Electrochemical Behaviour of Titanium in H_2SO_4 - MnSO_4 Electrolytes

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ABSTRACT

The corrosion of titanium in H_2SO_4 electrolytes (0.001-1.0 M) at temperatures from ambient to 98°C has been investigated using steady state polarization measurements. Four distinct regions of behaviour were identified; namely, active corrosion, the active-passive transition, passive region and the dielectric breakdown region. The active corrosion and active passive transition were characterized by anodic peak current (i_m) and voltage (E_m), which in turn were found to vary with the experimental conditions; *i.e.*, $d\log(i_m)/dpH = -0.8 \pm 0.1$ and dE_m/dpH which was -71 mV at 98°C, -58 mV at 80°C and -28 mV at 60°C. The activation energy for titanium corrosion, determined from temperature studies, was found to be 67.7 kJ mol⁻¹ in 0.1 M H_2SO_4 and 56.7 kJ mol⁻¹ in 1.0 M H_2SO_4 . The dielectric breakdown voltage (E_d) of the passive TiO_2 film was found to vary depending on how much TiO_2 was present. The inclusion of Mn^{2+} into the H_2SO_4 electrolyte, as is done during the commercial electrodeposition of manganese dioxide, resulted in a decrease in titanium corrosion current, possibly due to Mn^{2+} adsorption limiting electrolyte access to the substrate.

Keywords: titanium, active corrosion, passivation, electrolytic manganese dioxide

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1. INTRODUCTION

The electrochemical behaviour of titanium has been the subject of numerous investigations due to its widespread use as a strong and relatively lightweight construction material, and as a substrate in many commercial anodic electro-synthesis operations. Furthermore, titanium can be regarded as a “model” metal in the sense that it exhibits a wide range of electrochemical phenomena [1]. In this regard there are three types of behaviour that are of interest:

(i) An active state in which the titanium is oxidized to form soluble Ti(III) ions. In this area, previously reported works have focused on the kinetics and mechanism of the hydrogen evolution reaction, hydride formation and its role in the behaviour of titanium, the kinetics and mechanism of anodic titanium dissolution [2-20], the effects of added redox couples and various oxidants, as well as the role of alloying elements.

(ii) An active-passive transition region corresponding to the passivation process.

(iii) A passive state in which the metal is covered with an oxide film. Here the focus has been on the composition and structure of the oxide film, anodic film growth and film dissolution kinetics [22-33], and the semiconducting nature of the passive film, particularly how it relates to the kinetics of redox reactions at the oxide-electrolyte interface.

Of considerable importance to the battery industry is the production of electrolytic manganese dioxide (EMD), which is the preferred material for use in the very common aqueous alkaline Zn/MnO₂ cells. EMD is almost universally prepared by anodic deposition onto a titanium substrate from a hot acidic (H₂SO₄) solution of MnSO₄ [34]. A sulfate electrolyte is used for reasons of cost and also to avoid electrochemically active anions; *e.g.*, Cl⁻ and NO₃⁻. While each of the variables inherent with this synthetic approach have very broad ranges; *i.e.*, anodic current densities up to 100 Am⁻², temperatures greater than 90°C, and electrolyte compositions limited only by solubility, the EMD with the best electrochemical performance in a battery needs to be made under very specific conditions. Furthermore, for the sake of production quantities, EMD manufacturers would also prefer to operate using high anodic current densities to increase output.

What is not known is a detailed understanding of the role that the titanium substrate plays in determining the useable limits of the synthetic variables, and the quality of the EMD product. Empirically, manufacturers of EMD have found that the use of (either singularly or in combination) high anodic current densities, high H₂SO₄ concentrations and low temperatures lead to high anode voltages which decrease current efficiency due to the occurrence of oxygen evolution, and product quality. This is quite often cited as being a titanium passivation problem in which the resistance of the Ti-EMD interface has been increased. A number of studies have focused on avoiding this problem, including one in which a thin film of β-MnO₂ was deposited first onto the titanium substrate before bulk EMD deposition [35-37]. Fisher *et al.* [38] have studied the relationship

between electrolyte composition and the maximum possible anodic current density before passivation to assist in the design of uncoated titanium anodes for EMD production in sulfate solutions. The electrolyte composition was varied according to the ratio $[\text{MnSO}_4]/([\text{MnSO}_4]+[\text{H}_2\text{SO}_4])$ for which they found a value of 0.9 was most suitable, giving a maximum achievable current density of 115 Am^{-2} . A similar study was conducted by Mriyaaki *et al.* [39], although they were less definitive in their conclusions, stating that a sufficient supply of MnSO_4 to the anode surface, rather than H_2SO_4 , was essential to maintain a sound, non-passivated titanium anode. In a slightly different study, the behaviour of titanium for EMD production under neutral conditions has been reported by Tsagareli *et al.* [40]. They reported that the titanium anode voltage during EMD deposition was lower in neutral electrolytes compared to acidic electrolytes, hence providing more favorable conditions to avoid passivation. However, they did note that the titanium anode voltage increased during deposition, possibly due to the formation of a high resistance compound at the interface.

The work reported here can be best regarded as a continuation of the previous corrosion studies conducted on titanium in H_2SO_4 solutions, as well as an introductory study into the role that titanium corrosion and passivation has on EMD production. To achieve this the titanium active corrosion region, active-passive transition and passive region will be examined using steady-state anodic polarization in a variety of H_2SO_4 – MnSO_4 electrolytes at a range of temperatures.

2. EXPERIMENTAL

2.1. Electrode Preparation

The working electrode for our experiments consisted of a 2 cm^2 titanium sheet (Sigma-Aldrich, 99.99% purity) mounted in an epoxy body. Before each experiment, to remove any pre-existing oxide film, the titanium was mechanically polished with 300 grit emery paper, washed with acetone and then Milli-Q ultra-pure water ($18 \text{ M}\Omega$). The electrode was then immersed in 1 M H_2SO_4 and electrolyzed cathodically using 100 mA for 5 minutes . Following this it was washed thoroughly with Milli-Q ultra-pure water, patted dry with a lint free cloth and then immersed in the already deoxygenated electrolyte within the electrochemical cell.

2.2. Electrochemical Cell and Electrolytes

The electrochemical cell used in this work consisted of a thermally jacketed 250 mL multi-necked flask, in which the titanium working electrode, saturated calomel reference electrode (SCE) and platinum foil counter electrode were immersed. Note that all voltages reported in this work are with respect to the SCE unless otherwise stated. Also included were a thermocouple to monitor and control temperature via a feedback loop to a temperature controller, and an impellor used to assure

uniform sample heating, although before an electrochemical experiment was conducted the electrolyte was allowed to quiesce.

The electrolytes used were prepared from AR Grade H₂SO₄ and MnSO₄·H₂O with Milli-Q ultra-pure water, and varied in the concentration ranges 0.001-1.0 M for H₂SO₄ and 0.001-0.1 M for Mn²⁺. Experiments were conducted at temperatures of 22, 40, 60, 80 and 98°C (±1°C).

2.3. Electrochemical Profile

Control of electrochemical experiments was achieved through the use of a Perkin Elmer VMP multi-channel potentiostat. The first step in the profile involved removing any remaining oxide film by sweeping the potential of the titanium working electrode from its open circuit voltage (OCV) down to -0.8 V at 10 mVs⁻¹. From here the titanium voltage was stepped in 25 mV increments, with a 120 s residence time at each voltage, until an upper limit of 3.0 V was reached. After each voltage step the current was recorded as a function of time and found to have reached a steady state value well before the 120 s limit.

3. RESULTS AND DISCUSSION

3.1. Steady-State Anodic Polarization Curves

A typical polarization curve measured in this work is shown in Figure 1. Also shown in the figure are the voltage regions of active corrosion (I), the active-passive transition (II) and passivity (III). Region (IV) within the figure corresponds to the voltage beyond which dielectric breakdown of the passive film occurs, resulting in the evolution of oxygen as a result of water oxidation. Much debate in the literature has focused on the chemical and electrochemical processes occurring in each of these voltage regions. In general, two schools of thought have emerged; namely, those based on a monolayer mechanism, and those based on a phase-oxide mechanism. Of these the monolayer mechanism has the most support, due mainly to there being no conclusive *in-situ* or *ex-situ* evidence to suggest the presence of an oxide film during active corrosion, which is the key postulate of the phase-oxide mechanism. As such, the monolayer mechanism will only be considered.

The monolayer mechanism for titanium was developed from a similar study into the active dissolution of iron, and is based essentially on the behaviour of adsorbed titanium species at the solid-electrolyte interface. During active dissolution of the metal, the proposed mechanism is as follows [1]:

The steps in the mechanism represented by Eqns (4) and (5) represent the continued oxidation of the titanium substrate to Ti(III), which is different to the iron system in which case Fe(II) is the active state dissolution product. The formation of a soluble Ti(III) species then results from:

Of course this sequence of reaction steps is only for the active corrosion voltage region, or I in Figure 1. The maximum in the anodic polarization curve signifies the beginning of region II, which is the active-passive transition. In this region the reactions in Eqns (1)-(6) can continue, although they are now competing with additional reactions that limit current flow through the interface; *i.e.*, passivation is occurring. Such additional reactions have been proposed to include:

This scheme indicates that the formation of Ti(IV) species does not depend on Ti(III) species in solution; *i.e.*, the Ti(IV) surface entity ($[\text{Ti}(\text{OH})_2]_{\text{ad}}^{2+}$) is formed from surface Ti(III) species via Eqn (8) [6-7, 21]. Furthermore, it supports experimental data indicating that Ti(IV) can exist in solution in the active-passive transition region. The declining current in region II is of course due to the build up of a passive oxide film (TiO_2 in this case, as in Eqn (11)) which inhibits current flow for the continued oxidation.

An interesting feature of the data shown inset in Figure 1 is the dip and then slight increase in steady-state current apparent at -0.4 V. This is consistent with previous reports focused on the role that soluble Ti(III) species have on the corrosion process [6-7, 21]. In particular, the current after the dip is a combination of direct TiO_2 formation from species adsorbed in the monolayer, as is described by Eqn (11), and soluble Ti(III) oxidation to TiO_2 . This result indicates that some of the Ti(III) formed during active passivation escaped from the electrode surface, at least into the electrode diffusion layer given that our solution was not stirred.

Beyond the active-passive transition region we enter the passive region in which we would presume there is a film of titanium oxide (TiO_2) covering the metallic titanium. Given the poor conductivity of TiO_2 , minimal current flows within this voltage region. What current that does flow is most likely due to the continued oxidation of titanium at the metal-oxide interface as a result of the acidic electrolyte penetrating the almost impermeable (slightly porous) oxide layer. At even higher voltages we enter the dielectric breakdown region of the passive layer where oxygen is now

evolved on the oxide surface. The voltage at which dielectric breakdown occurs is of course dependent on thermodynamics; *i.e.*, the electrode voltage must be higher than the oxygen evolution potential, as well as the thickness and conductivity of the oxide layer.

3.2. Correction for the Hydrogen Evolution Reaction

While the corrosion of titanium is an anodic process, the overall current that flows is a combination of both titanium corrosion and cathodic hydrogen evolution. Therefore, to determine the anodic titanium corrosion current we must correct for the current due to hydrogen evolution [1]. Figure 2, which is a plot of $\log(i)$ vs V for an actively corroding system, demonstrates how this correction can be made. For hydrogen evolution (i_H) at voltages less than the corrosion potential (E_{corr}), $\log(i)$ can be extrapolated linearly to more positive potentials. The slope of the data shown in Figure 2 was in all cases close to the anticipated value from $(\partial \log|i_H|/\partial E) = -F/2(2.303RT)$ [1]. These extrapolated current values then form the baseline for correcting the current due to titanium corrosion. As can be seen, the as measured current (i_d) is significantly less than the corrected current ($i_{d,c}$), particularly so at potentials near to E_{corr} . This correction leads to small changes in both the voltage (E_m) and current (i_m) of the corrosion maxima. As such, all future reported values for E_m and i_m will be corrected for the hydrogen evolution reaction, and as we shall see this will be most significant for the more concentrated H_2SO_4 solutions, and for experiments carried out at elevated temperatures.

3.3. Effect of H_2SO_4 Electrolyte Concentration and Temperature

Typical examples of the effects of H_2SO_4 concentration and temperature on the corrosion of titanium are shown in Figures 3(a) and (b), respectively. Note the changes in each of the voltage regions indicated in Figure 1(a), especially the considerable variation in active corrosion current (Region I) and the voltage at which dielectric breakdown of the oxide layer occurs (Region IV). Of particular interest is the absence of any substantial anodic dissolution current at both low H_2SO_4 concentrations and low temperatures. This is clearly demonstrated in Figure 4 which shows the maximum corrosion current (i_m) as a function of both H_2SO_4 concentration and temperature. The absence of an active corrosion region under these mild conditions is contrary to previous reports [1] which clearly show significant corrosion currents, for example in pH 2.00 electrolytes ($[\text{H}^+] = 0.01 \text{ M}$). A possible explanation for these differences involves knowing what the precise pretreatment (*e.g.*, thermal and mechanical history, *etc.*) of the titanium in these instances was, and if it is different, what effect it has had on both anodic titanium dissolution, as well as the cathodic hydrogen evolution reaction. More specifically, if the crystal structure of the titanium substrate is different (*e.g.*, crystal orientation, size, defect content, *etc.*) it may lead to different corrosion and

hydrogen evolution kinetics. Certainly there are many examples in the literature of where proper crystal orientation is essential for electrochemical reactions to occur [41]. The results obtained here suggest that titanium corrosion is another such example. Such behaviour will be the subject of a future report.

To quantify the relationship between H_2SO_4 concentration (pH), temperature, and i_m and E_m a number of previous studies have reported the following relationships [7]:

$$\frac{d \log(i_m)}{dpH} = -\frac{2}{3} \quad \dots(12)$$

$$\frac{dE_m}{dpH} = -\frac{4}{3} \left(2.303 \frac{RT}{F} \right) \quad \dots(13)$$

For the experiments in this work in which titanium corrosion was apparent, the average $d \log(i_m)/dpH$ value measured was -0.8 ± 0.1 , which is slightly larger than the expected -0.67 (Eqn (12)), though certainly comparable with other experimental data [3, 13, 16]. Similarly, our experimentally determined values of dE_m/dpH (-71 mV (98°C), -58 mV (80°C) and -28 mV (60°C)) were comparable to the predicted values of -98 mV, -93 mV and -88 mV, respectively.

From the changes in i_m with temperature, the activation energy (E_A) for the dissolution process can be determined using an Arrhenius-like equation:

$$\ln(i_m) = B - \frac{E_A}{RT} \quad \dots(14)$$

where B is a constant. A key feature of using Eqn (14) is that the i_m values used must all be at the same voltage (E_m), otherwise the equation loses validity [42]. It has been reported previously that E_m remains constant for titanium dissolution [19], and our work is consistent (Figure 4(b)); *i.e.*, for 1.0 M H_2SO_4 $E_m = -0.522 \pm 0.029$ V, while in 0.1 M H_2SO_4 $E_m = -0.597 \pm 0.035$ V. Therefore, the use of Eqn (18) is plotted in Figure 5, from which the activation energy was determined to be 67.7 kJ mol^{-1} in 0.1 M H_2SO_4 , and 56.7 kJ mol^{-1} in 1.0 M H_2SO_4 . These values are comparable to previously reported activation energies of 59.9 kJ mol^{-1} in 1 N H_2SO_4 [6]. We might also speculate on the observed trend of increasing activation energy with decreasing H_2SO_4 concentration. Perhaps this is an indication as to the reason why no substantial titanium anodic dissolution current was observed when 0.01 and 0.001 M H_2SO_4 solutions were used; *i.e.*, the activation energy in these electrolytes was too high to allow for any substantial corrosion to occur. Alternatively, anodic dissolution of Ti(III) may have been limited by its solubility in the H_2SO_4 electrolyte used. This also has the potential to influence our determination of the activation energy using this approach. These phenomena will be examined further in future work.

Another key feature of our experimental data is the dielectric breakdown voltage (E_d) of the passive film to allow oxygen evolution to occur. Before discussing the data, bear in mind that the

voltage at which dielectric breakdown occurs should be very much dependent on the thickness of the oxide film, or alternatively, the amount of charge passed in film formation, as well as the temperature of oxidation. Of course it is reasonable to assume that the thicker the oxide film the higher the dielectric breakdown voltage. Firstly, the dielectric breakdown voltage for the matrix of experiments conducted is shown in Figure 6(a). In comparison with i_m (Figure 4(a)) we can qualitatively say that the higher the corrosion current the higher the dielectric breakdown voltage. In an attempt to quantify this we need to assess in some way the thickness of the oxide film formed. An approach to achieving this is to determine the amount of anodic charge (Q_A ; C) passed between E_m and E_d in the steady-state polarization curves for each experiment. E_m was chosen as the starting voltage because it has been suggested that this is the minimum voltage at which titanium oxidation to Ti(IV) begins, with subsequent precipitation of a passive oxide layer. There is certainly the possibility that within the passivation region (Region II in Figure 1) there is still oxidation of the titanium to soluble Ti(III) occurring which could influence the calculated anodic charge. However, after E_m the current drops quite rapidly indicating the passive nature of the oxide film, and hence we might expect the charge associated with Ti(III) formation to be only a small contribution. For those experiments that did not exhibit an active corrosion region, Q_A was determined from the anodic current that flowed up to E_d . Figure 6(b) compares E_d with Q_A for all experiments with the distinction being made between those experiments that did or did not show an active corrosion region, as well as the experimental temperature. As can be seen, there is a degree of linearity between the experiments based on whether substantial active corrosion occurred. In general, more anodic dissolution was observed at higher temperatures; however, as the $\log([H^+])$ values next to the points in the 98°C series in Figure 6(b) indicate, electrolyte composition also had a significant effect on behaviour. For those experiments that did not exhibit an active corrosion region we have assumed that the anodic current that flows is due to the direct formation of an oxide layer on the titanium surface; *i.e.*, no dissolution occurs perhaps also due to low Ti(III) solubility. For these samples E_d increases quite sharply (5.71 V C⁻¹), reflecting the change from an almost bare surface to a complete oxide layer coverage. There are two samples within this category that exhibit anomalous behaviour (circled data points in Figure 6(b)), although their values of E_d are consistent with those experiments that exhibited an active corrosion region. For these experiments the change in E_d is relatively small (0.07 V C⁻¹), indicating that a critical electrode voltage had been reached, beyond which E_d does not need to increase substantially for oxygen evolution to occur on the substrate. This upper line in Figure 6(b) will also include contributions from the experimental temperature on oxygen evolution.

3.4. Effect of Mn²⁺ Inclusion in the Electrolyte

The effects of including soluble Mn^{2+} on titanium corrosion has been investigated using an electrolyte of 1.0 M H_2SO_4 to ensure extensive corrosion. The reason for studying such a system is due to the popularity of titanium as a substrate for the electrolytic production of manganese dioxide. As mentioned in the Introduction, the interface between the titanium and the manganese dioxide has to be conductive, as well as mechanically robust to allow for efficient electrodeposition. In other words, the titanium substrate must not be significantly passivated by an oxide layer otherwise current flow across the interface will be inhibited, hence raising the electrodeposition voltage substantially, and thus increasing the likelihood that oxygen evolution would be the preferred anodic reaction.

A typical example of steady-state anodic polarization in the presence of Mn^{2+} is shown in Figure 7. At low voltages the system exhibits the expected titanium corrosion followed by the passivation process. The most significant difference arising as a result of the inclusion of Mn^{2+} is the presence of an anodic wave beginning at ~ 1.2 V due to the oxidation of Mn^{2+} to MnO_2 ; *i.e.*,

Of course the plateau in current attained at higher voltages is the diffusion limiting current for Mn^{2+} arrival at the electrode surface. At voltages approaching 3.0 V, the electrolyte without Mn^{2+} undergoes dielectric breakdown of the oxide layer, while in the presence of Mn^{2+} this has apparently been pushed to higher voltages since such behaviour was not observed in the polarization curves. Throughout the course of this work characterization of titanium corrosion has been through the analysis of the peak corrosion current (i_m) and voltage (E_m). The effect of including Mn^{2+} on these characteristics is shown in Figure 8. In general, the inclusion of Mn^{2+} in the electrolyte suppresses titanium corrosion. This is particularly true at high temperatures (80°C and 98°C) where the drop in i_m is substantial. Commercial electrodeposition of manganese dioxide occurs at these higher temperature which means that the Mn^{2+} in the plating electrolyte is actually contributing to the prevention of titanium passivation. The mechanism through which the Mn^{2+} prevents corrosion is proposed to involve adsorption of Mn^{2+} ions onto the titanium substrate in such a fashion:

Through such an adsorption process a barrier is established to either inhibit charge transfer in the titanium system ($\text{Ti} \rightarrow \text{Ti(III)}$), or to prevent access of electrolyte species (H^+ in particular) to the electrode surface. It is also such an adsorption process that forms the interface between the titanium substrate and the manganese dioxide deposit.

The changes in E_m for titanium corrosion with the addition of Mn^{2+} are less distinctive, as shown in Figure 8(b). Essentially, for those systems in which corrosion occurred, increasing the

temperature caused a decrease in E_m . The presence of Mn^{2+} at various levels appeared not to have a significant effect on E_m .

Another interesting consequence of Mn^{2+} inclusion in the electrolyte is the apparent overpotential (η) for the manganese dioxide deposition reaction, compared to oxygen evolution. The relevant half reactions and Nernst equations for each process are as follows [43]; *i.e.*,

$$MnO_2 + 4H^+ + 2e^- \leftrightarrow Mn^{2+} + 2H_2O \quad (E^0 = 1.23 \text{ V})$$

$$E = E^0 + \frac{RT}{2F} \ln \left(\frac{(a_{H^+})^4}{a_{Mn^{2+}}} \right) \quad \dots(17)$$

$$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \quad (E^0 = 1.23 \text{ V})$$

$$E = E^0 + \frac{RT}{4F} \ln \left(P_{O_2} \cdot (a_{H^+})^4 \right) \quad \dots(18)$$

To be able to determine the overpotential we have assumed that activities can be replaced by concentrations, and that the partial pressure of oxygen (P_{O_2}) is 0.1 atm. For Mn^{2+} it is reasonable to presume that concentration is the same as activity, except in the more concentrated solutions (0.05 and 0.1 M), in which case we should expect some deviation. In the case of proton activity, given that 1.0 M H_2SO_4 was used as the supporting electrolyte, we should expect there to be some deviation from the concentration. However, given that manganese dioxide deposition has only a two-times greater dependence on proton activity compared to oxygen evolution (Eqns (17) and (18)), any deviation should not be too great. After calculating the equilibrium potentials for both half reactions (also taking into account temperature effects on the standard reduction potential using the Gibbs-Helmholtz equation), the overpotential can be determined as the difference between the experimentally observed oxygen evolution or manganese dioxide deposition voltage and the equilibrium potential. Figure 9 shows the resultant overpotentials. Clearly manganese dioxide deposition on titanium is a much more facile process compared to oxygen evolution, with substantially lower overpotential.

The reasons for the much lower overpotential for manganese dioxide deposition may be due to a similar mechanism as that proposed for the suppression of titanium corrosion. If Mn^{2+} is able to adsorb with oxygen on the titanium substrate, as proposed in Eqn (16), then it should be in an ideal position close to the substrate for it to be oxidized. When this occurs, the resultant manganese dioxide remains *in-situ* on the substrate with the titanium oxide layer merging into the manganese dioxide deposit. The structural transition from the titanium dioxide (for instance) layer to manganese dioxide is also advantageous in the sense that these oxides have similar crystal structures [44] which also means they are more likely to mix with one another. On the other hand, for oxygen evolution to occur either one of two energy intensive processes must occur. The first

possibility involves the oxidation of oxide ions associated with the passive titanium oxide layer. Clearly, these oxide ions are going to be very tightly bound to the titanium ions present, and so would require a very high voltage to be oxidized. In the second case, water molecules from the electrolyte are the source of oxygen. They adsorb on the passive oxide layer and for charge transfer (oxidation) to occur electrons have to tunnel through the passive layer (dielectric breakdown). Given the relatively short distance that electrons can tunnel, again a very high voltage is required to cause oxidation. Overall, the much lower overpotential for manganese dioxide deposition compared to oxygen evolution, does suggest a very close interaction between the starting Mn^{2+} and the titanium substrate.

4. SUMMARY AND CONCLUSIONS

The following key points have arisen from this work:

(i) Steady-state anodic polarization data has been collected for the corrosion of titanium in H_2SO_4 electrolytes ranging in concentration from 0.001-1.0 M, at temperatures from ambient to 98°C. In general, the polarization curves were consistent with previously reported data, exhibiting active corrosion, an active-passive transition, and passive voltage regions. At even higher voltages dielectric breakdown of the passive layer occurred resulting on oxygen evolution.

(ii) For the dilute H_2SO_4 solutions considered our results did not show any evidence of corrosion which is inconsistent with previous work. This was believed to be due to the nature (crystallinity, *etc*) of the titanium substrate, and proposed that future work focus on the role that this material property has on corrosion.

(iii) Active corrosion of titanium was characterized by the peak current (i_m) and voltage (E_m), and how these properties changed as a function of experimental conditions. In particular, $d\log(i_m)/dpH$ was found to be -0.8 ± 0.1 , while dE_m/dpH was determined to be -71 mV at 98°C, -58 mV at 80°C and -28 mV at 60°C. In both instances, our data was consistent with previous experiments. The activation energy for titanium corrosion (E_A) was found to be 67.7 kJ mol^{-1} in 0.1 M H_2SO_4 and 56.7 kJ mol^{-1} in 1.0 M H_2SO_4 , which is consistent with previous data and also is a possible indicator of the reasons why corrosion in more dilute H_2SO_4 solutions did not occur; *i.e.*, increasing activation energy.

(iv) In terms of the dielectric breakdown voltage (E_d), two regions of correlation were found when compared to the estimated amount of anodic charge passed (Q_A) in the formation of the passive TiO_2 layer. With very little charge passed, such as when the titanium did not actively corrode, there was a sharp increase in E_d with Q_A (5.71 V C^{-1}). Beyond this when more anodic charge was passed, such as for those samples that actively corroded, the tendency was still an

increase in E_d with Q_A ; however, the increase was now much less dramatic (0.07 V C^{-1}), perhaps indicating a critical electrode voltage had been reached.

(v) With the inclusion of Mn^{2+} ions in the H_2SO_4 electrolyte, corrosion of the titanium substrate was suppressed substantially. The cause of this was suggested to be due to adsorption of Mn^{2+} ions on the titanium substrate inhibiting active corrosion.

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Figure 1. Typical example of a steady-state anodic polarization curve obtained in this work showing the (I) active, (II) transition, (III) passive, and (IV) dielectric breakdown voltage regions. Inset: Expanded voltage region showing the anodic current dip and rise due to soluble Ti(III).

Figure 2. Current correction for cathodic hydrogen evolution.

(a)

(b)

Figure 3. Typical examples of the effect of (a) H_2SO_4 concentration (60°C) and (b) temperature on titanium corrosion.

(a)

(b)

Figure 4. Data summary of (a) peak corrosion current (i_m) and (b) peak voltage (E_m) as a function of H_2SO_4 concentration and temperature.

Figure 5. Determination of the activation energy for anodic dissolution of titanium.

(a)

(b)

Figure 7. Steady-state anodic polarization curves showing the effects of including Mn^{2+} in the electrolyte. $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$; $T = 80^\circ\text{C}$.

(a)

(b)

Figure 8. Effect of Mn^{2+} inclusion on (a) i_m and (b) E_m for titanium corrosion.

Figure 9. Overpotential (η) for oxygen evolution compared to manganese dioxide deposition as a function of $[\text{Mn}^{2+}]$ and temperature.