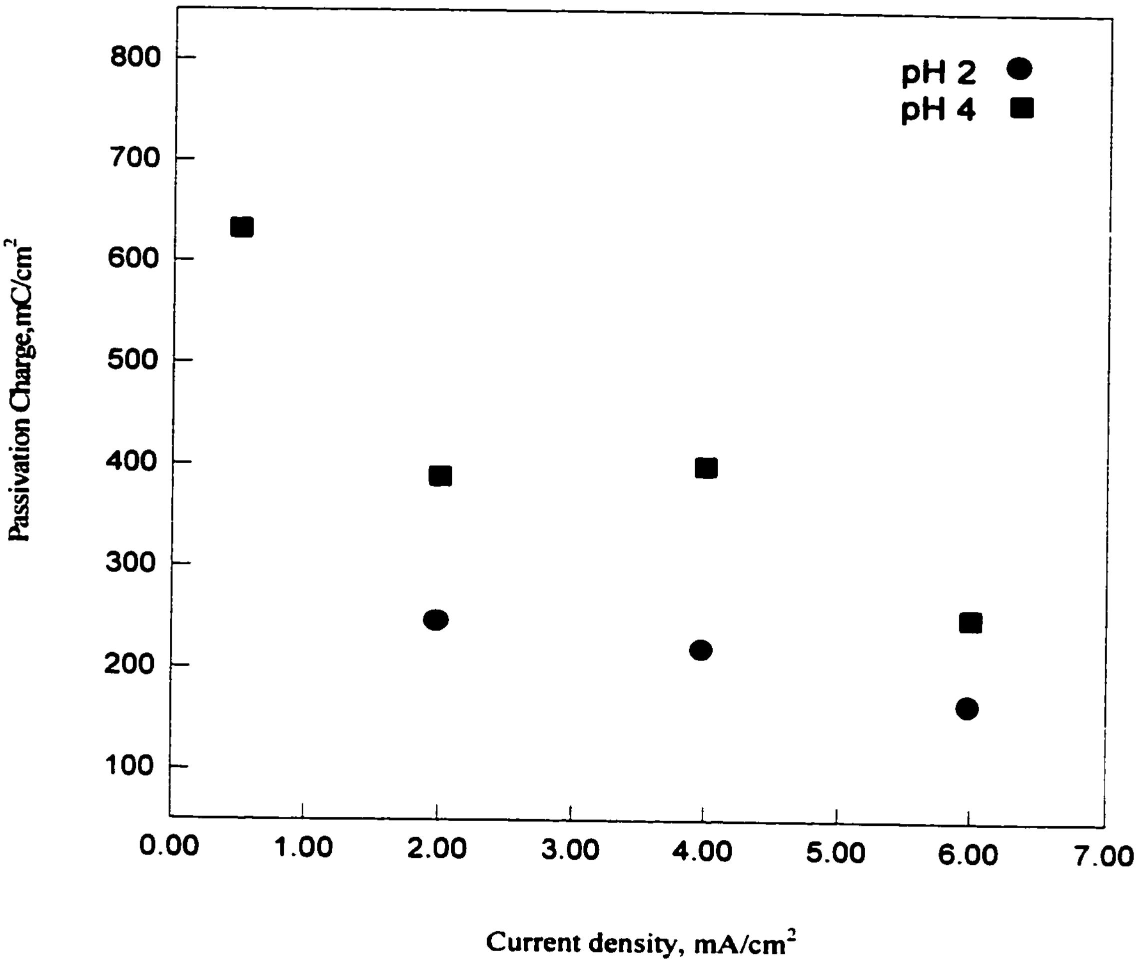


Figure 4.9 Passivation charge vs current density for acidic media at T= 25 °C

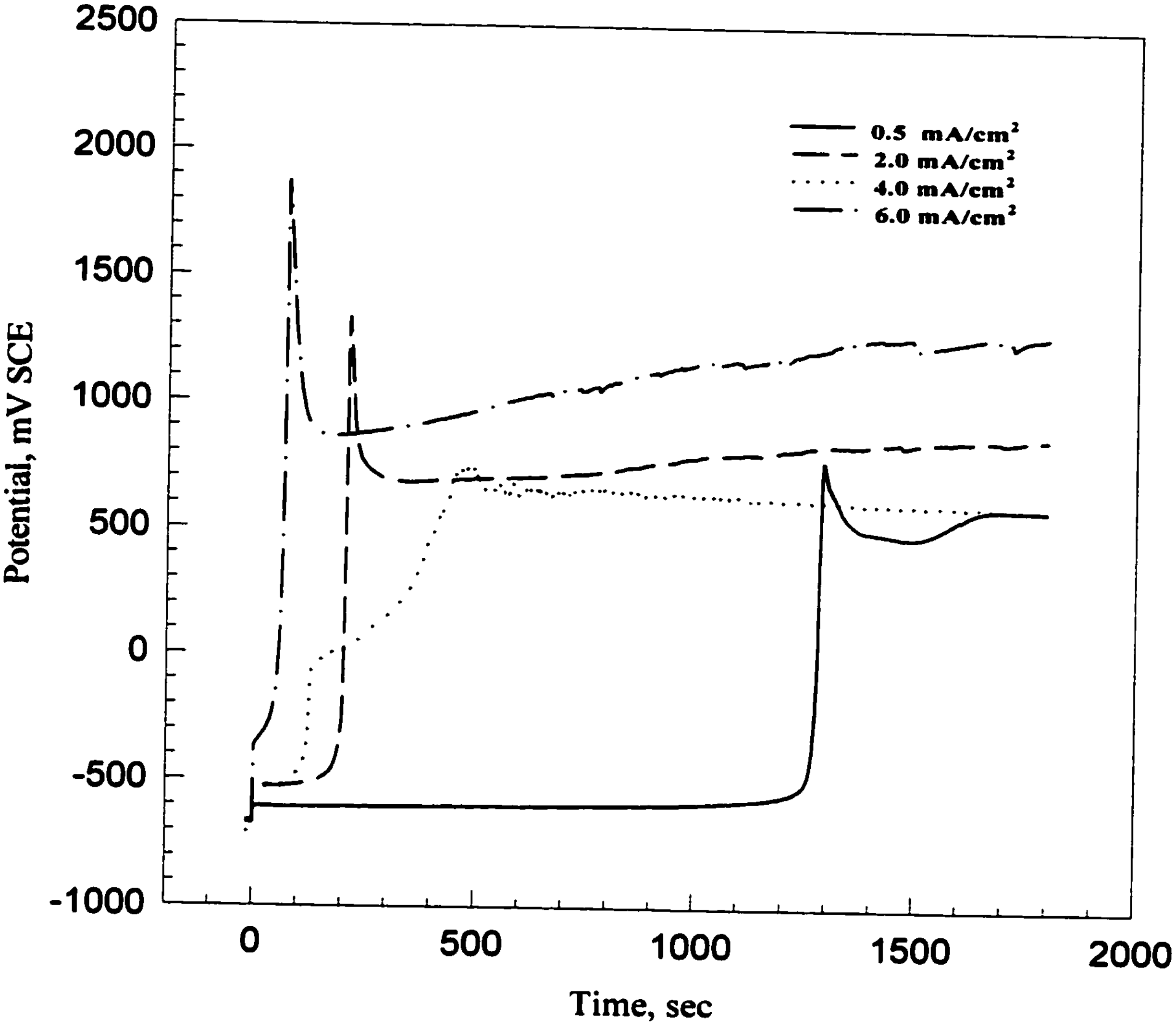


Figure 4.10 Potential vs time at pH 4.0 and T= 25 °C

With slower reaction, it takes more time to achieve the required degree of passivation for initiation of pyrrole oxidation. The induction time and passivation charges are plotted against current densities in Figure 4.8 and 4.9 respectively. The linear plots in Figure 4.8 for pH= 4.0 suggest following relationship

$$\ln\tau = 6.24 - 1.32 \ln i \qquad (3)$$

For the reaction medium of pH 4.0, it showed a higher passivation charge than those of the other system but its passivation charge decreased very rapidly with further increase of current density.

At higher current densities, e.g. 4.0 and 6.0 mA/cm^2, the oxidation potential increases with time. The increase in oxidation potential with time at pH 6.0 and at 5.63 mA/cm^2 was also observed by Su and Iroh [20]. This phenomenon is not well understood. Nevertheless, an increase in potential with time could be explained if the conductivity of film is significantly low. In this case additional IR drop in the film will be manifested as increased potential. The constant potential at lower current densities and also at higher current densities at pH 2.0 could be due to thinner film and higher film conductivities.

B. Effect at higher temperature

Chronopotentiometric plots of polypyrrole deposition at 2.0 pH and higher temperature (i.e. 35, 45, 55 and 65 °C) shown in Figures 4.11-4.20 show similar trend as at 25 °C. At 35 °C, a very thin polypyrrole film was observed when the applied current density was 0.5 mA/cm^2.

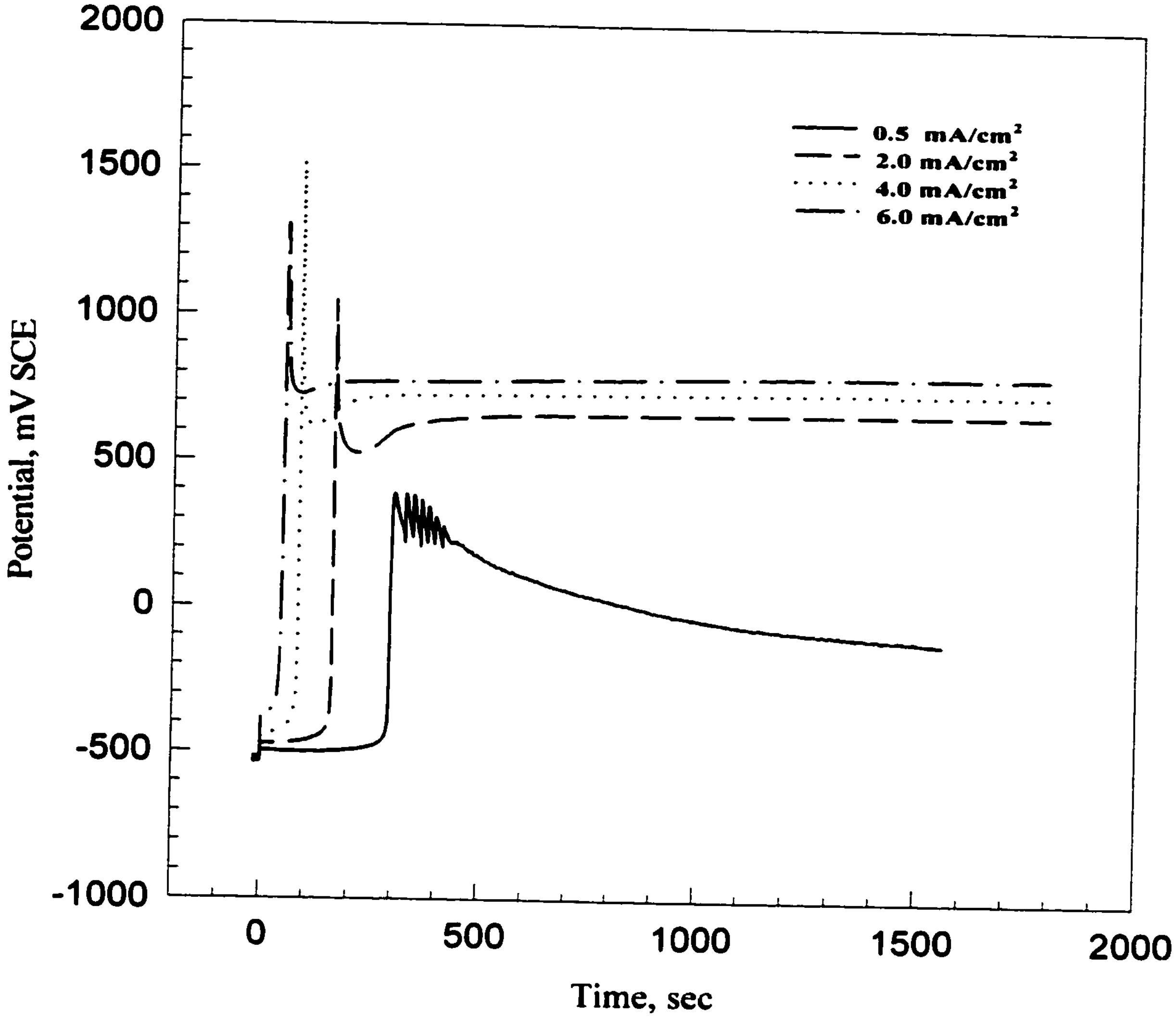


Figure 4.11 Potential vs time at pH 2.0 and T= 35 °C

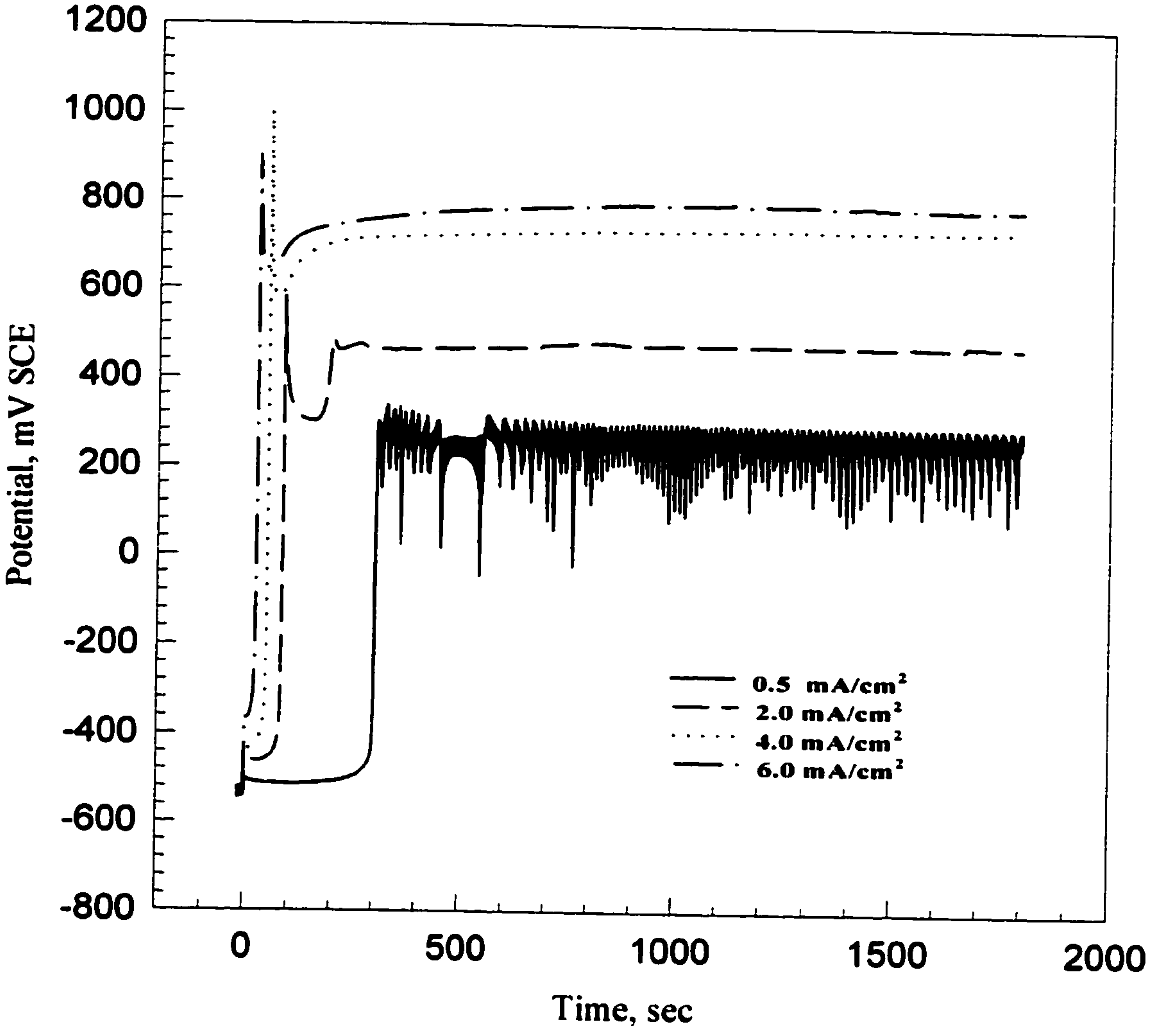


Figure 4.12 Potential vs time at pH 2.0 and T= 45 °C

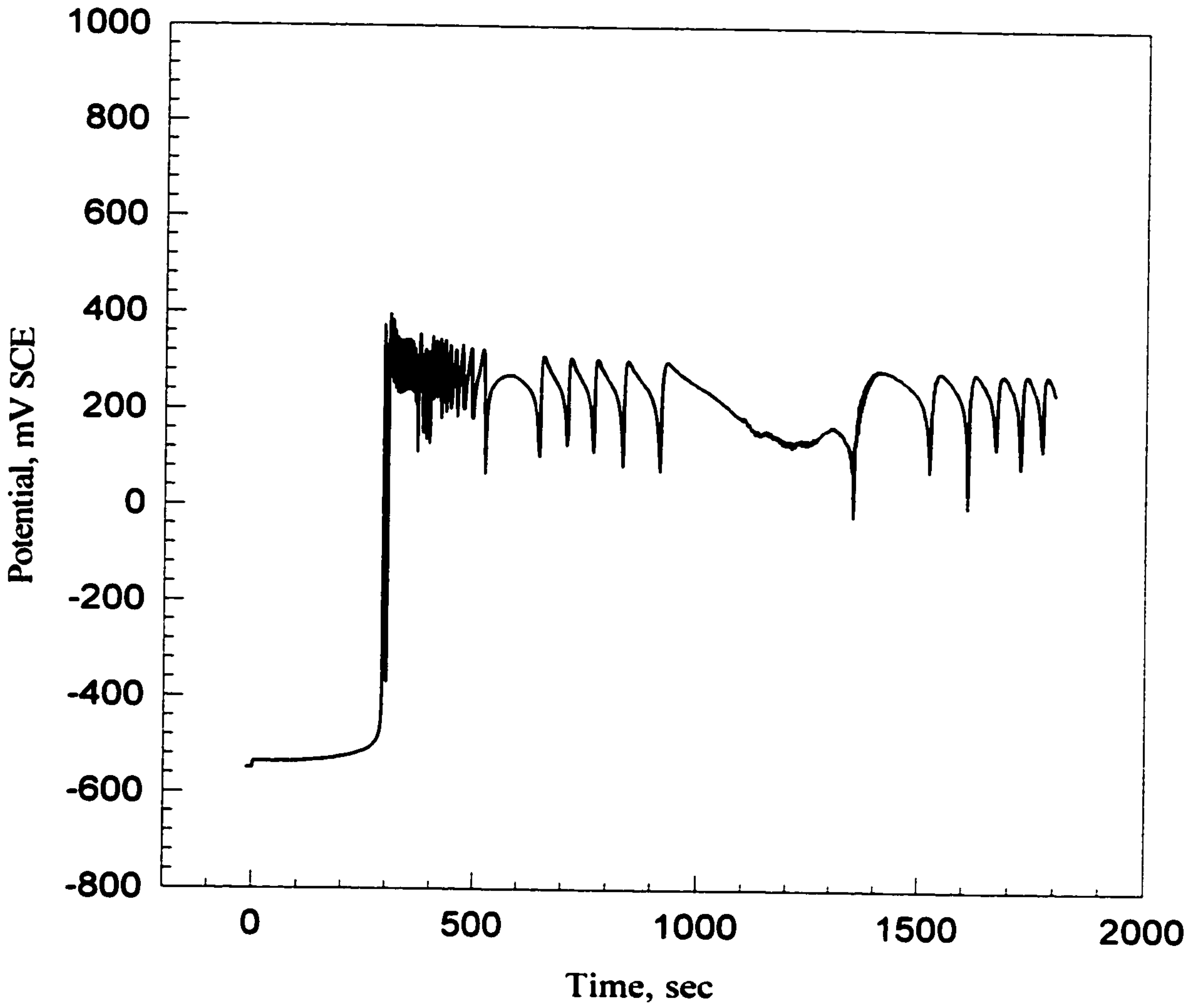


Figure 4.13 Potential vs time at pH 2.0 ,T= 55 °C and current density of 0.5 mA/cm^2

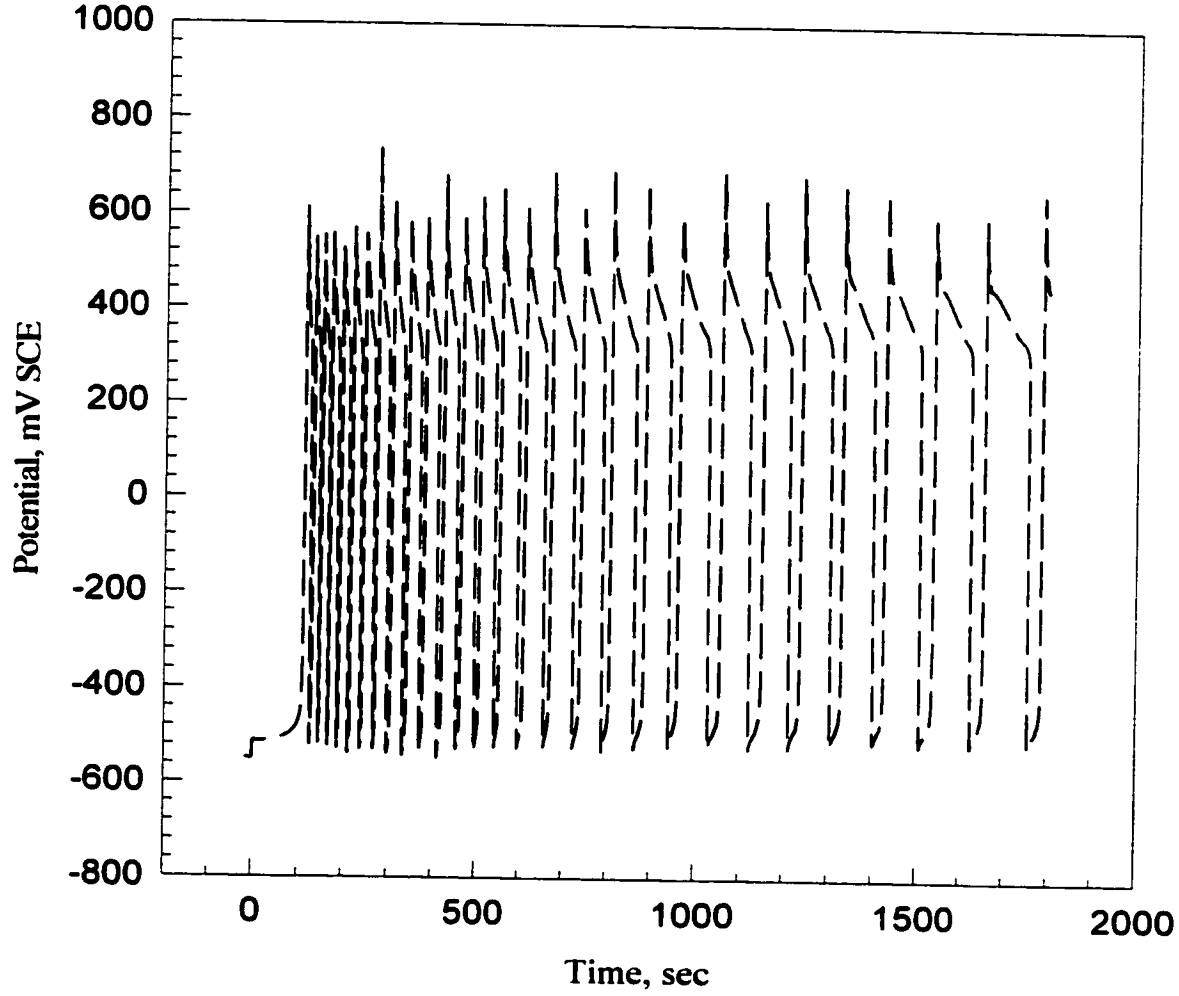


Figure 4.14 Potential vs time at pH 2.0 ,T= 55 °C and current density of 2.0 mA/cm^2

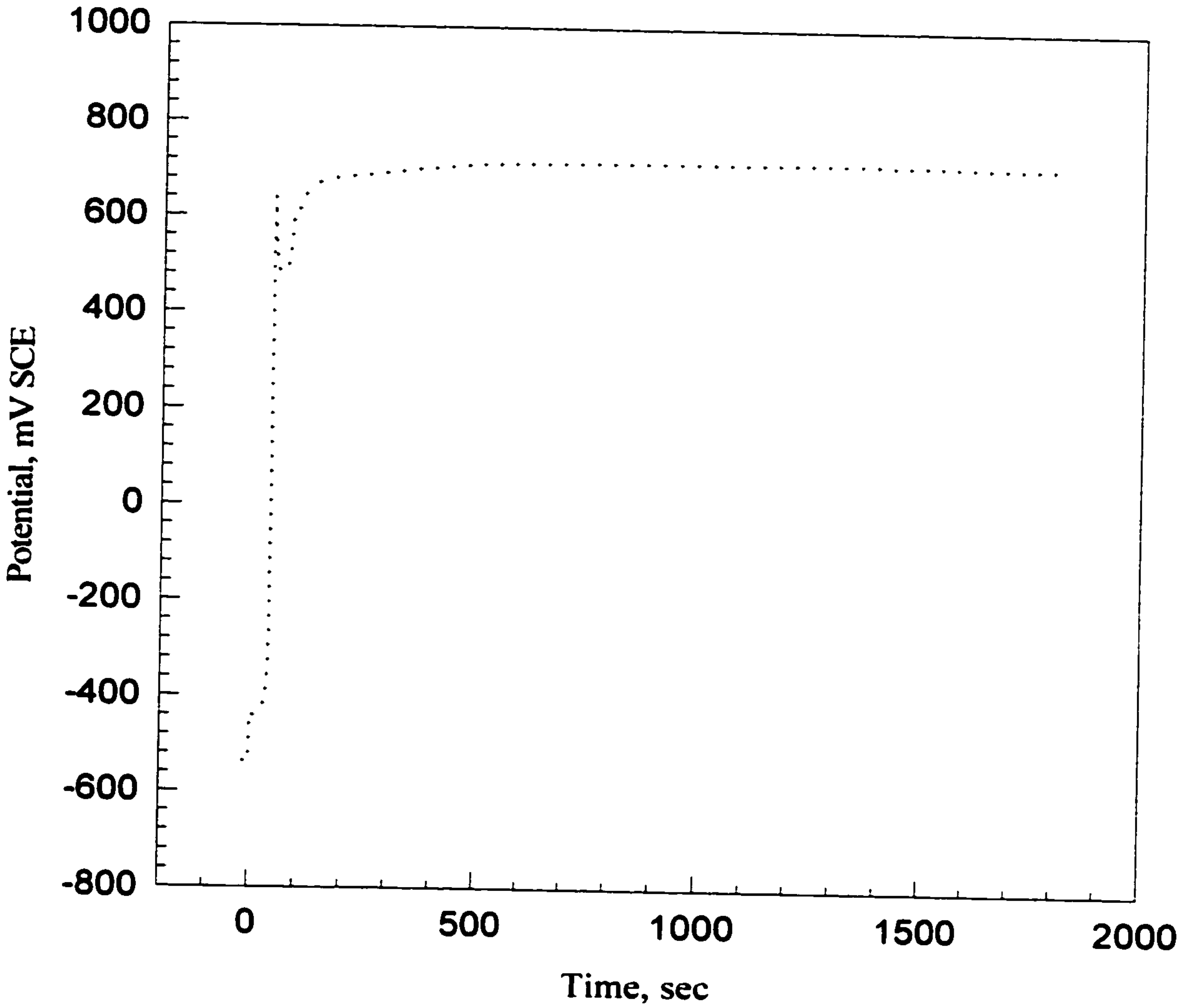


Figure 4.15 Potential vs time at pH 2.0 ,T= 55 °C and current density of 4.0 mA/cm^2

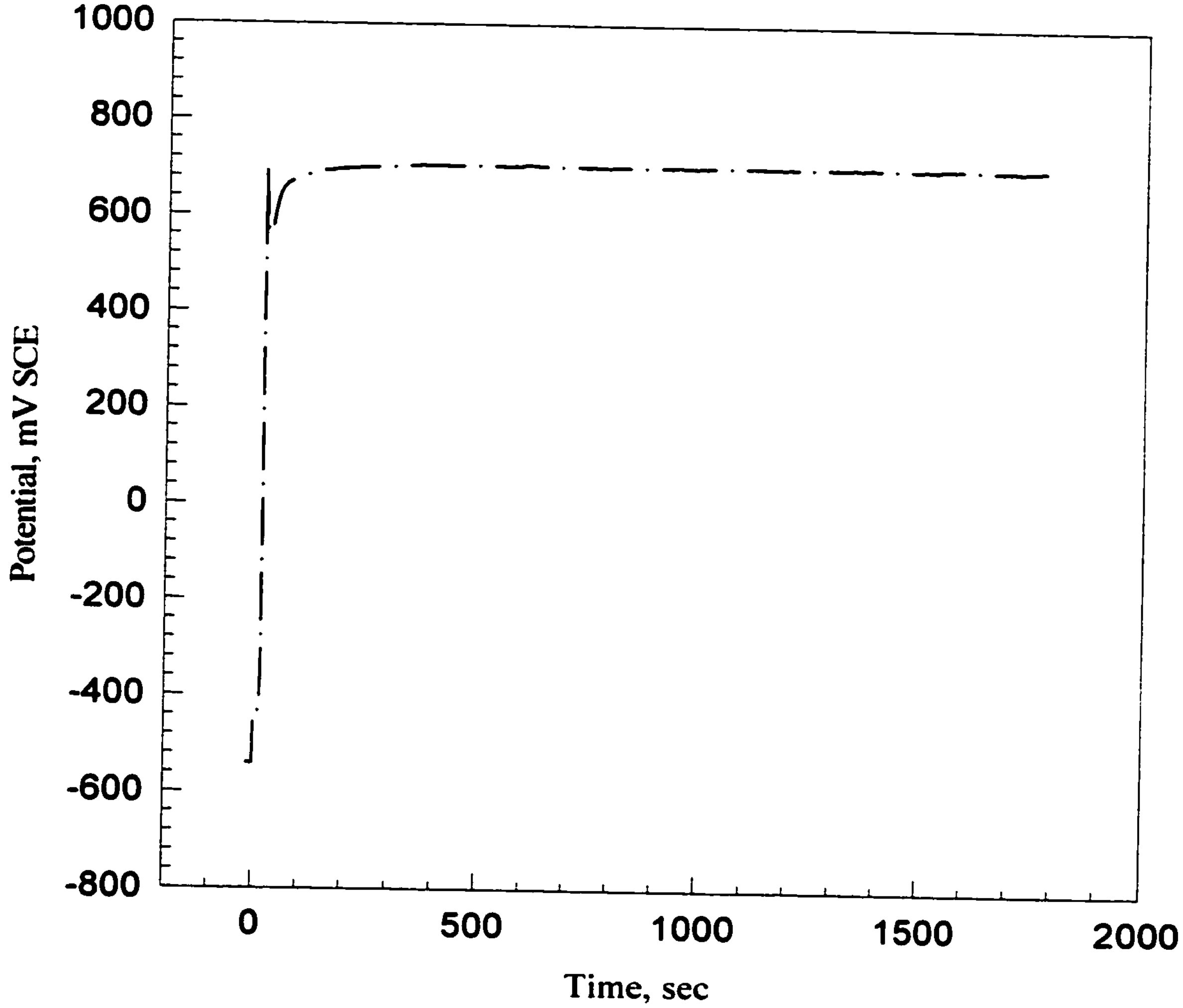


Figure 4.16 Potential vs time at pH 2.0 ,T= 55 °C and current density of 6.0 mA/cm^2

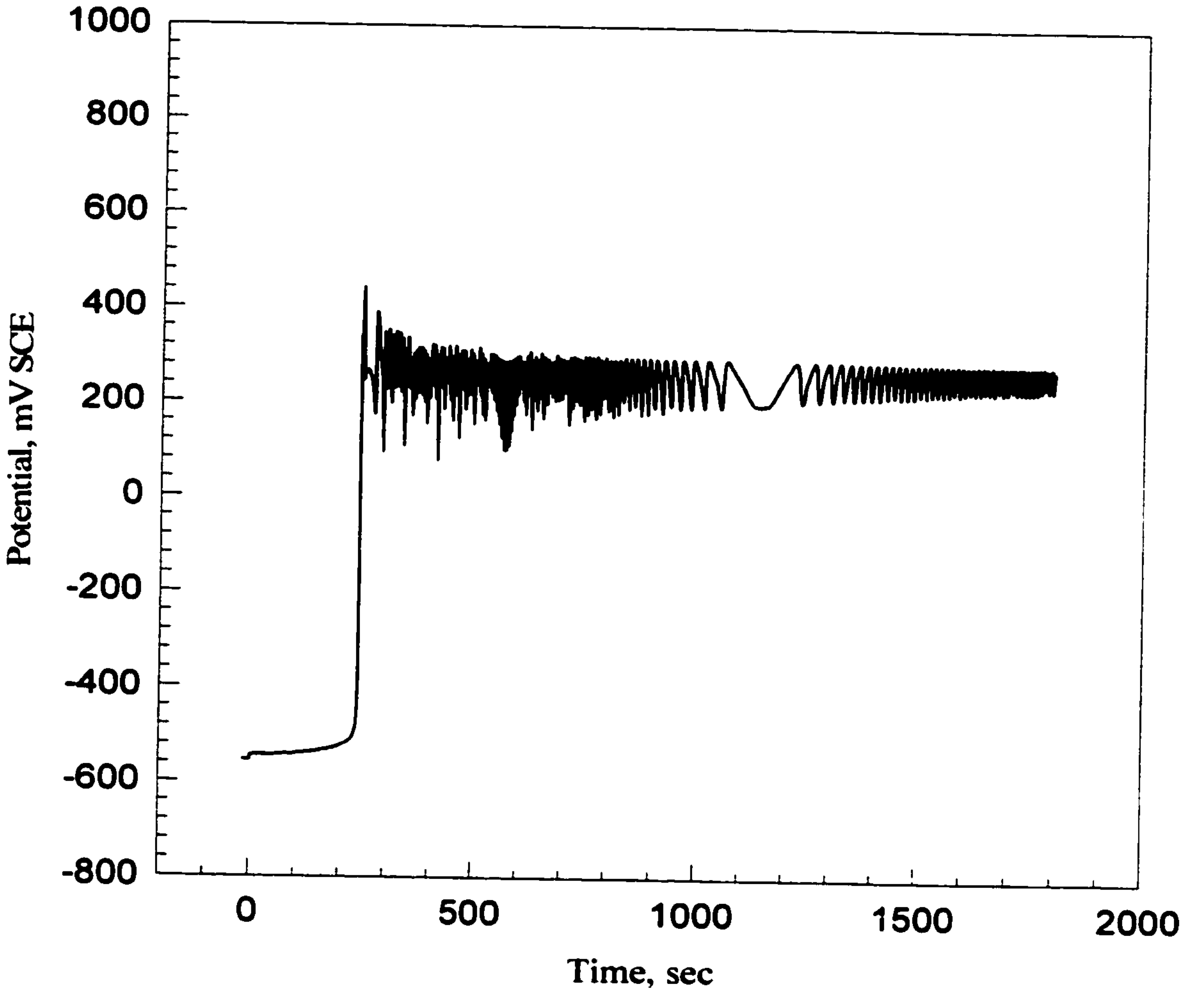


Figure 4.17 Potential vs time at pH 2.0, T= 65 °C and current density of 0.5 mA/cm^2

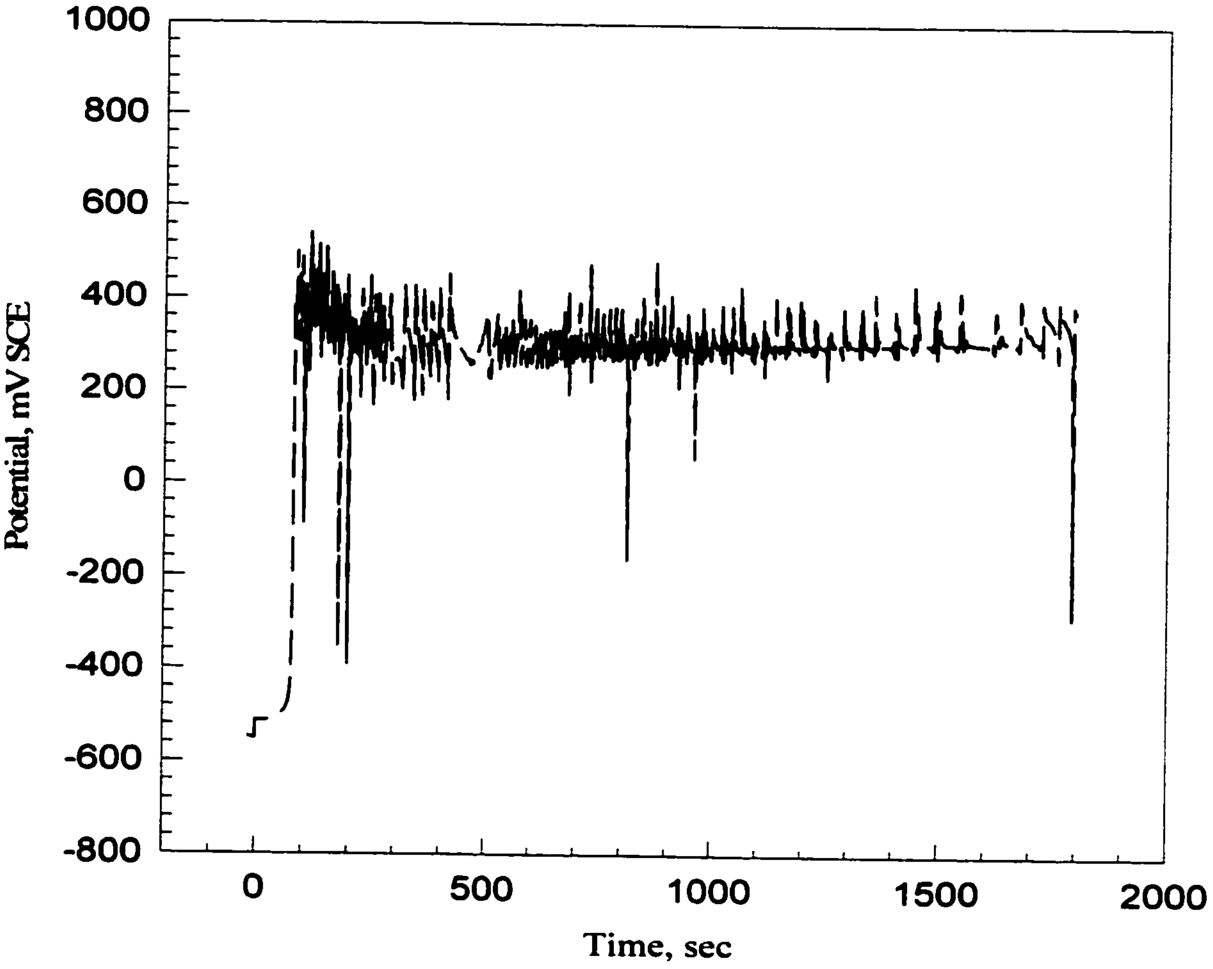


Figure 4.18 Potential vs time at pH 2.0, T= 65 °C and current density of 2.0 mA/cm^2

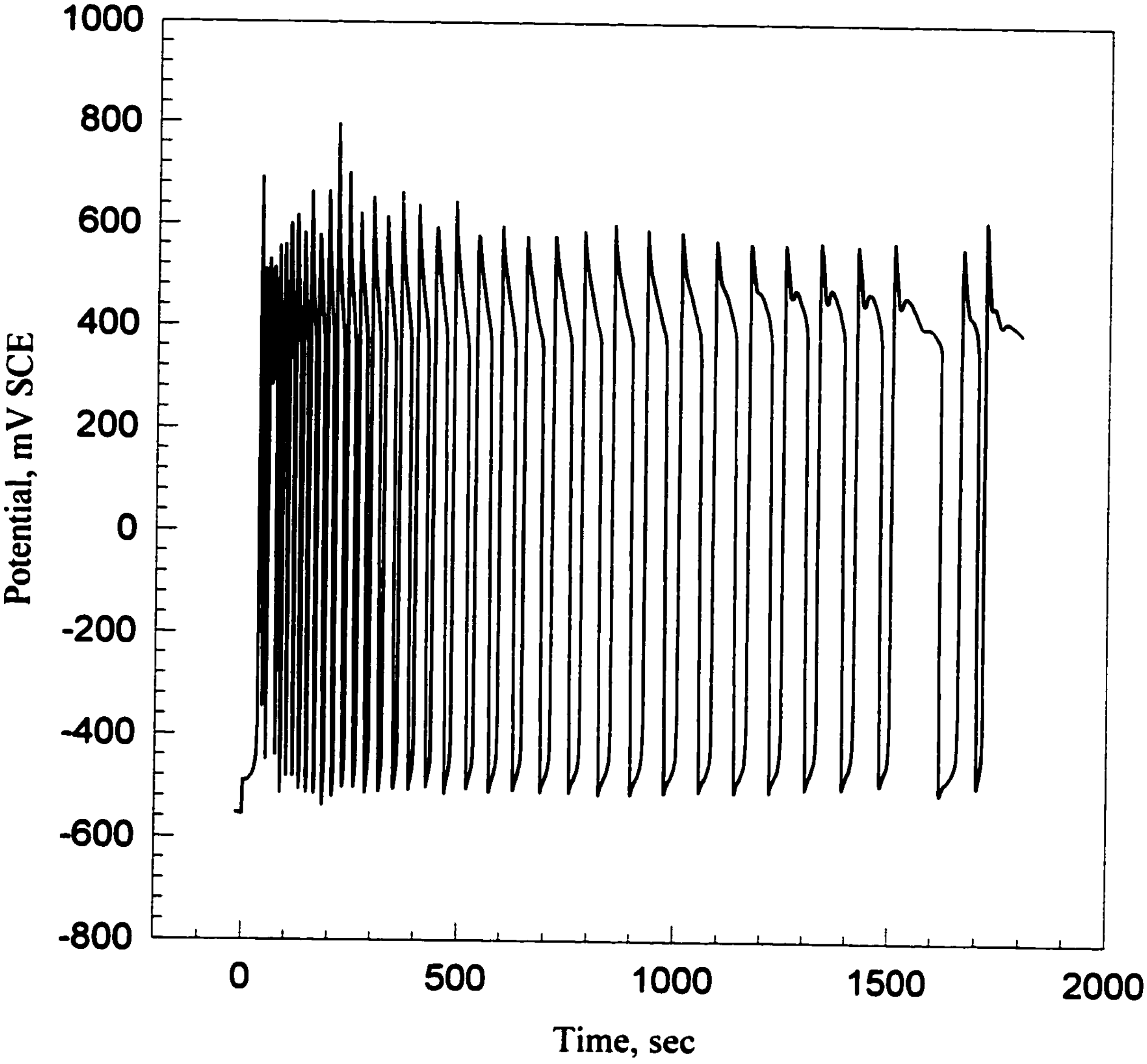


Figure 4.19 Potential vs time at pH 2.0, T= 65 °C and current density of 4.0 mA/cm^2

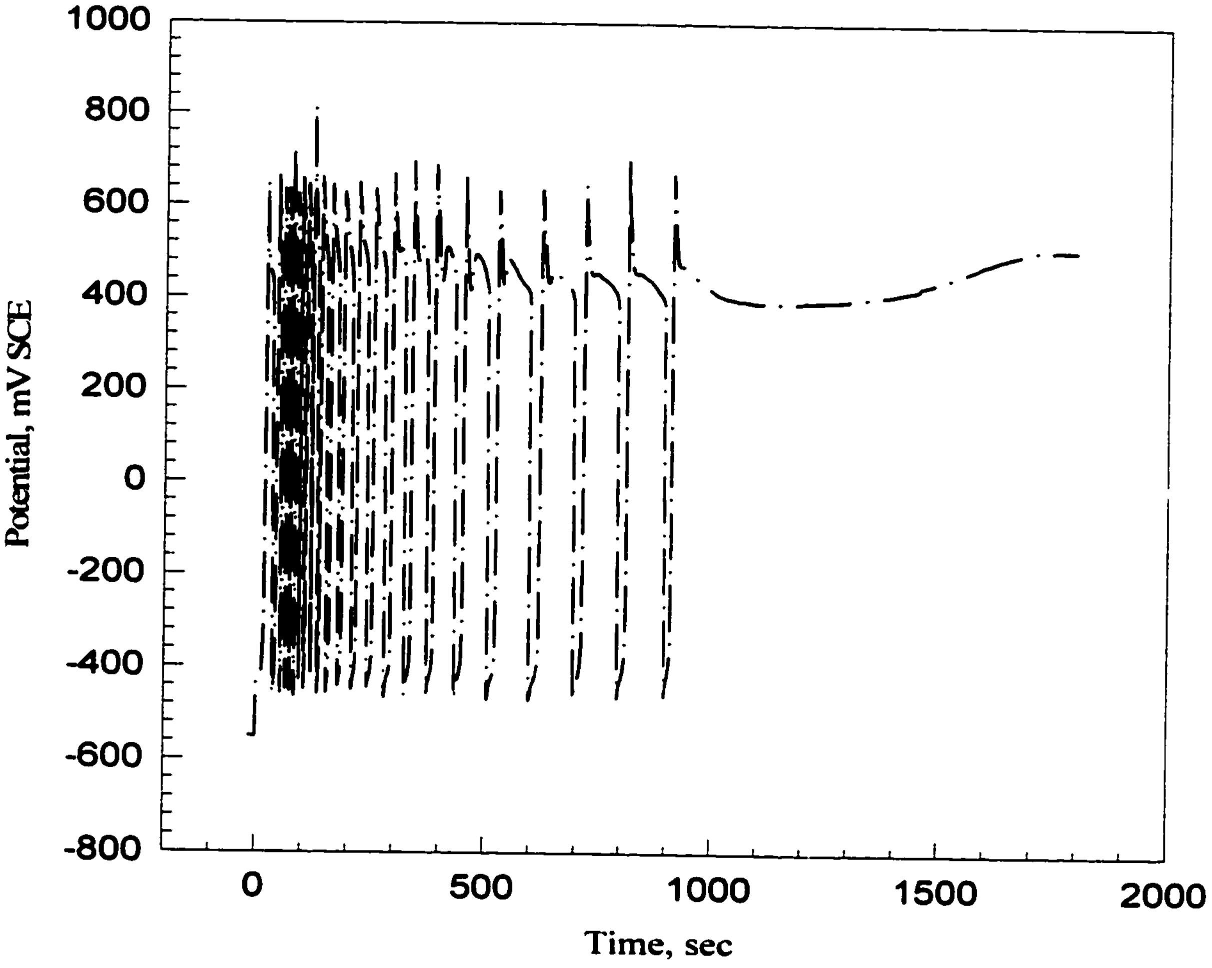


Figure 4.20 Potential vs time at pH 2.0, T= 65 °C and current density of 6.0 mA/cm^2

A better deposition was noticed at higher current density e.g. 2.0 and 4.0 mA/cm^2. However, pinholes and rough surface were observed at 6.0 mA/cm^2 current density. The same observations were made even at higher temperature. Increasing the temperature for the same applied current density resulted into thinner polypyrrole film than those obtained at lower temperature. This is apparently because of higher dissolution rate of steel at high temperature.

A new oscillatory phenomenon was observed only at 0.5 mA/cm^2 current density when the applied temperature either 35 or 45 °C. This observation was also noticed at 55 °C even at current density of 2.0 mA/cm^2. At 65 °C, the oscillations were recorded for the whole range of applied current density. Figures 4.11 through 4.14 and 4.17 through 4.20 show the oscillation in potential. This observation will be discussed later in this chapter.

The oxidation potential increases with increased current density as mentioned earlier for room temperature. However, the induction time decreased with increasing the current density for the whole range of temperatures. The induction time versus current density plots are shown in Figures 4.21 through 4.24. It seems that the temperature does not have significant effect on the induction time. A linear expression of the data can be put in the following form for different temperatures at pH 2.0.

For T=35°C

$$\ln\tau = 5.69 - 1.07\ln i \qquad (4)$$

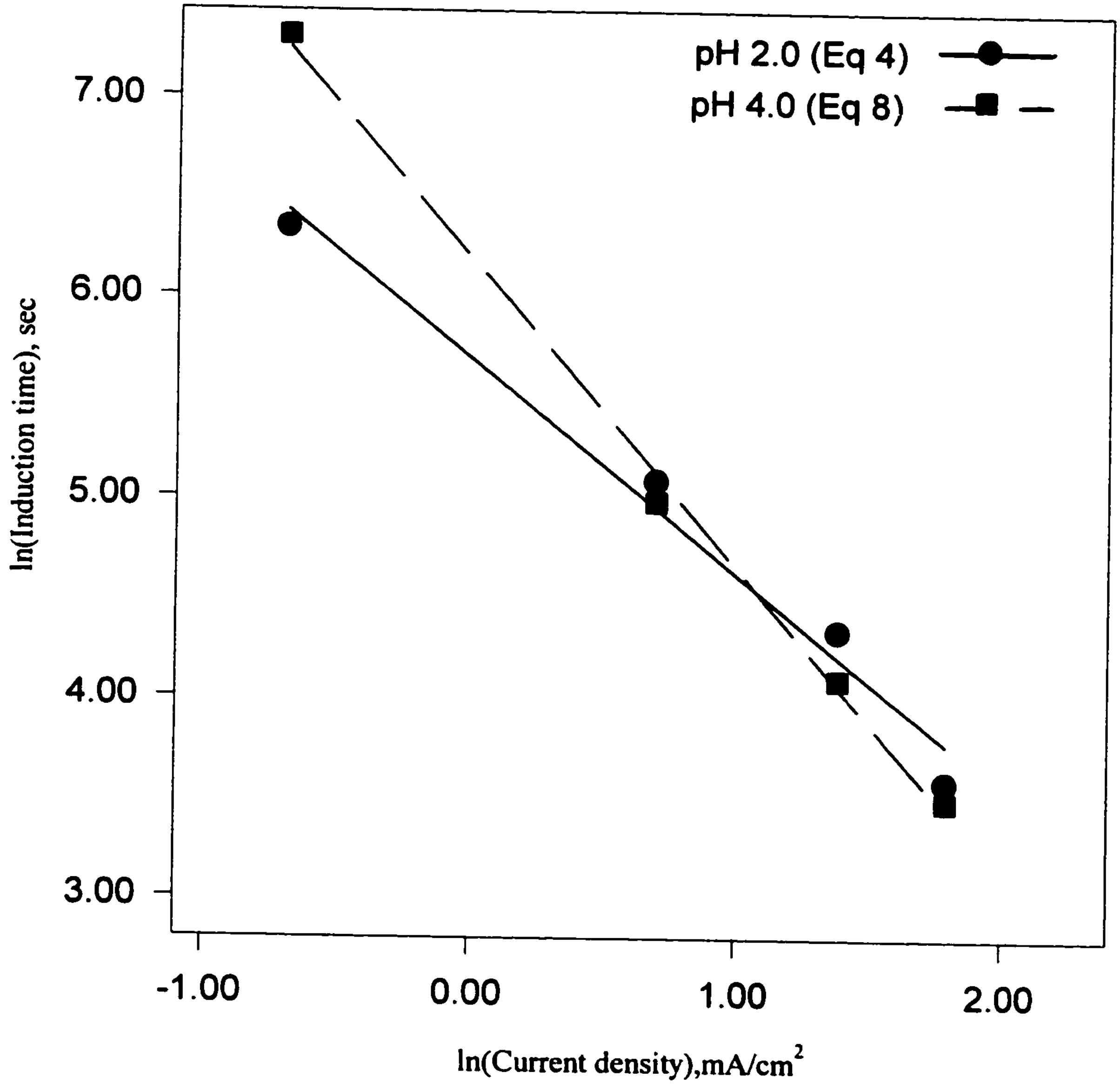


Figure 4.21 Dependence of induction time on the applied current density in acidic media (T=35 °C)

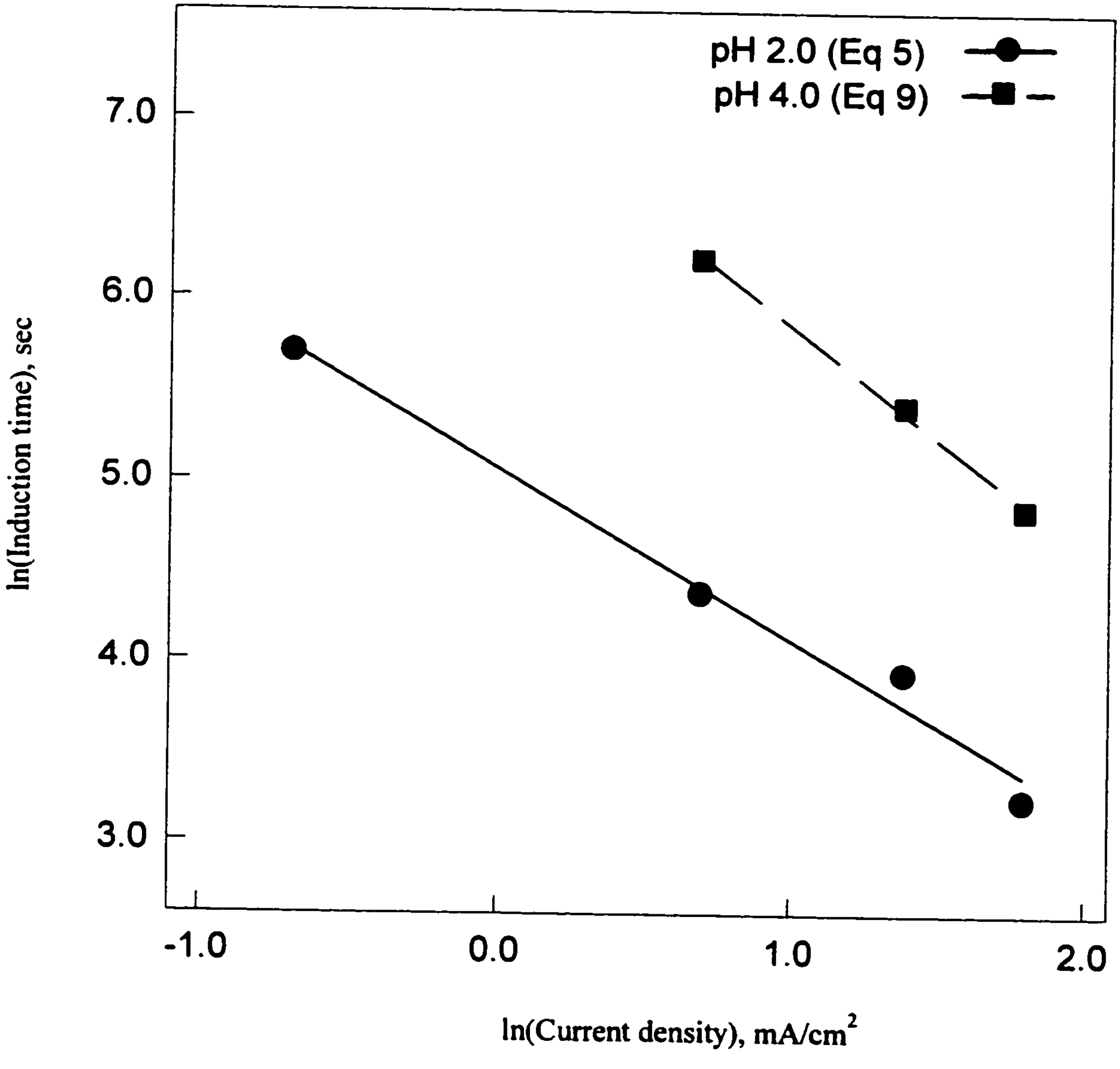


Figure 4.22 Dependence of induction time on the applied current density in acidic media (T=45 °C)

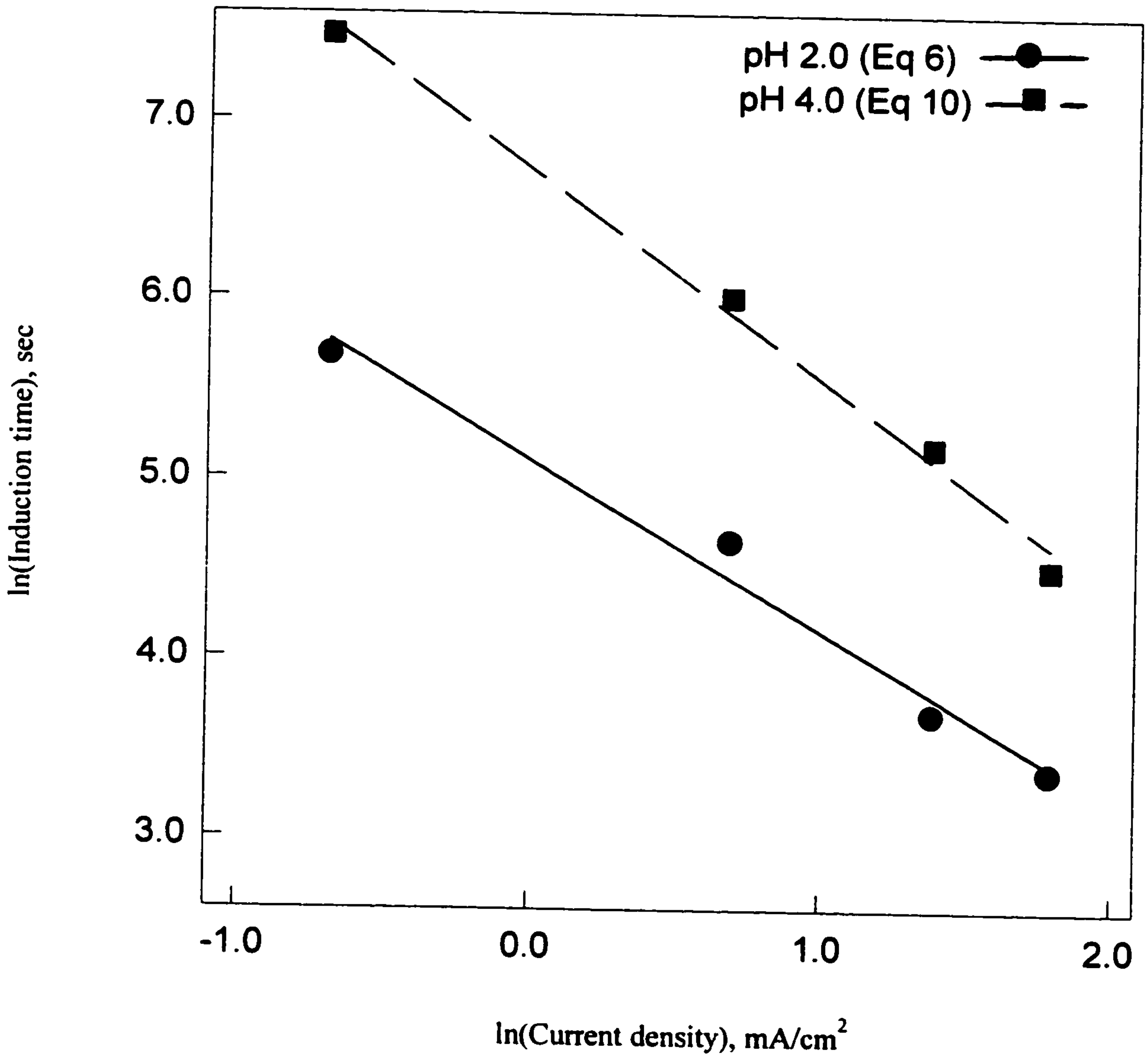


Figure 4.23 Dependence of induction time on the applied current density in acidic media (T=55 °C)

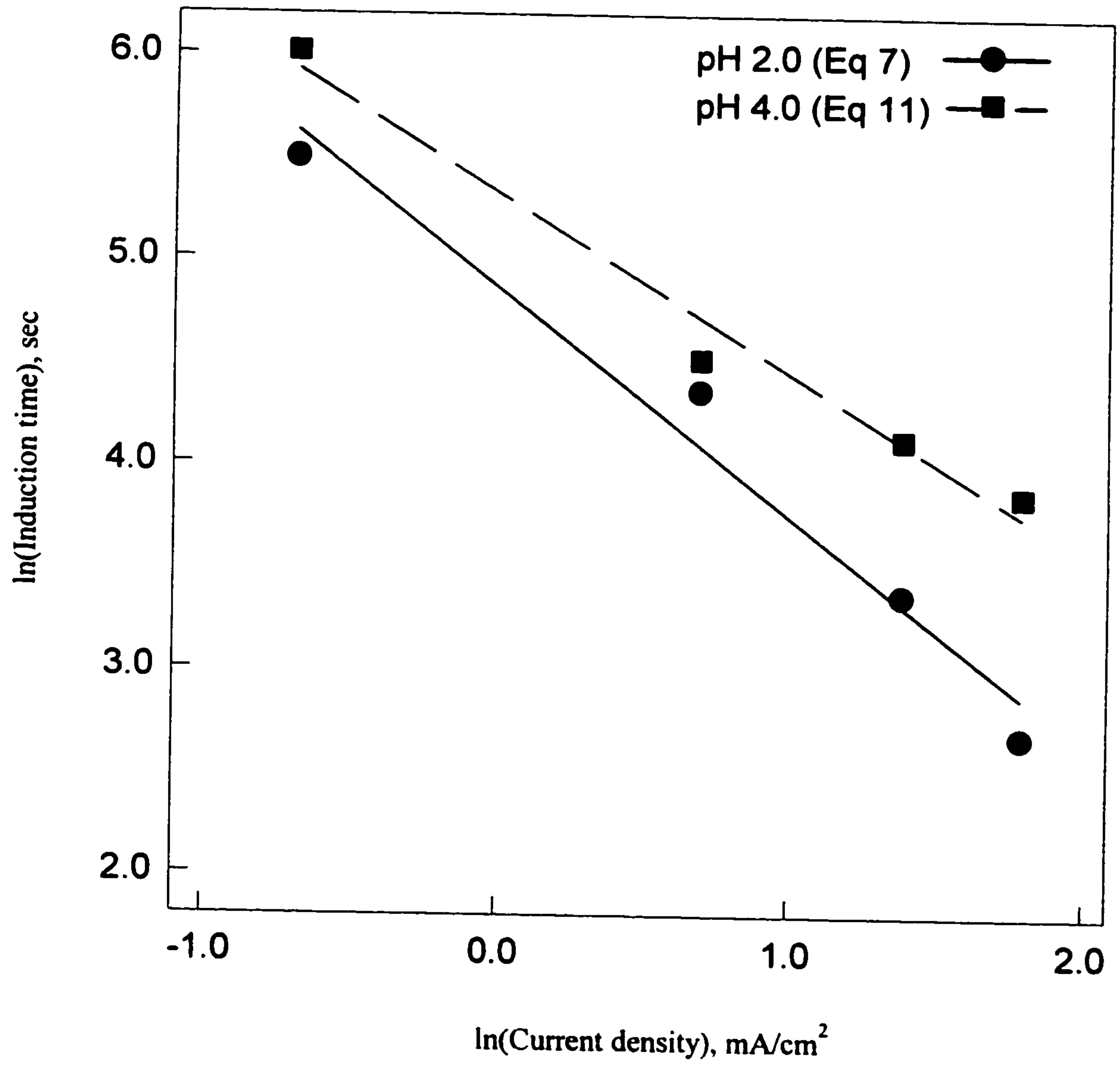


Figure 4.24 Dependence of induction time on the applied current density in acidic media (T=65 °C)

For T=45°C

$$\ln\tau = 5.10 - 0.95 \mathrm{n}i \tag{5}$$

For T=55°C

$$\ln\tau = 5.10 - 0.95 \mathrm{n}i \tag{6}$$

For T=65°C

$$\ln\tau = 4.85 - 1.10 \mathrm{n}i \tag{7}$$

Figures 4.25 through 4.28 show the change of charge consumed during the induction period with applied current density for the acidic medium. The passivation charge decreased with increasing current density for all temperatures. A lesser amount of charge was required to passivate the surface at high current density and it takes longer time to passivate the surface at lower current density.

Potential-time curves of polypyrrole coating at pH 4.0 and higher temperature (i.e. 35, 45, 55 and 65 °C) are shown in Figures 4.29 through 4.35. The curves are similar as those obtained at 25 °C. No good polypyrrole film was formed at current density of 0.5 mA/cm^2 even at high temperature. The effect of increasing current density is also similar at higher temperature. Increasing the current density gives more adherent polypyrrole film but the surface becomes rough when the applied current density was 6.0 mA/cm^2. The film surfaces obtained at pH 4.0 were usually smoother than those obtained at pH 2.0. For the same applied current density, increasing the temperature would result into smooth but thin polypyrrole deposition. This may be due to high dissolution rate and low polymerization rate at high temperature. However, the oscillatory phenomenon which will be explained later was also observed

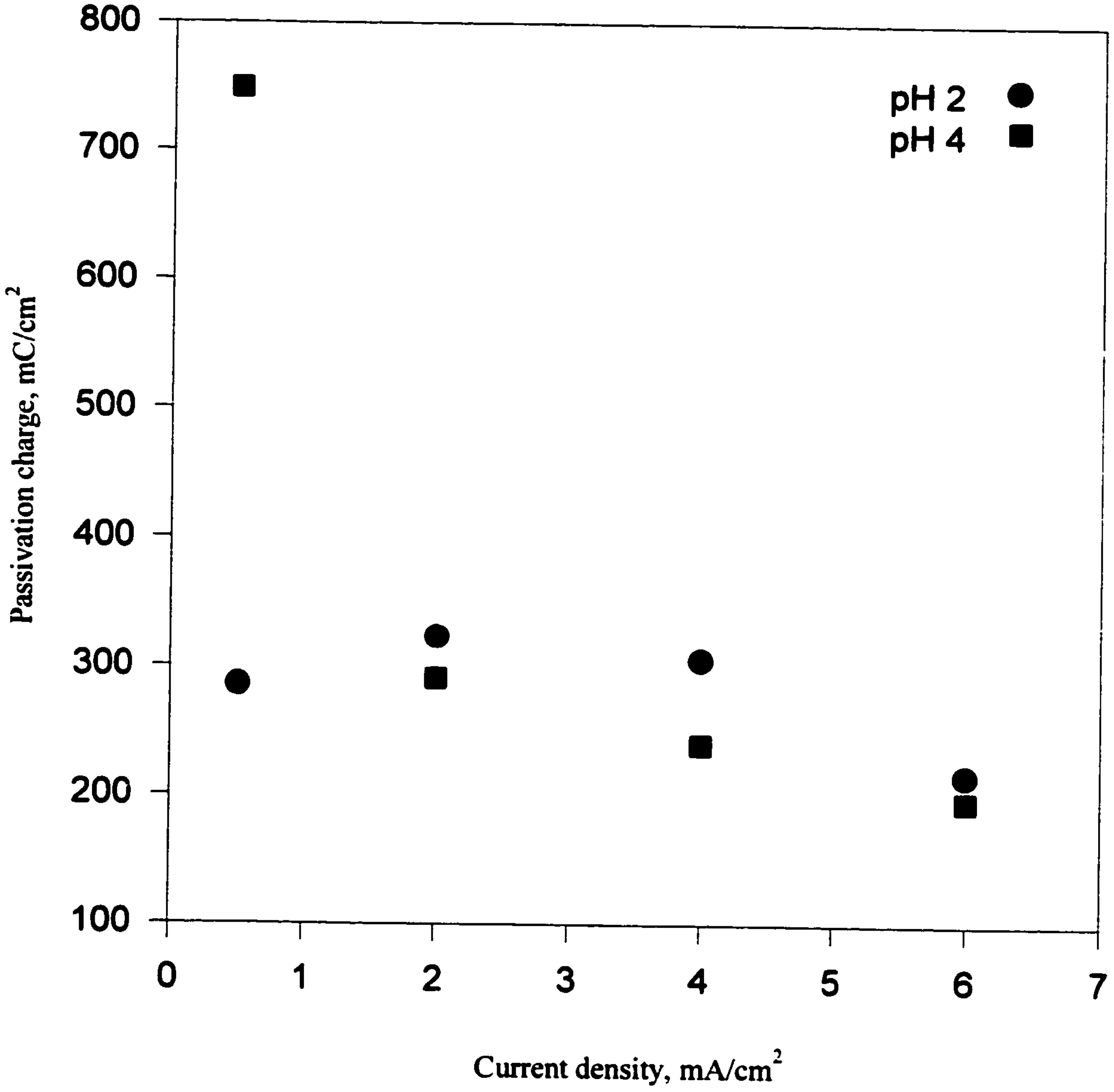


Figure 4.25 Passivation charge vs current density for acidic media at T=35°C

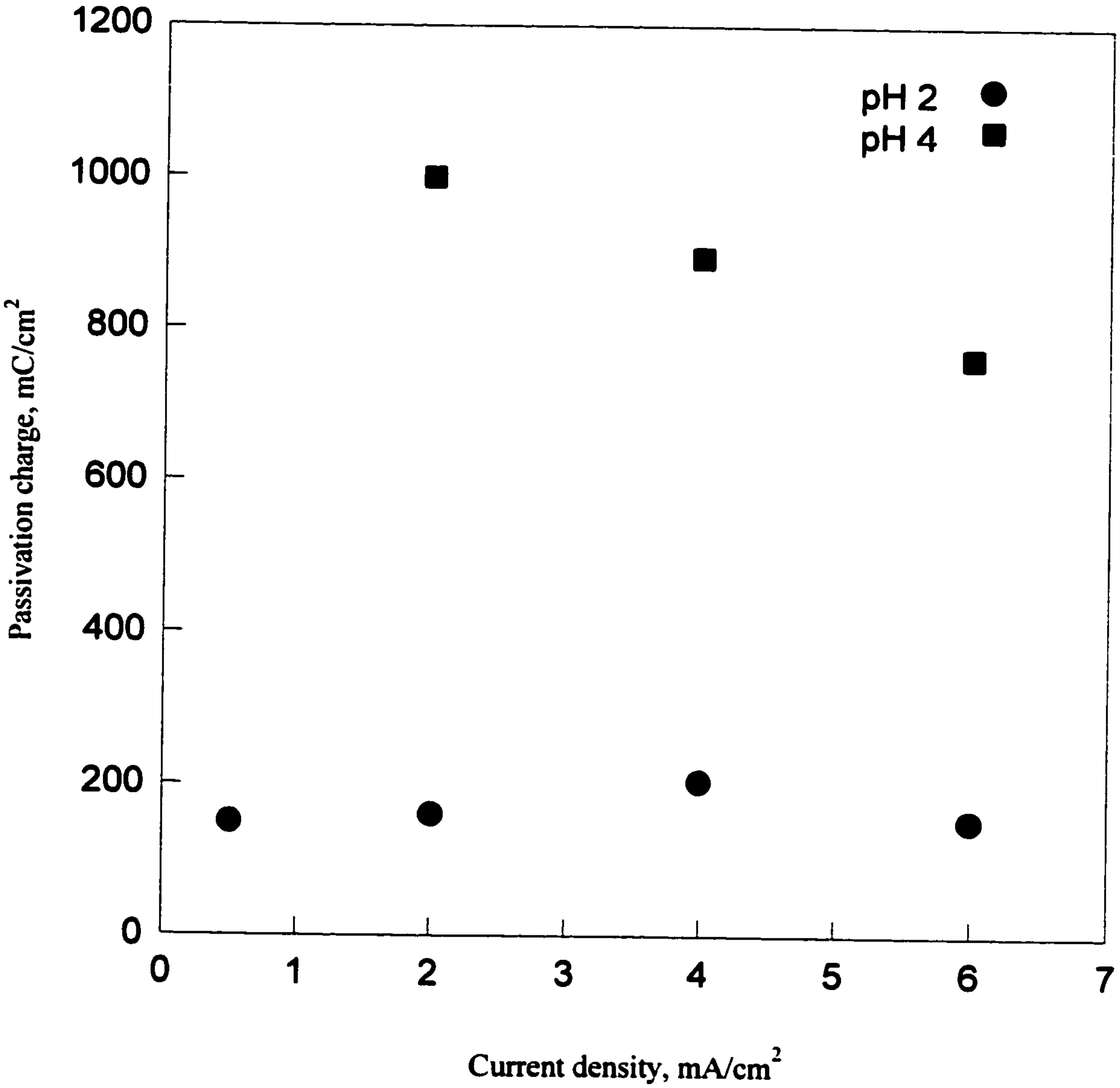


Figure 4.26 Passivation charge vs current density for acidic media at T=45°C

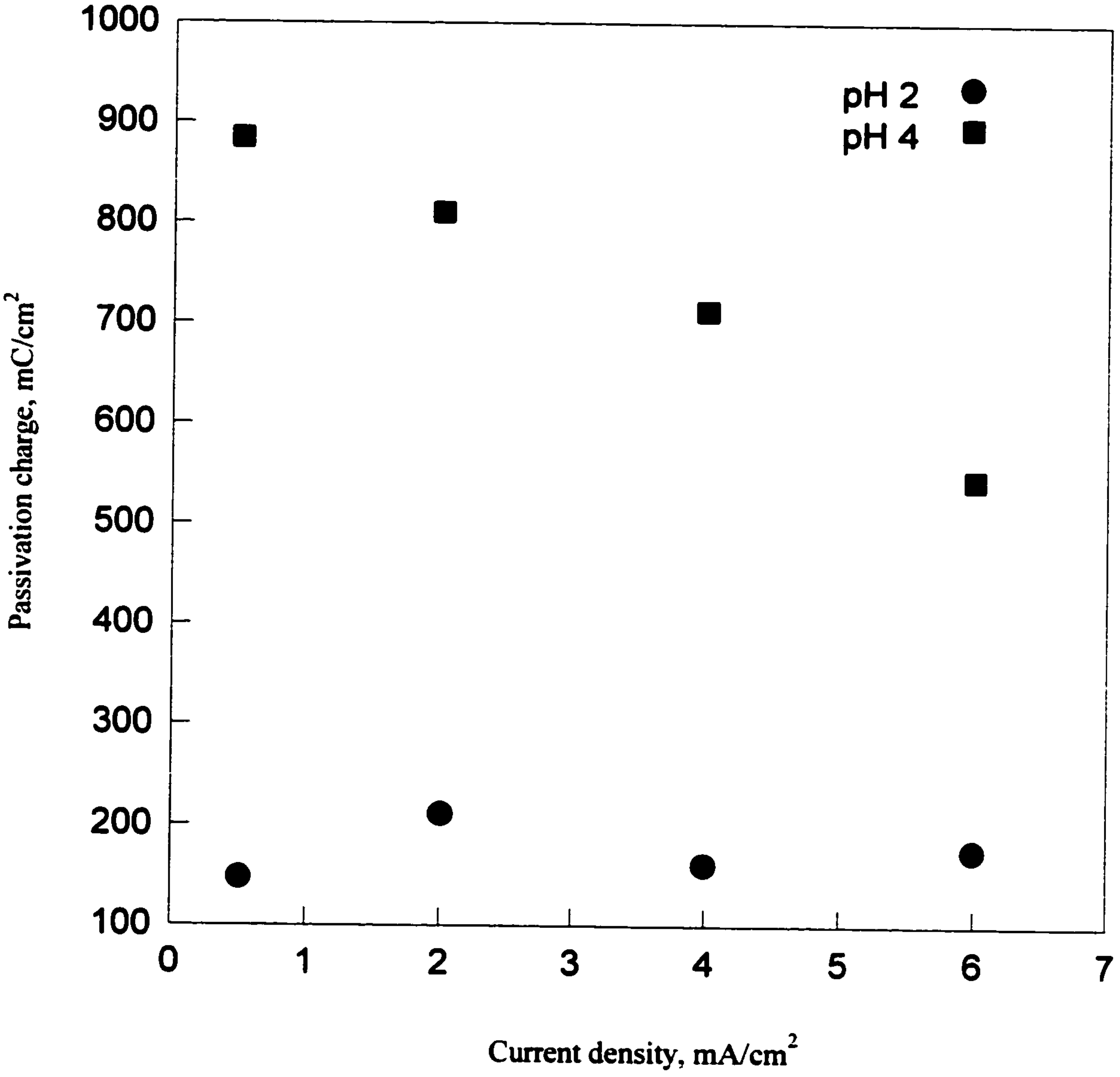


Figure 4.27 Passivation charge vs current density for acidic media at T=55 °C

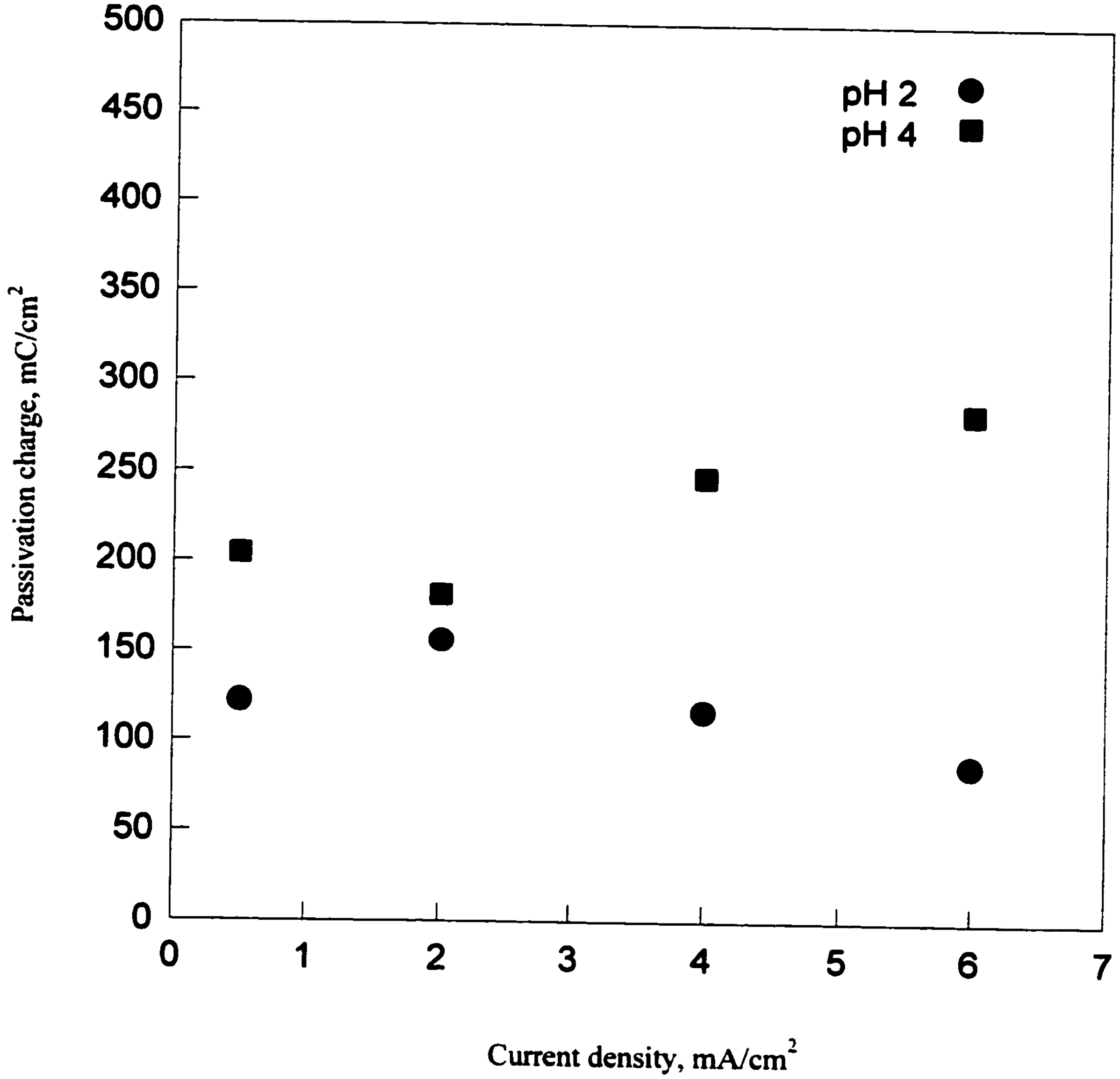


Figure 4.28 Passivation charge vs current density for acidic media at T=65 °C

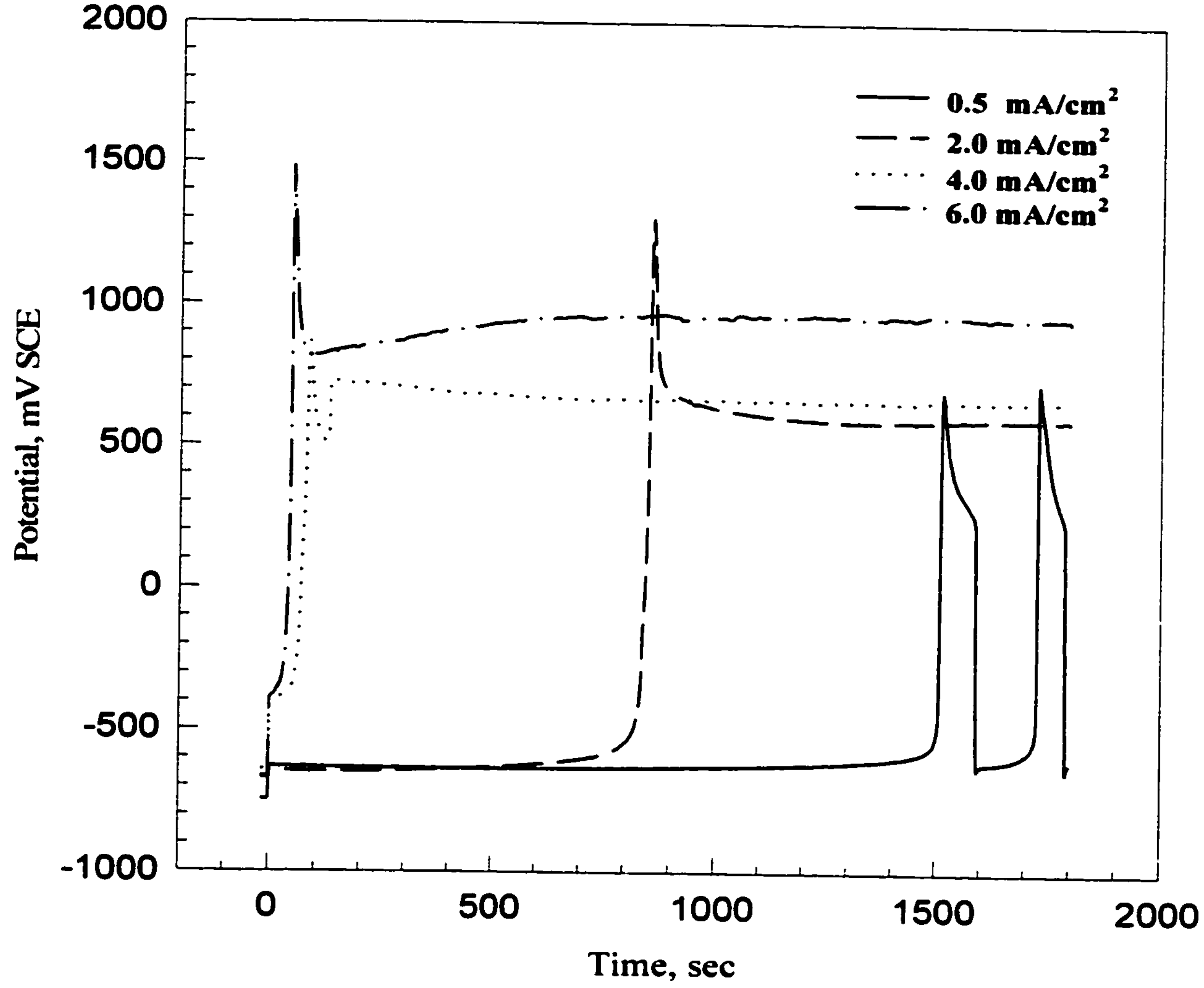


Figure 4.29 Potential vs time at pH 4.0 and T= 35 °C

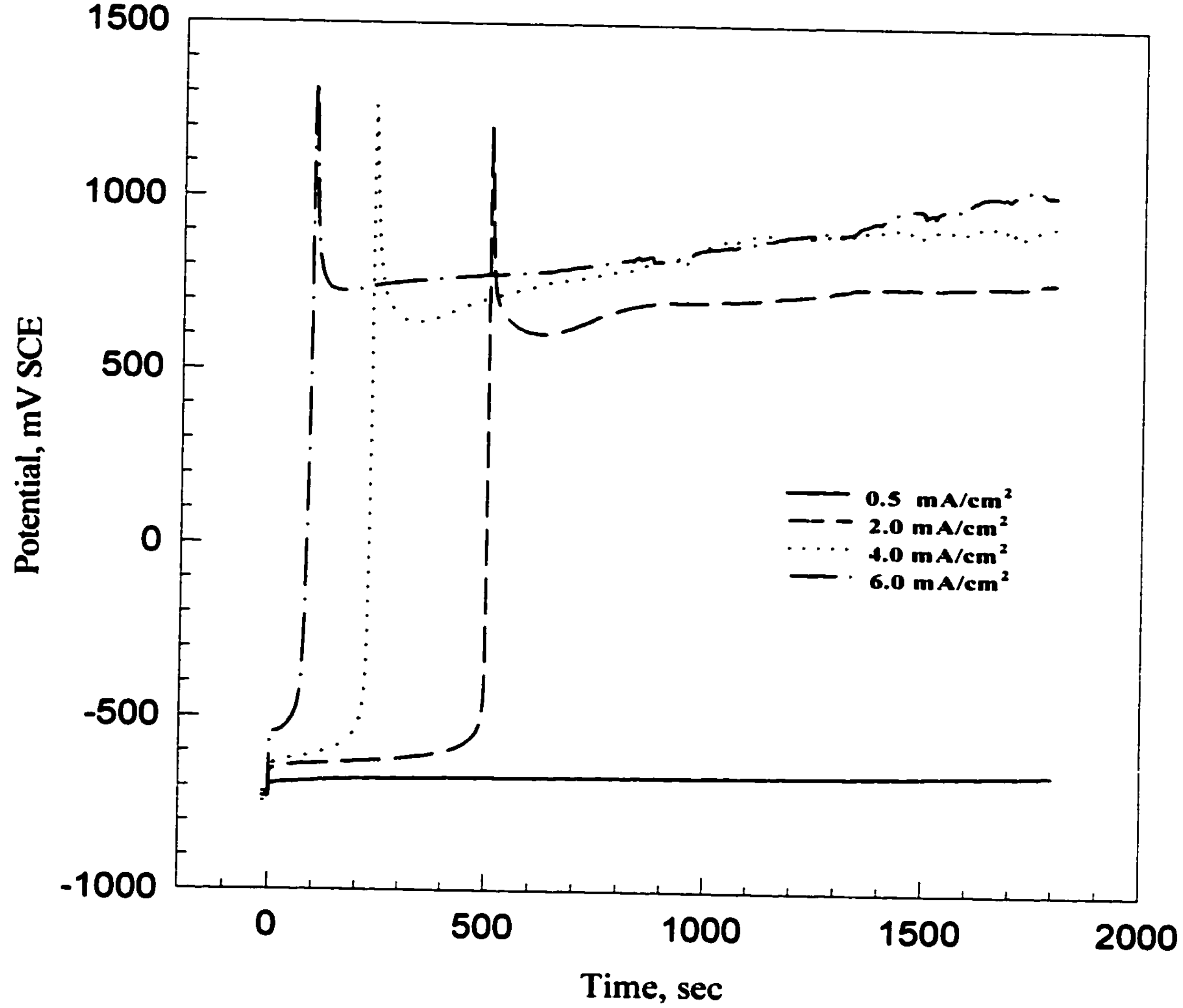


Figure 4.30 Potential vs time at pH 4.0 and T= 45 °C

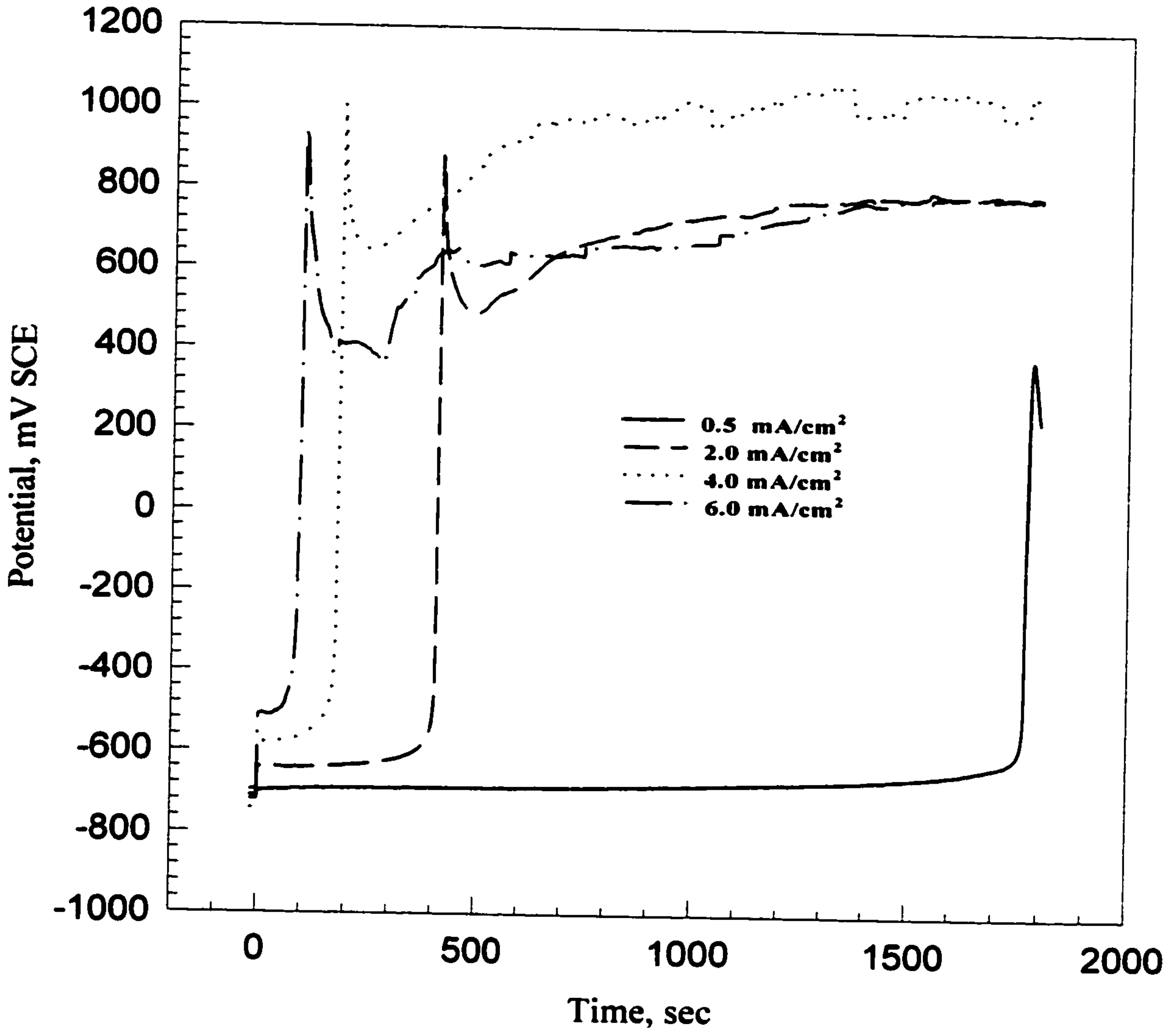


Figure 4.31 Potential vs time at pH 4.0 and T= 55 °C

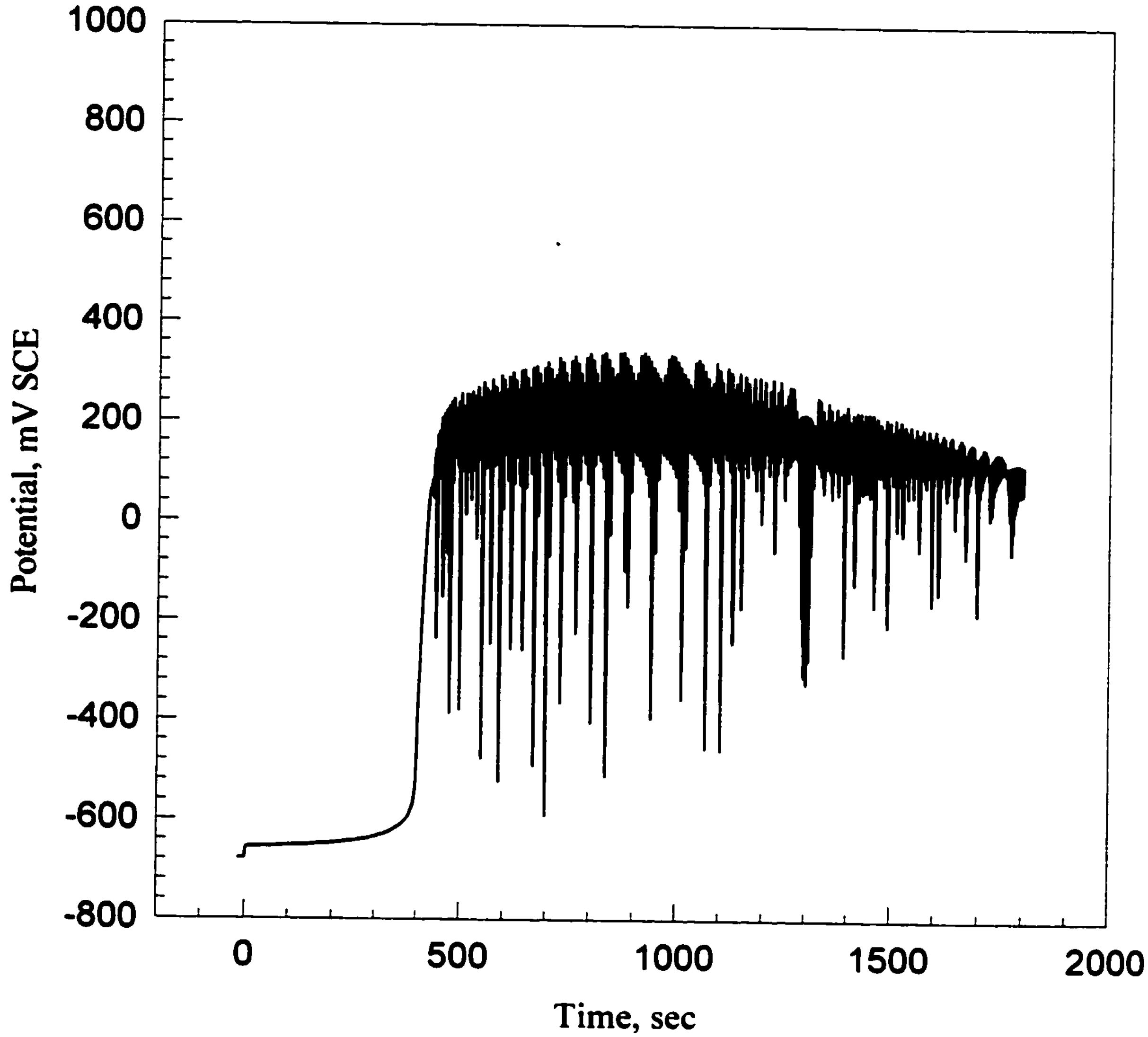


Figure 4.32 Potential vs time at pH 4.0, T= 65 °C and current density of 0.5 mA/cm^2

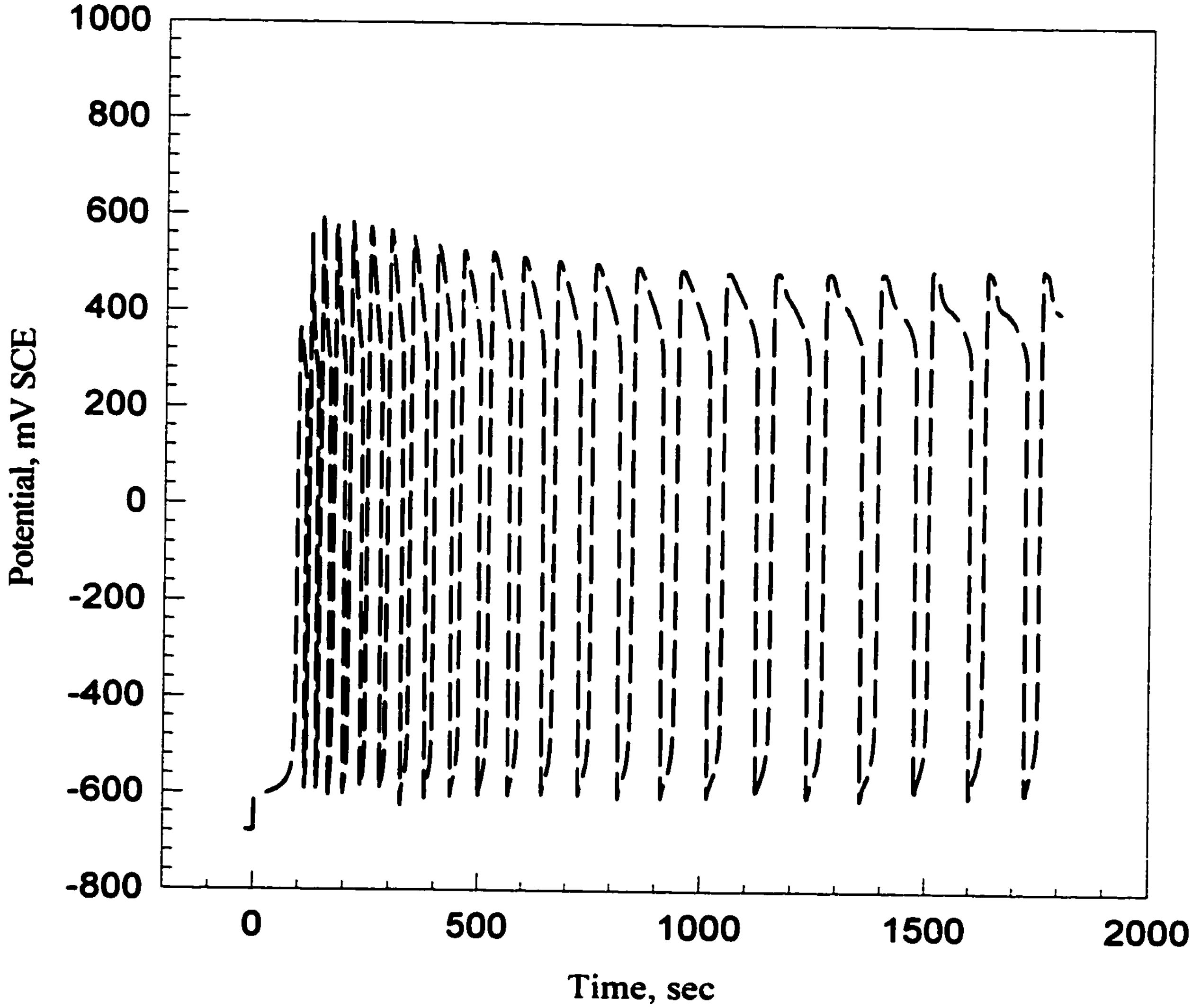


Figure 4.33 Potential vs time at pH 4.0, T= 65 °C and current density of 2.0 mA/cm^2

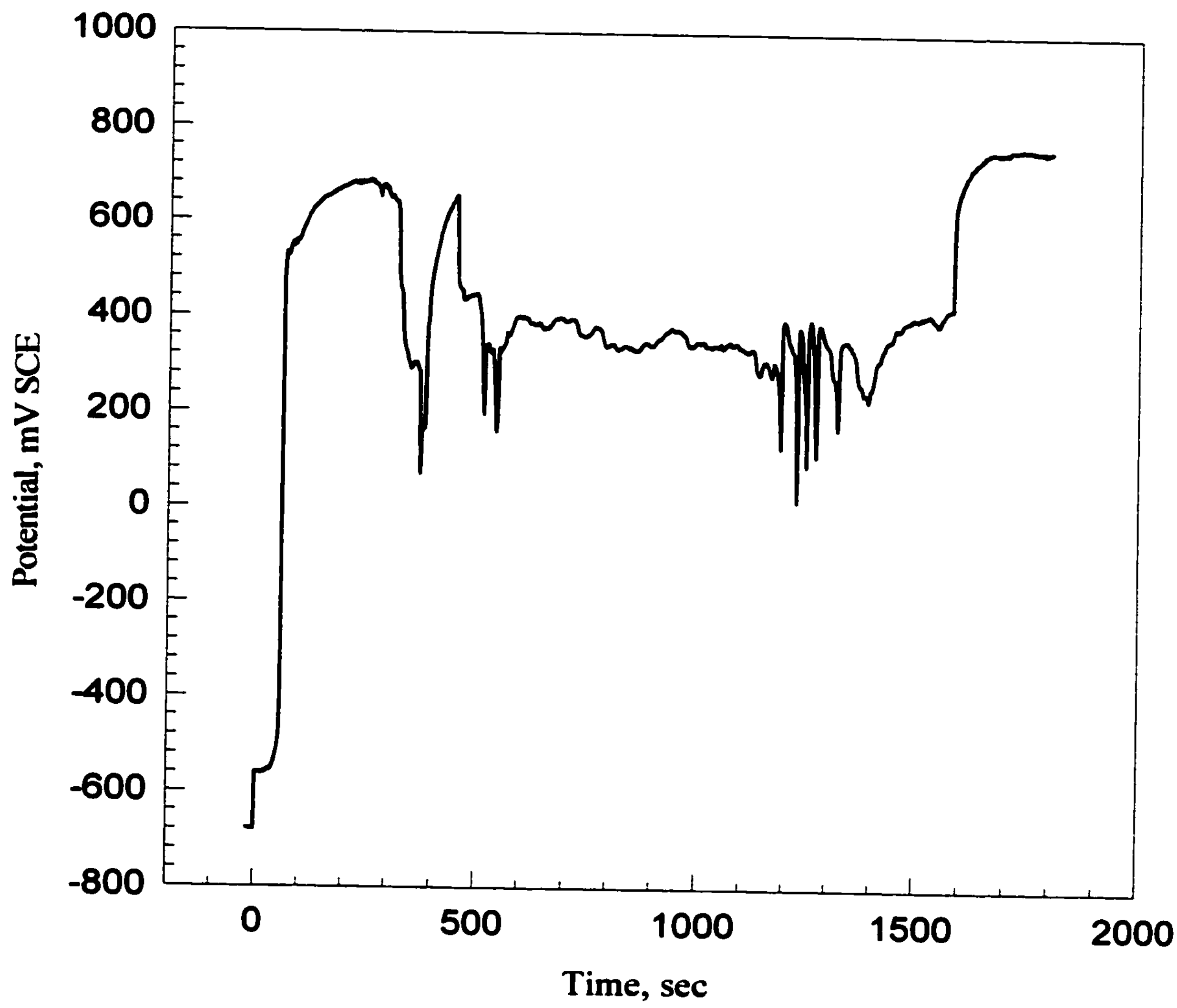


Figure 4.34 Potential vs time at pH 4.0, T= 65 °C and current density of 4.0 mA/cm^2

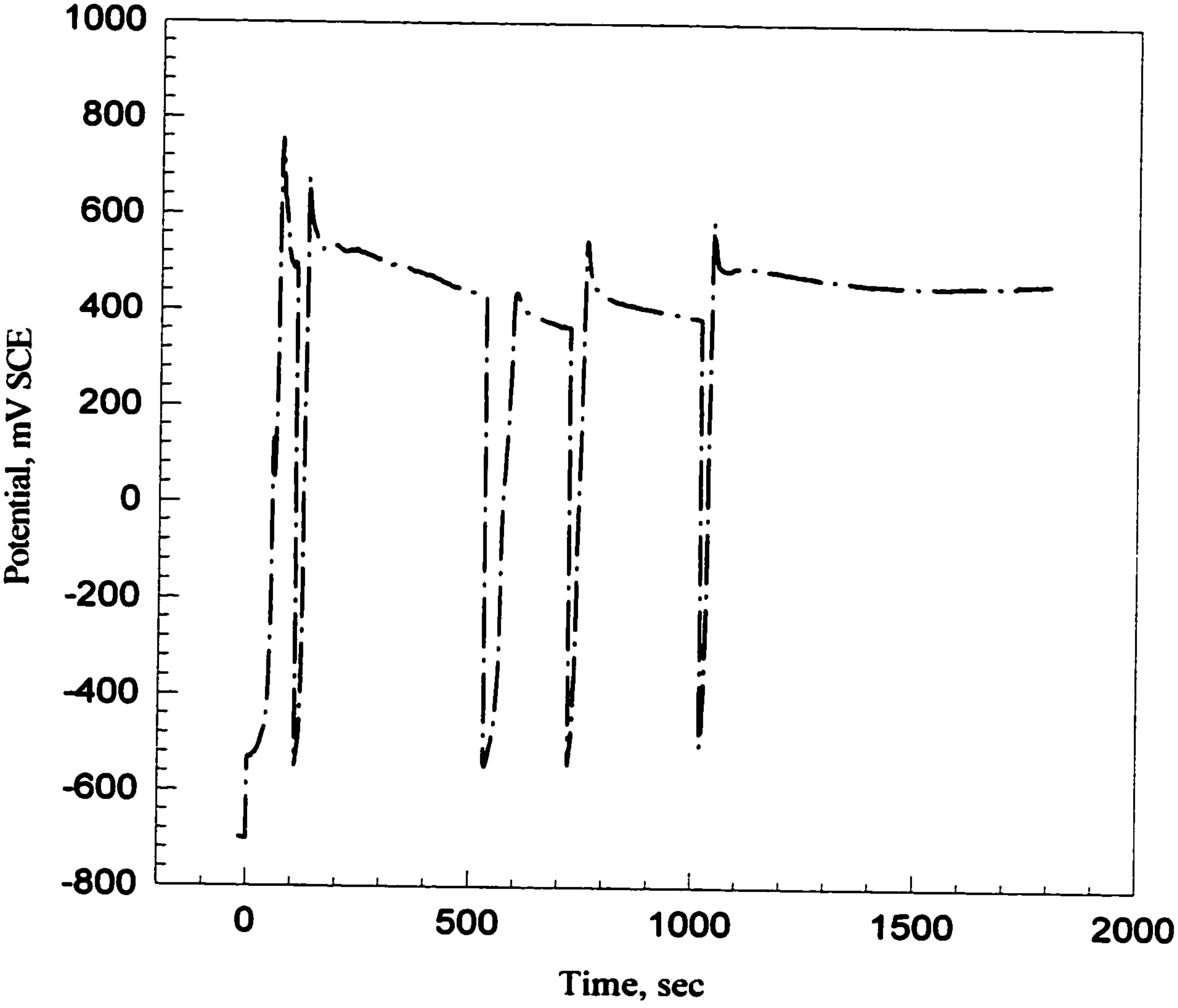


Figure 4.35 Potential vs time at pH 4.0, T= 65 °C and current density of 6.0 mA/cm^2

when the applied temperature was 65 °C for the whole range of current density.

The induction time at pH 4.0 is generally higher than the one obtained at pH 2.0 for the same temperature. The dissolution rate of iron is low at high pH with slow reaction. So, more time is required to get sufficient passivation as pH increased. Increasing the temperature did not have significant effect on the induction time especially at high current density. For example, the induction time was 55 seconds at 35 °C while it was 60 seconds at 65 °C for the same applied current density (4 mA/cm^2). The induction time and passivation charges are plotted against current density in Figures 4.21 through 4.24 and Figures 4.25 through 4.28 respectively. For each reaction medium, a linear relationship is obtained, which can be expressed by the following equations:

For T=35°C

$$\ln\tau = 6.19 - 1.53\ln i \tag{8}$$

For T=45°C

$$\ln\tau = 7.0 - 1.23\ln i \tag{9}$$

For T=55°C

$$\ln\tau = 6.71 - 1.20\ln i \tag{10}$$

For T=65°C

$$\ln\tau = 5.32 - 0.87\ln i \tag{11}$$

The oxidation potential has tendency to increase with time especially at 45 and 55 °C for high current density, e.g. 2.0, 4.0 and 6.0 mA/cm^2 that may be due to low conductivity of polypyrrole film.

C. Description of the oscillatory phenomenon

Oscillation in electrode potential were observed during the electropolymerization of pyrrole on mild steel at higher temperatures. At 25 °C, no oscillation was recorded for whole range of pH and current densities. At 35 °C and 45 °C, this oscillatory phenomenon was observed at the lowest current density 0.5 mA/cm^2 only at pH 2.0. At 55 °C, the oscillation appeared also at current density of 2.0 mA/cm^2 at pH 2.0. At 65 °C the oscillation occurred in acidic medium of pH 2.0 and 4.0 for the four applied values of current densities. These oscillations are shown in Figures 4.11-4.14, Figures 4.17 through 4.20 and Figures 4.32 through 4.35. Petitjean, et al. [22] observed a series of current oscillations during the electropolymerization of pyrrole on an iron electrode in aqueous acetonitrile solution containing tetrabutylammonium-hexafluorophosphate. They concluded that the oscillations was occurred particularly in the studied electrolyte.

This oscillatory phenomenon is a complex process that depends on current density, pH and temperature of the solution. The amplitude, periodicity and the shape of the oscillations might depend on the combination of these parameters or on the monomer or electrolyte concentrations. Further investigations are needed in this field. The phenomenon, to our knowledge, was never observed previously in electropolymerization of pyrrole in oxalic acid. It is because that the previous studies were conducted at room temperature only.

During the electropolymerization process, two reactions are possible, the first corresponds to dissolution of iron (reaction A) (E_1= - 0.29 V vs. SCE), and the second to pyrrole oxidation (reaction B) (E_2= 0.8 V vs SCE).

$$Fe \rightarrow Fe^{3+} + 3e^{-} \qquad (A)$$

$$nPy \rightarrow PPy + (2n-2)H^{+} + (2n-2)e^{-} \qquad (B)$$

The oscillatory behavior is explained with the help of Figure 4.36. The first step represents the dissolution of the metal and pyrrole molecules try to come on the surface but the metal surface is still active and would not allow the polymerization. The electrode potential is negative and is in the corrosion range. Reaction A occurres at this step. After certain time, the corrosion products start forming a passive film. This happens at lower electrode potential. Reaction B initiates after sufficient passivation in achieved. This will cause an increase in the potential (step 2). The formed film is unstable and it can easily undergo breakdown allowing the dissolution of the metal to take place. The corresponding electrode potential is low. This constitutes step 3. Step 2 and 3 will alternate with the passing of time. The oscillation will stop/reduce when passivation is strong enough to allow deposition of stable polypyrrole film.

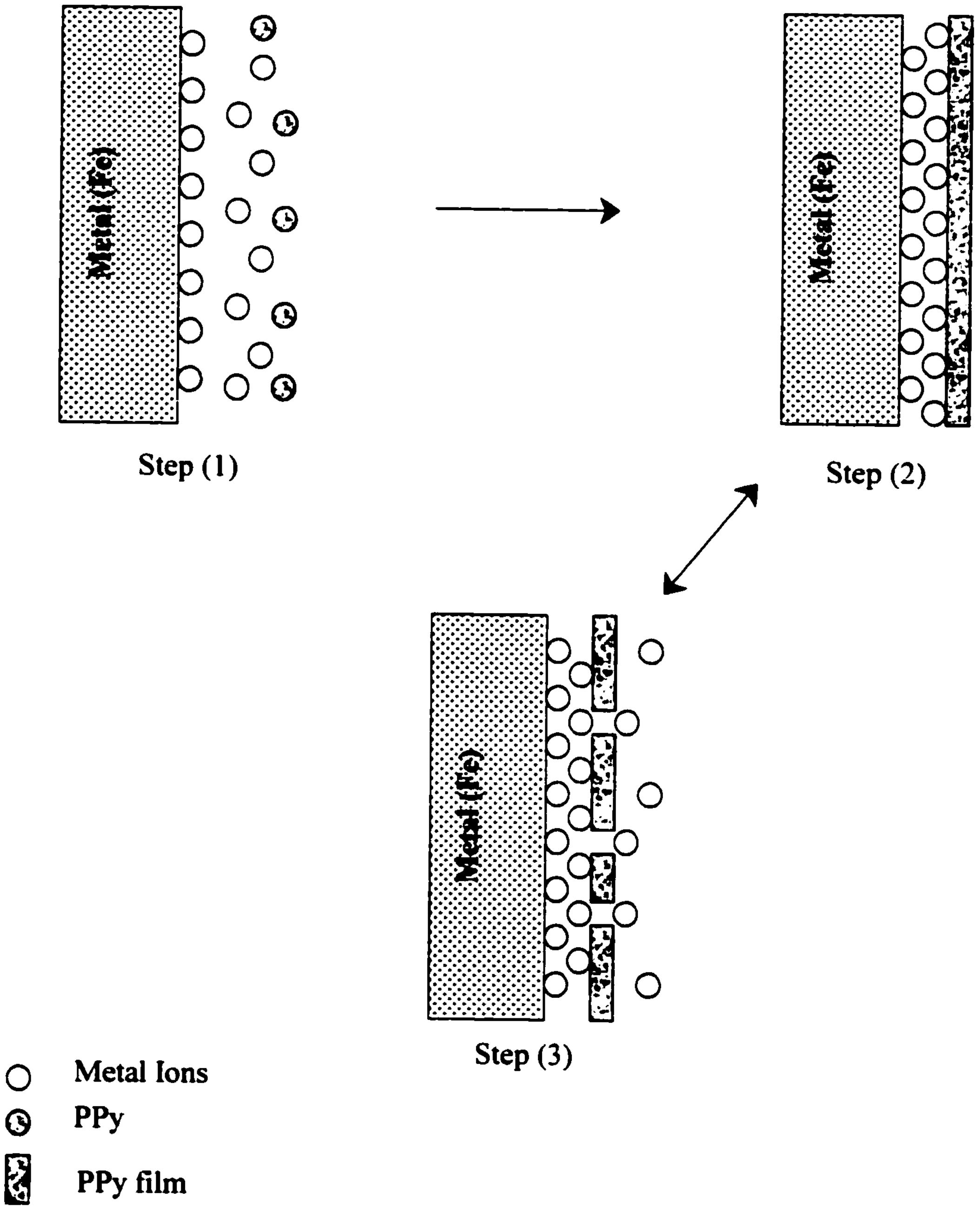


Figure 4.36 Apparent proposed mechanism for the oscillatory phenomenon

4.3.2 Effect of Temperature and Current Density in Neutral Media

Chronopotentiometric plots of polypyrrole coating at neutral medium and different temperatures are shown in Figures 4.36 through 4.40. Photos of steel samples are shown in Appendix A. For neutral solution at same applied temperature, no good deposition was observed at applied current densities of 0.5 and 2.0 mA/cm^2. At higher current densities, e.g. at 4.0 and 6.0 mA/cm^2, a thin polypyrrole deposition was noticed even at high temperature. However, increasing the temperature does not have positive effect on the deposition. At high temperature, the deposition became smooth but very thin. It seems that polymerization rate did not increase as fast with temperature as rate of dissolution reaction did.

Figures 4.37 through 4.41 show the potential-time curves for pH 7.0 at different temperature. The inverse proportionality relation between the current density and induction time was still applicable here. The figures show that at the lowest applied current density, the surface needs much time to be passivated. A neutral solution would require high current density in order to passivate the steel surface and to allow the deposition of polypyrrole on the surface.

The neutral solution gave induction time higher than that obtained in acidic media. For neutral solution and low value of current density of 0.5 and 2.0 mA/cm^2, the induction time was almost constant even at elevated temperature. For the other two values of current density i.e. 4.0 and 6.0 mA/cm^2, increasing the temperature would require longer induction time or in other words, it required longer time for the surface

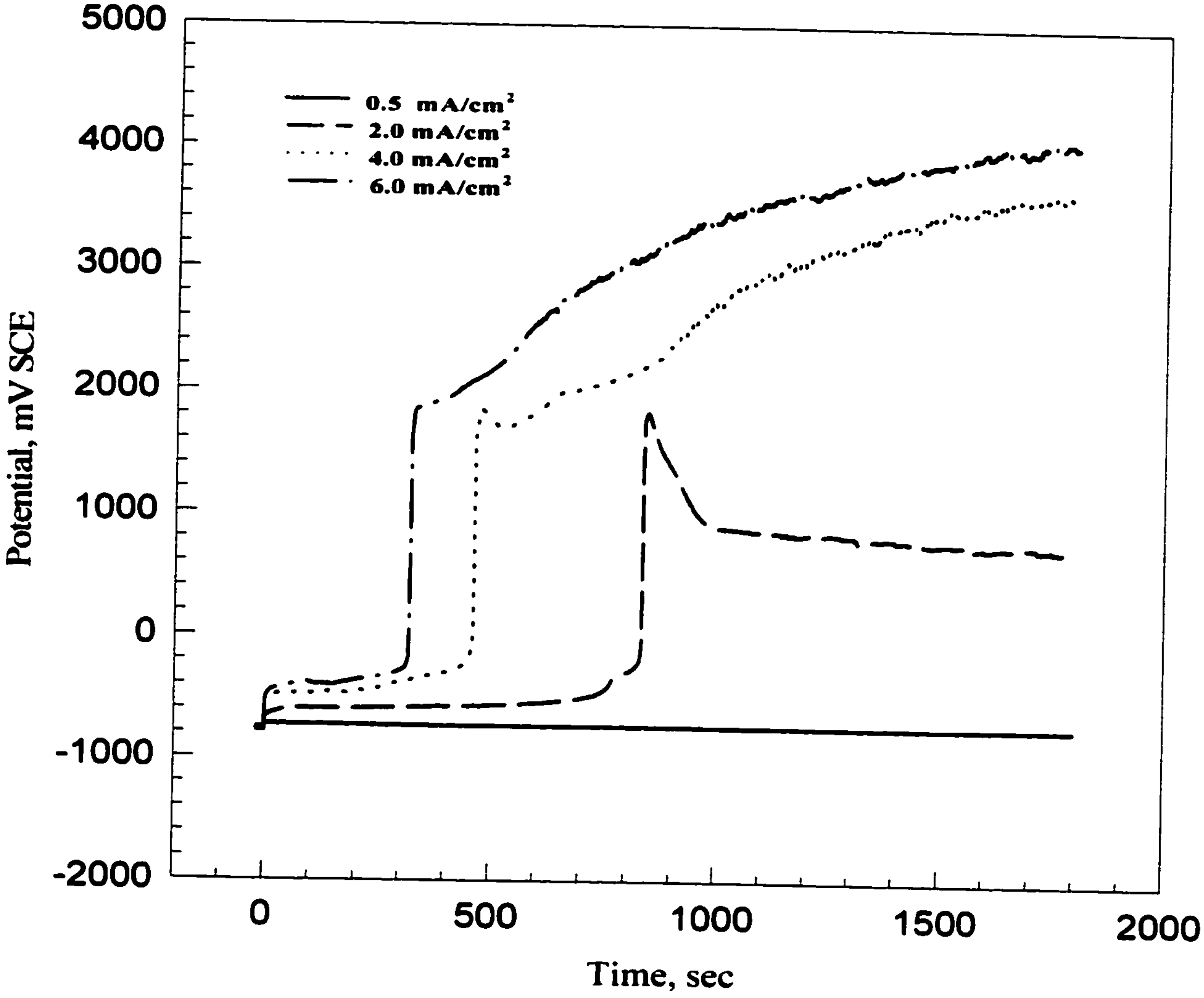


Figure 4.37 Potential vs time at pH 7.0 and T= 25 °C

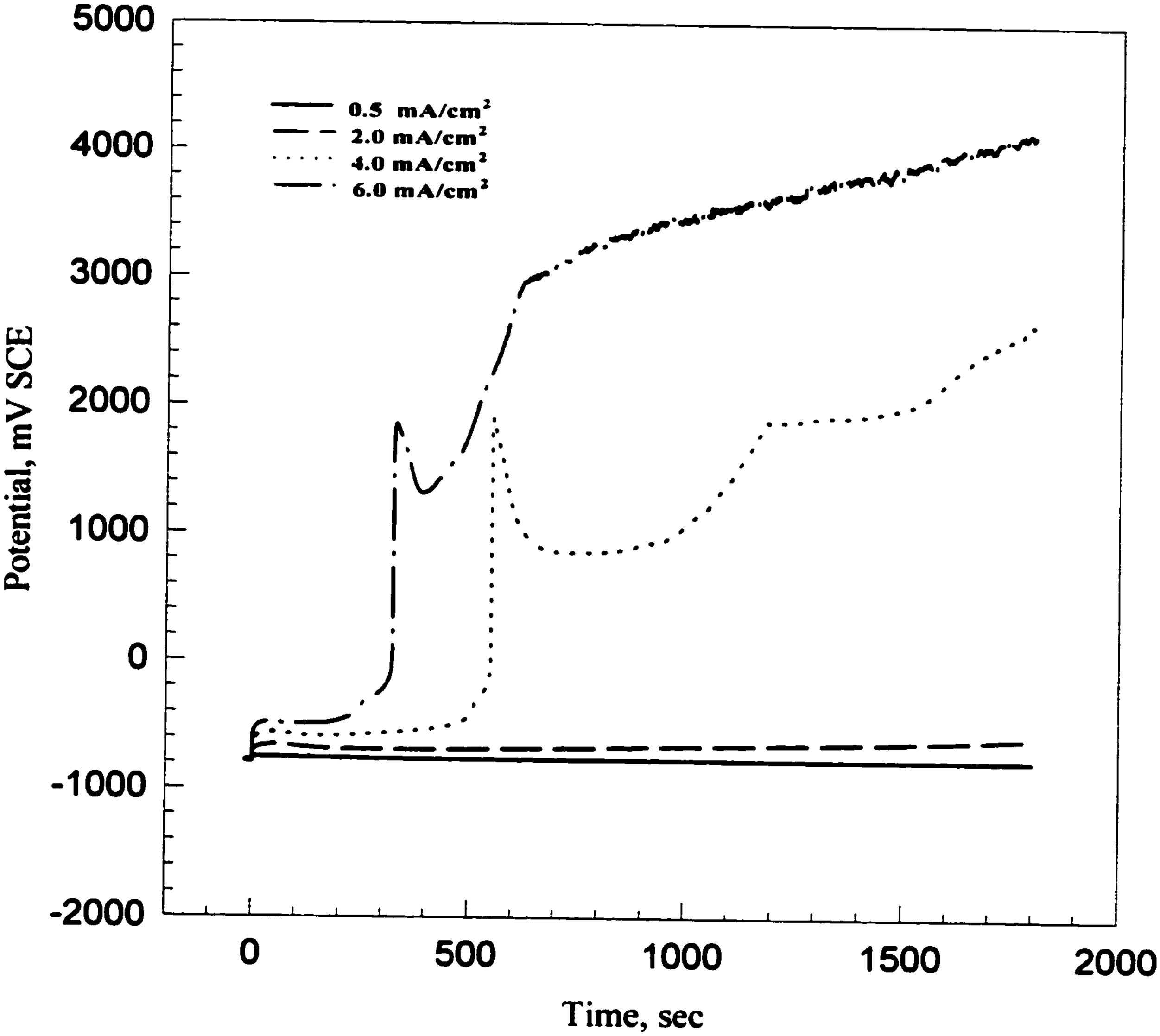


Figure 4.38 Potential vs time at pH 7.0 and T= 35 °C

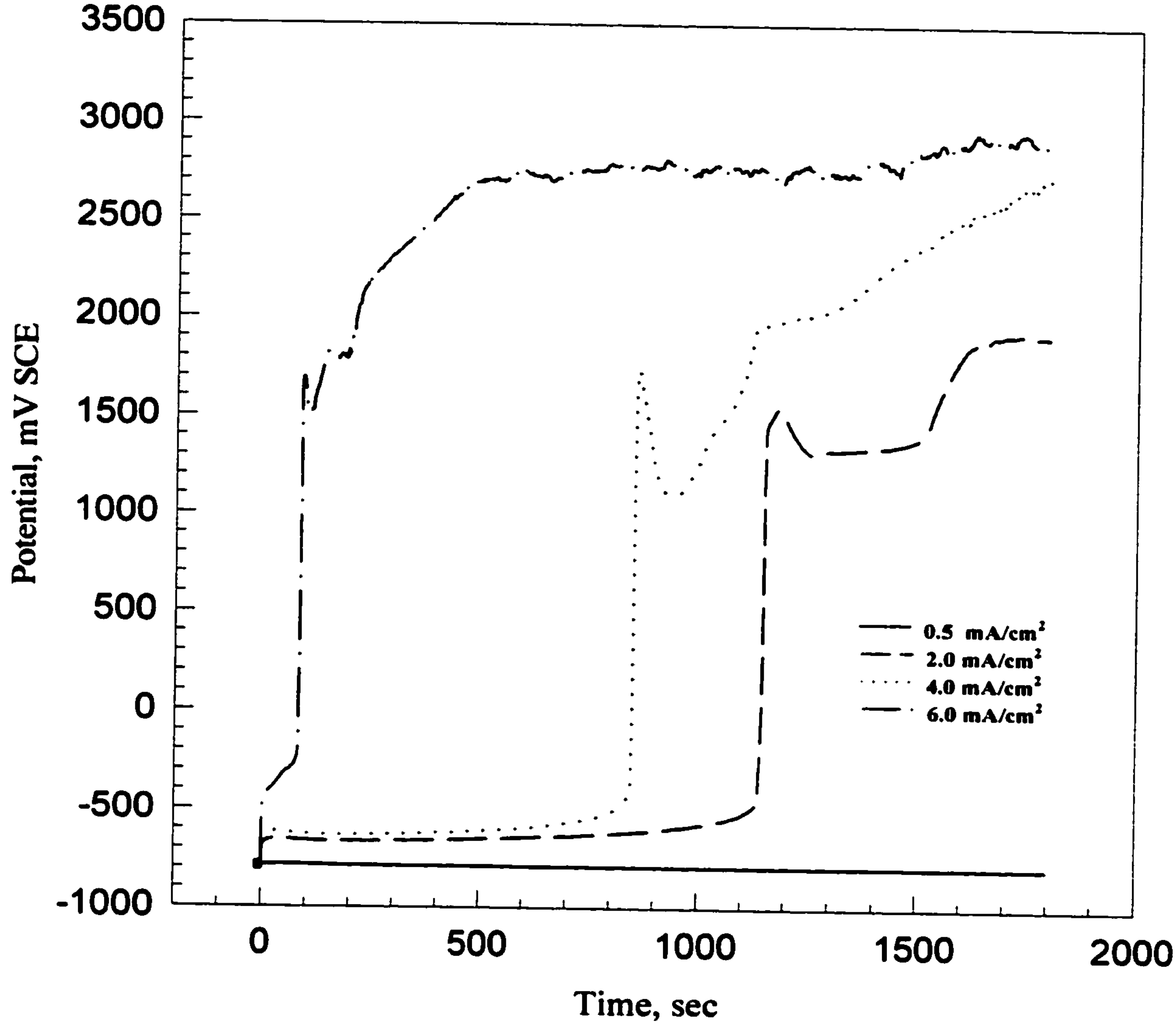


Figure 4.39 Potential vs time at pH 7.0 and T= 45 °C

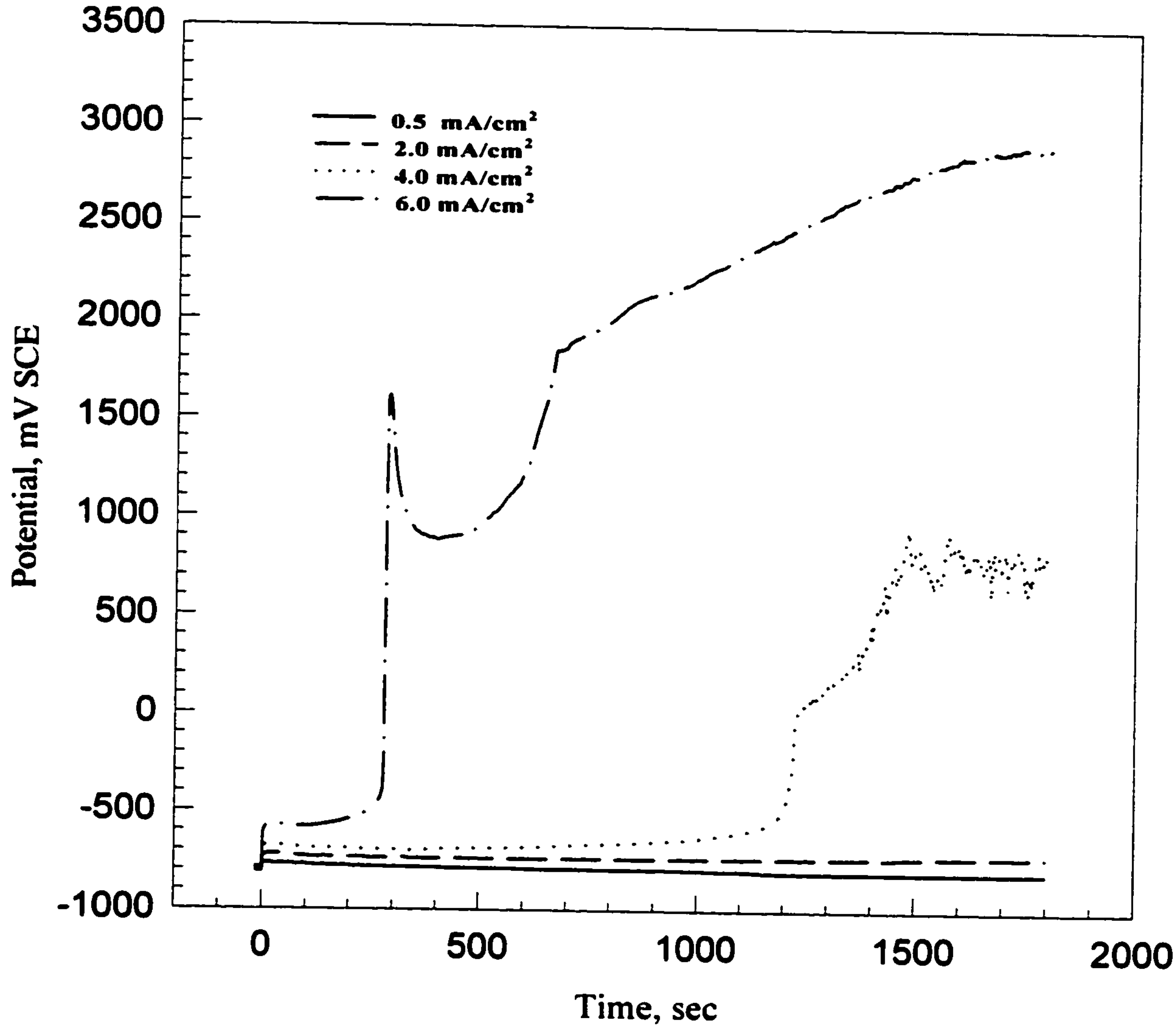


Figure 4.40 Potential vs time at pH 7.0 and T= 55 °C

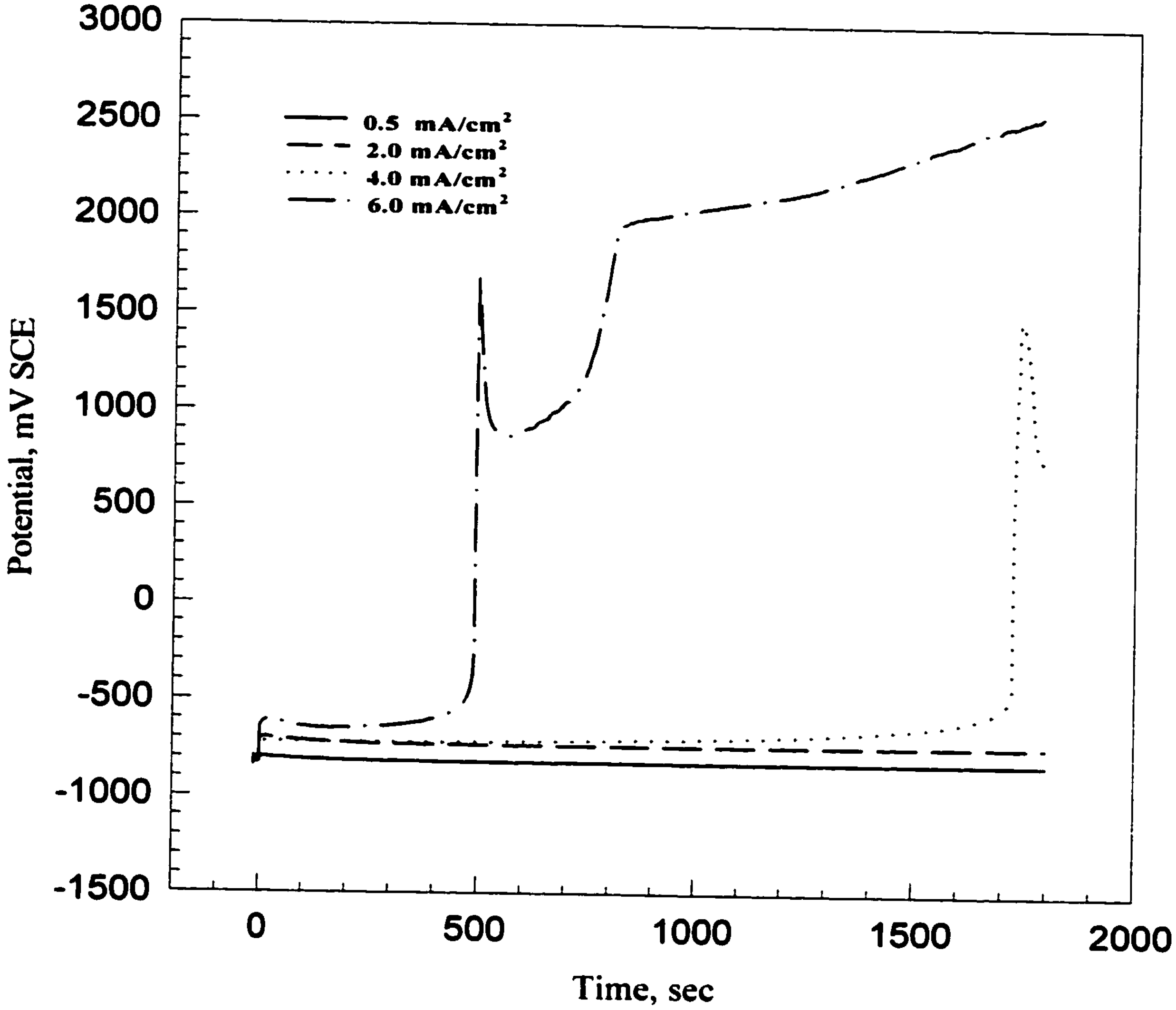


Figure 4.41 Potential vs time at pH 7.0 and T= 65 °C

to be passivated. For example, at current density of 4.0 mA/cm^2, the induction time was about 450 seconds at 25 °C while it increased to 1715 seconds at 65 °C. Since the corrosion rate is low at pH 7.0, it takes longer to achieve the required passivation for initiation of polypyrrole oxidation.

The oxidation potential increases with increased current density. Normally the oxidation potential in neutral solution was higher than that in acidic media. This was also observed by Su and Iroh [20]. They mentioned that the detailed mechanism of this phenomenon is not clear. In addition, the oxidation potential especially at current density of 4.0 and 6.0 mA/cm^2 has a tendency to increase. It may be due to film's high resistance or low conductivity.

4.3.3 Effect of Temperature and Current Density in Alkaline Media

Chronopotentiometric plots of polypyrrole coating at alkaline medium (pH= 8.5) and different temperatures are shown in Figures 4.42 through 4.46. Photos of steel samples are shown in Appendix A. For alkaline solution at 25°C, no good deposition was observed at applied current densities of 0.5 and 2.0 mA/cm^2. For the same temperature, increasing the current density increased the polymerization rate and better compact deposition was formed. The film surface was smooth even at high current density.

It appears that for the same applied current density, increasing the temperature would result into adherent, smoother and better polypyrrole film. Apparently, the polymerization rate was higher than the dissolution rate of iron as temperature

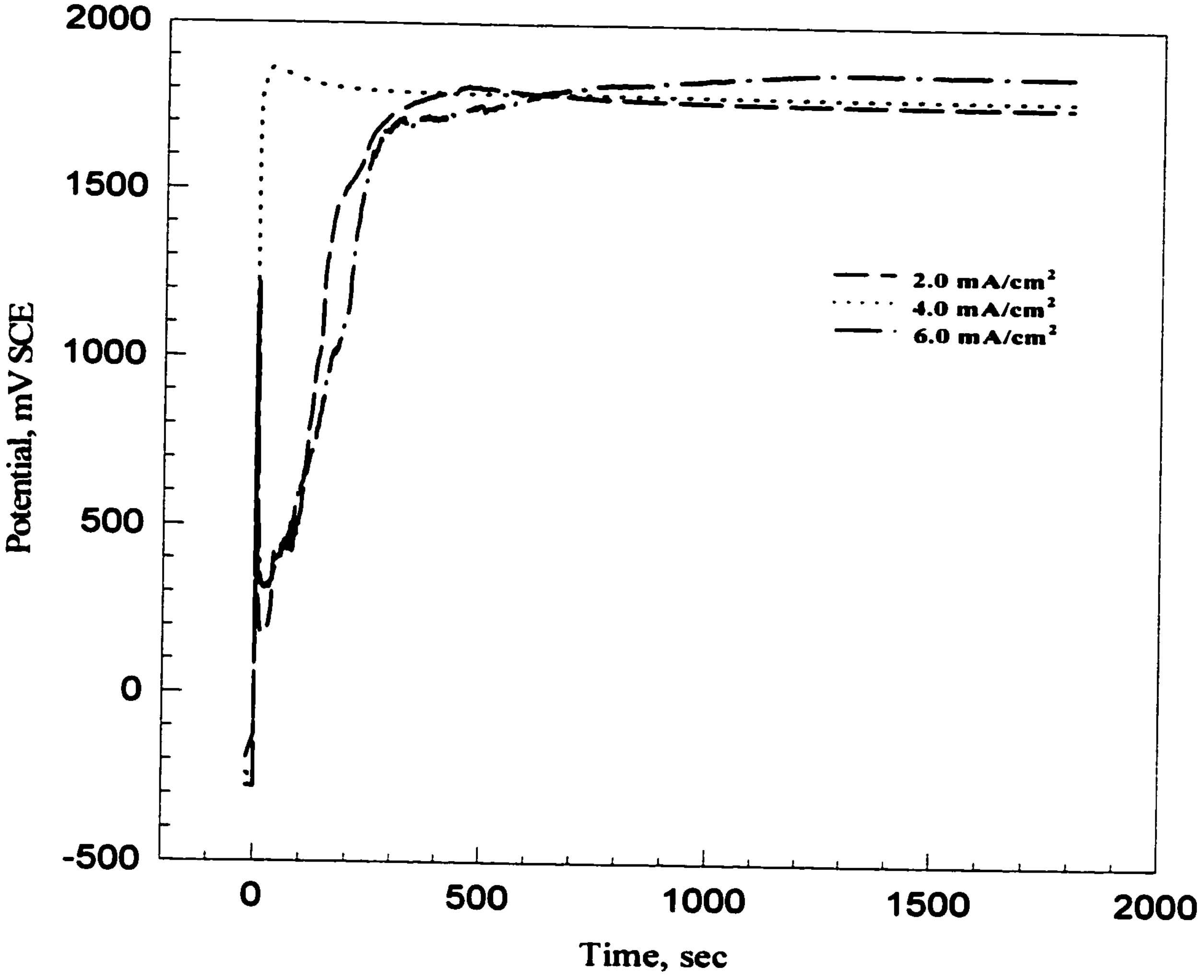


Figure 4.42 Potential vs time at pH 8.5 and T= 25 °C

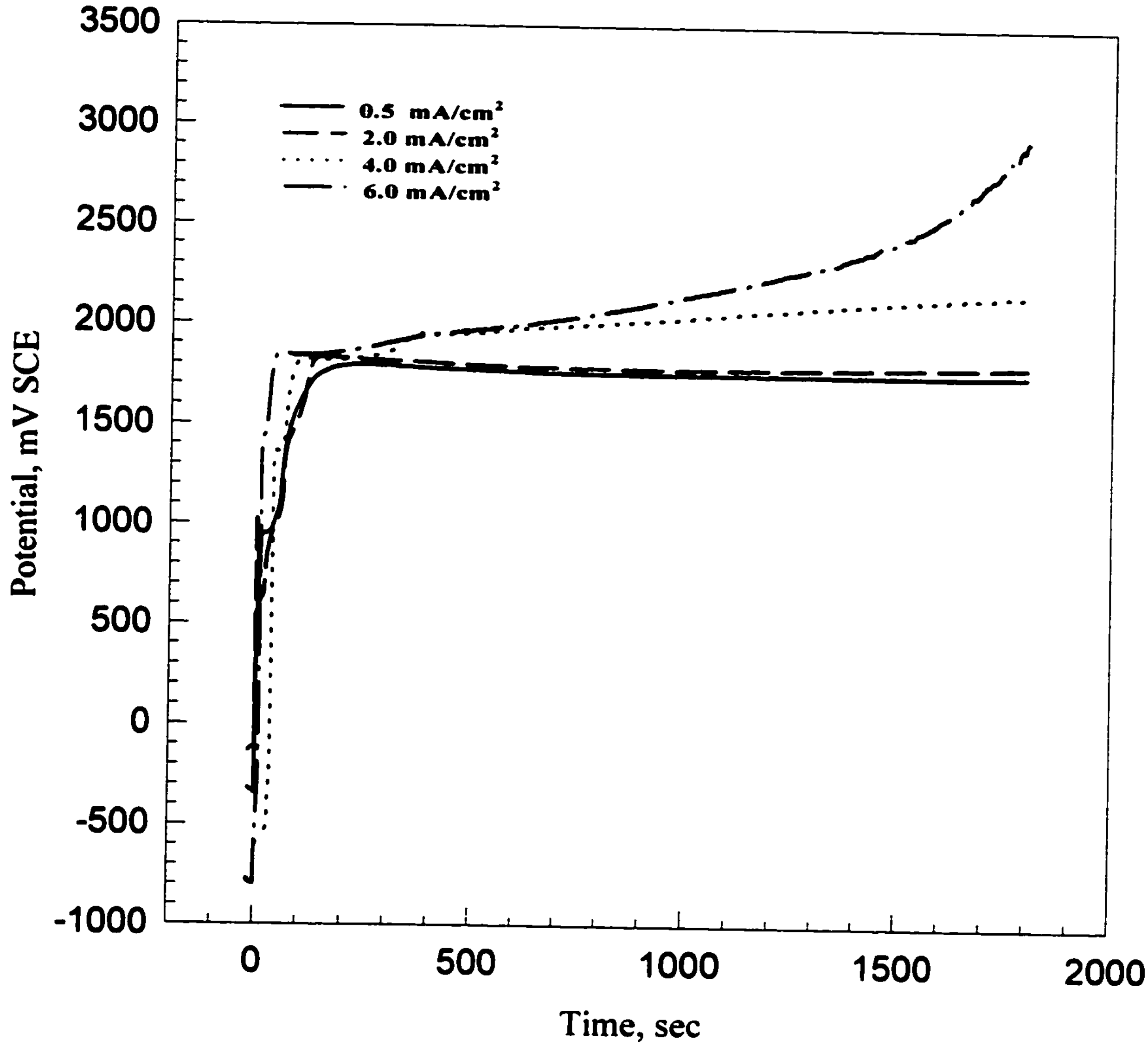


Figure 4.43 Potential vs time at pH 8.5 and T= 35 °C

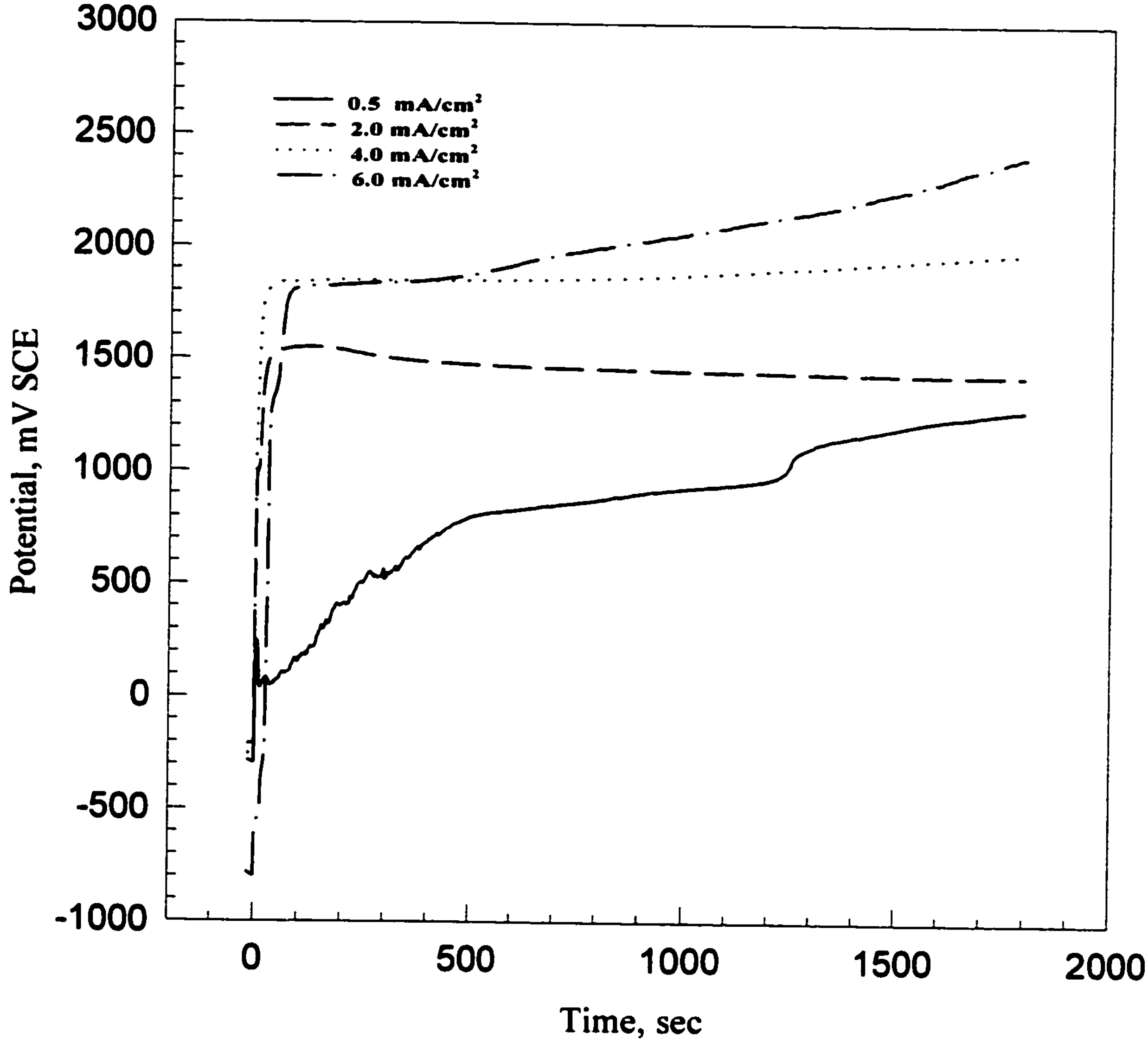


Figure 4.44 Potential vs time at pH 8.5 and T= 45 °C

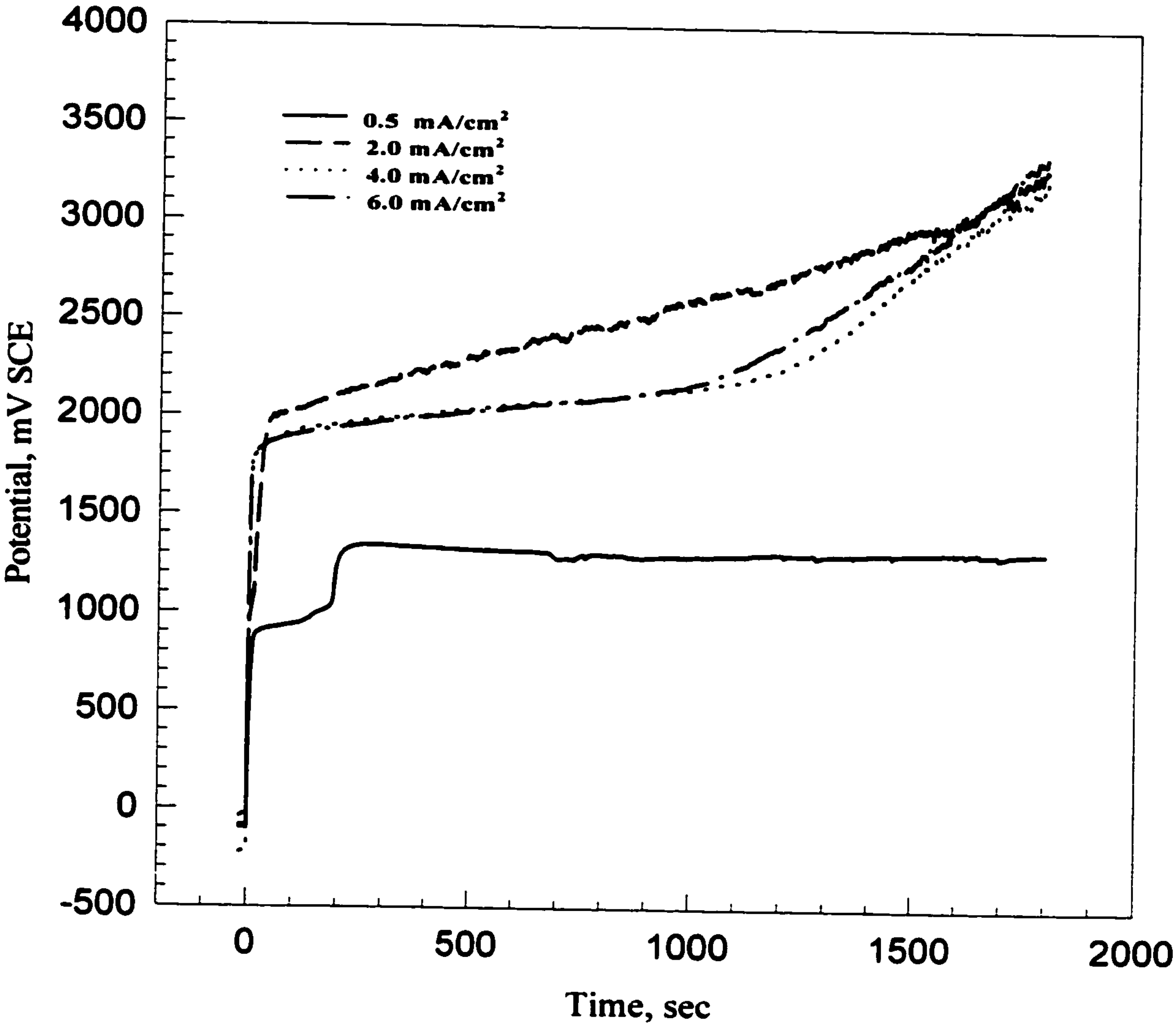


Figure 4.45 Potential vs time at pH 8.5 and T= 55 °C

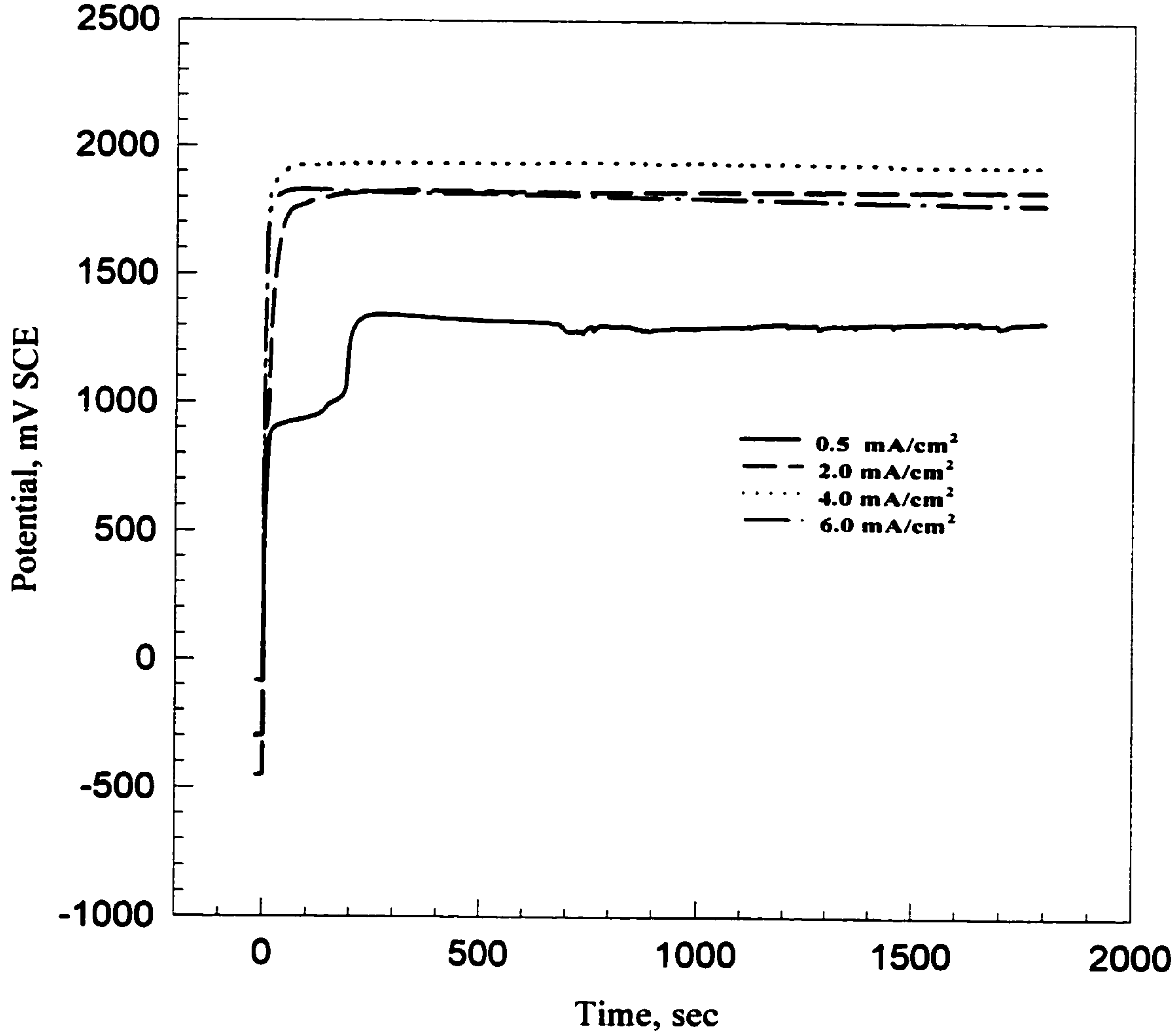


Figure 4.46 Potential vs time at pH 8.5 and T= 65 °C

increased in alkaline media. A very thin deposition was observed at low current density only at high temperature. However, the deposition noticed at high temperatures was better than that observed at room temperature for the same applied current density.

The formation process of polypyrrole in alkaline medium was quite different from that in acidic medium. It can be seen from Figures 4.42 through 4.46 that the potential first increased sharply with time, then tended to a steady state value. These figures clearly show that no induction time was observed even at high temperatures when the pH of the reaction medium was 8.5. Increasing the temperature in the alkaline medium did not have any effect on the induction time for all values of applied current densities. The induction time observed in the alkaline medium was much lower than that observed at either acidic or neutral solution. These results are not unusual. According to a Pourbaix diagram, the application of an anodic potential to an iron sheet immersed in alkaline medium will bring about the passivation of the iron.

The oxidation potential of pyrrole in alkaline medium was much higher than that in acidic medium for the same applied current density even at high temperatures. The mechanism is not clear and the reproducibility of the potential-time curves was poor as mentioned by Su and Iroh [20]. Temperature did not have clear effect on the oxidation potential of pyrrole. An increase in potential was noticed at different values of current density and temperature. Figures 4.42 through 4.45 show this behavior. This increase may be due to low conductivity of polypyrrole film.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study casts light on the electropolymerization of pyrrole on mild steel for corrosion protection. Four different methods available in open literature were studied with the help of Scanning Electron Microscopy (SEM) and visual inspection in order to select the best method with uniform and adherent polypyrrole deposition. Subseguently, a parametric study was undertaken for the best method to find the effect of several parameters such as current density, pH and temperature. The following can be concluded from the study:

1. Beck's method gives the most adherent film of polypyrrole on mild steel compared with the other methods tested in this work and mentioned previously. The electrolyte used in this method was (0.1 M oxalic acid) and (0.1 M pyrrole).

2. At low value of current density (0.5 mA/cm^2), no good deposition was observed for the studied range of pH and temperatures.

3. Increasing the current density will enhance the electropolymerization process but it will increase the roughness of the surface in acidic and neutral media because the rate of the polymerization will be high and the deposition will be formed randomly on the surface. Pinholes were noticed at 6.0 mA/cm^2.

4. In general, induction or passivation time (τ) decreases with increasing the current density.

5. Electropolymerization potential of pyrrole increases with increasing the current density.

6. No deposition is observed for neutral or alkaline solution except at high value of current density.

7. Increasing the pH up to 7.0 will increase the induction time (ι). However, The lowest induction time was recorded for the alkaline media.

8. The neutral and alkaline solution give much higher oxidation potential than that from acidic media. Also, potential in neutral solution had a tendency to increase because of low conductivity of the film.

9. Increasing the temperature does not have significant effect on the induction time especially at high value of current density for acidic and alkaline medium. However, the temperature had major effect on the induction time for the neutral medium.

10. Increasing the temperature results into poor deposition in acidic or neutral medium and good deposition in alkaline media.

11. For better deposition, in acidic or neutral media, it is better to work with low temperature and intermediate value of current density while high temperature and high value of current density is better for alkaline media.

12. A new oscillatory phenomenon was observed in acidic media at temperature higher than room temperature.

5.2 RECOMMENDATION

It is recommended for future work to:

1. Study the effect of temperature and other parameters on the conductivity of the film.
2. Study the effect of temperature on degree of polymerization of polypyrrole.
3. Compare deposition in galvanostatic and potentiostatic modes.
4. Copolymerize the pyrrole with another polymer to improve its properties
5. Use rotating disc electrodes to elucidate the newly observed oscillatory phenomenon.

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APPENDIX-A

Photographs of Steel Samples

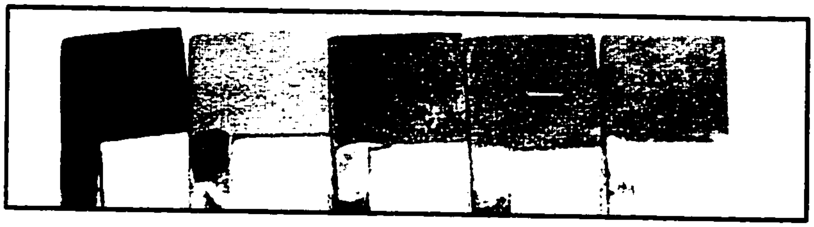

Figure A.1 Photograph of the samples for pH 2.0, current density 0.5 mA/cm^2 and varying temperature from 25 to 65 °C

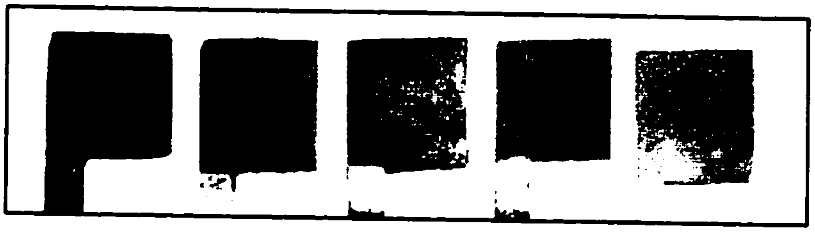

Figure A.2 Photograph of the samples for pH 2.0, current density 2.0 mA/cm^2 and varying temperature from 25 to 65 °C

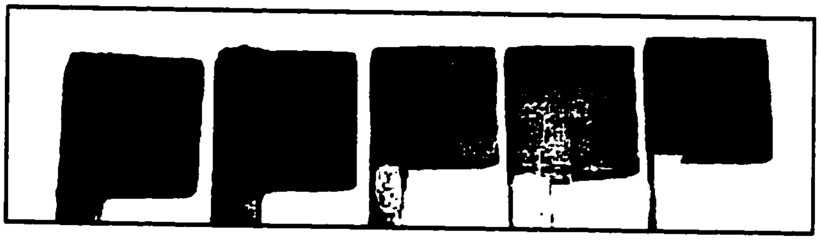

Figure A.3 Photograph of the samples for pH 2.0, current density 4.0 mA/cm^2 and varying temperature from 25 to 65 °C

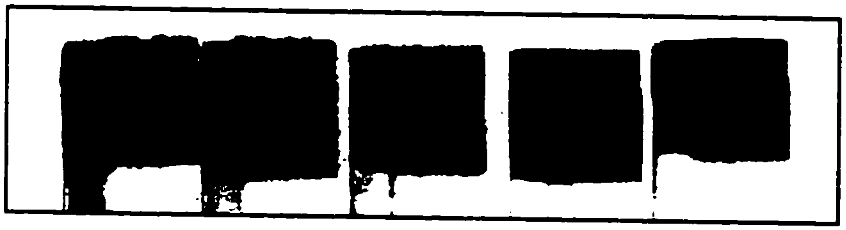

Figure A.4 Photograph of the samples for pH 2.0, current density 6.0 mA/cm^2 and varying temperature from 25 to 65 °C

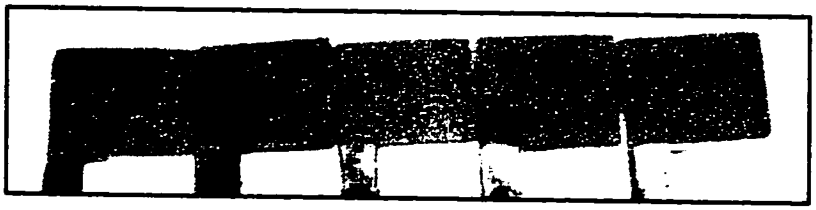

Figure A.5 Photograph of the samples for pH 4.0, current density 0.5 mA/cm^2 and varying temperature from 25 to 65 °C

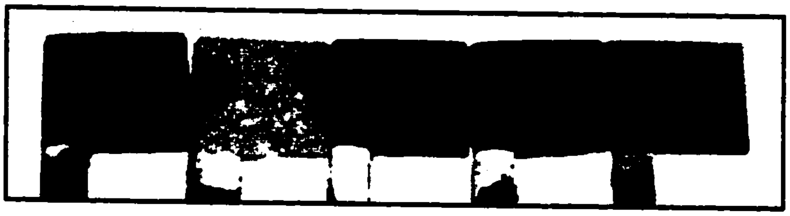

Figure A.6 Photograph of the samples for pH 4.0, current density 2.0 mA/cm^2 and varying temperature from 25 to 65 °C

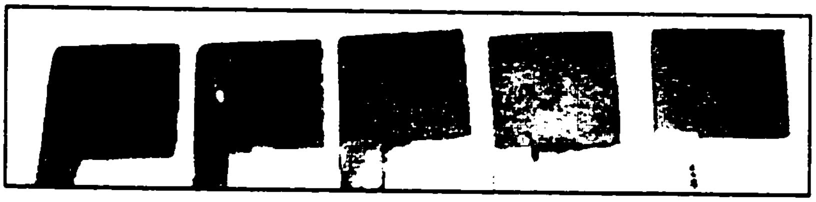

Figure A.7 Photograph of the samples for pH 4.0, current density 4.0 mA/cm^2 and varying temperature from 25 to 65 °C

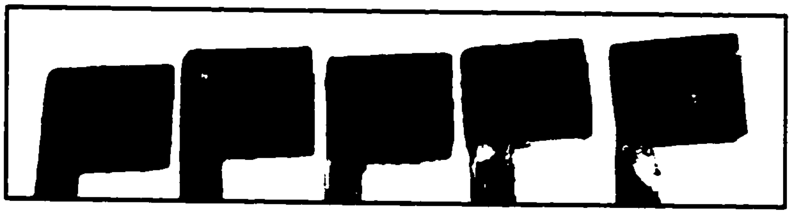

Figure A.8 Photograph of the samples for pH 4.0, current density 6.0 mA/cm^2 and varying temperature from 25 to 65 °C

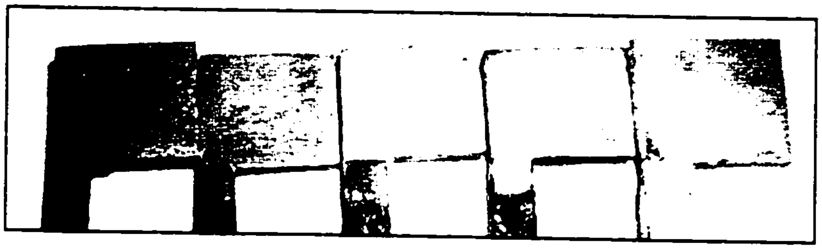

Figure A.9 Photograph of the samples for pH 7.0, current density 0.5 mA/cm^2 and varying temperature from 25 to 65 °C

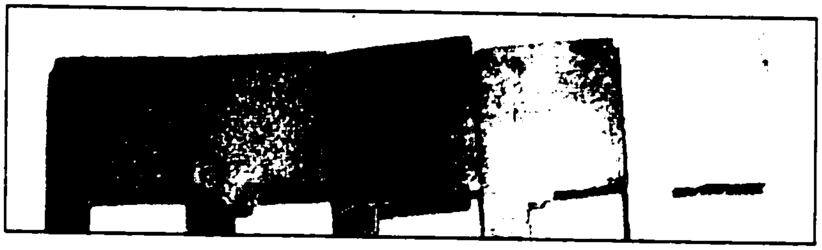

Figure A.10 Photograph of the samples for pH 7.0, current density 2.0 mA/cm^2 and varying temperature from 25 to 65 °C

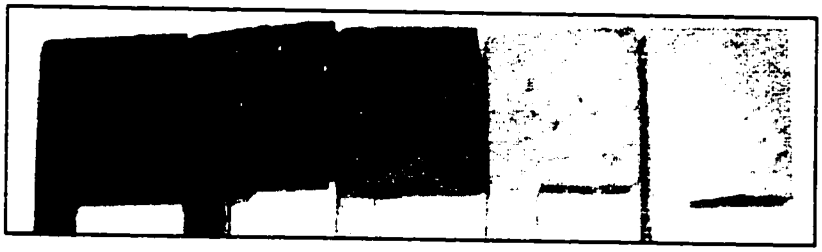

Figure A.11 Photograph of the samples for pH 7.0, current density 4.0 mA/cm^2 and varying temperature from 25 to 65 °C

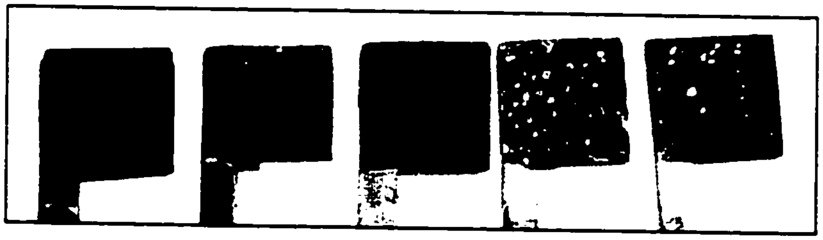

Figure A.12 Photograph of the samples for pH 7.0, current density 6.0 mA/cm^2 and varying temperature from 25 to 65 °C

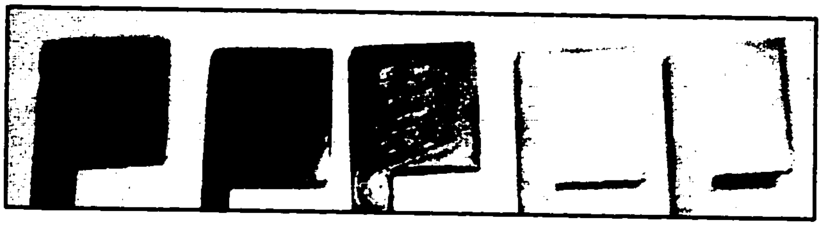

Figure A.13 Photograph of the samples for pH 8.5, current density 0.5 mA/cm^2 and varying temperature from 25 to 65 °C

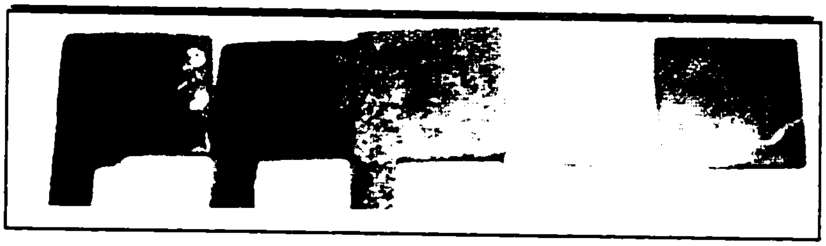

Figure A.14 Photograph of the samples for pH 8.5, current density 2.0 mA/cm^2 and varying temperature from 25 to 65 °C

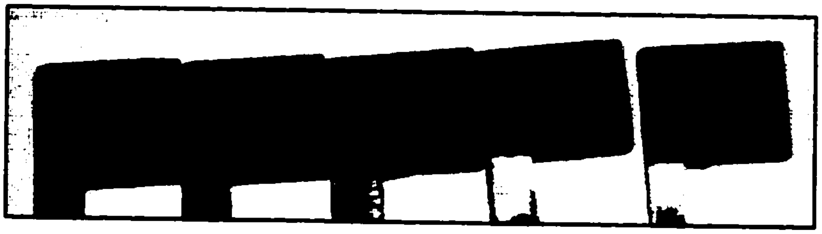

Figure A.15 Photograph of the samples for pH 8.5, current density 4.0 mA/cm^2 and varying temperature from 25 to 65 °C

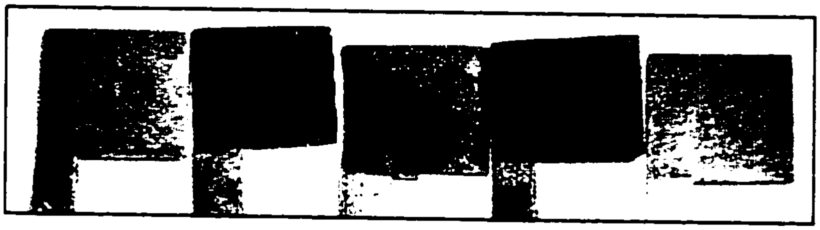

Figure A.16 Photograph of the samples for pH 8.5, current density 6.0 mA/cm^2 and varying temperature from 25 to 65 °C