PHYSICAL AND ELECTROCHEMICAL PROPERTIES OF COATED TITANIUM ANODES

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DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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ABSTRACT

The service life and electrocatalytic activity of tantalum oxide/iridium oxide coated titanium plate and mesh anodes used in the electrolytic production of chromic acid were investigated by performing accelerated life tests, voltammetric and chronoamperometric measurements in chrome (VI) solutions.

Experimental results showed that the service life for the coated mesh anode was 1059 hours, compared to 828 hours for the plate anode at a current density of 1.2 A cm^{-2}. In addition, the coating failed earlier in higher chromic acid concentration. Physical analysis by SEM and EDS before and after accelerated life test confirmed that the deactivation was a result of corrosion of IrO_2 followed by titanium substrate passivation.

A simple and rapid method for assessing the electrocatalytic activity of iridium–tantalum oxide coating based on a chronoamperometric technique was developed.

DEDICATION

To my family,

Ntunka

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- All other people with whom I came into contact with for all their cooperation and friendliness.
- My Heavenly Father, without whom, nothing is possible.

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List of symbols and abbreviations

A	area of electrode (m^2)
e^-	elementary charge of an electron (1.60217646 × 10^{-19} coulombs)
c_O	concentration of oxidising species in the bulk solution (mol m^{-3})
c_R	concentration of reducing species in the bulk solution (mol m^{-3})
C_k	kinetic term of current response in the chronoamperometry experiment (A cm^{-2})
C_{k+d}	kinetic and diffusionnal term of current density response in the chronoamperometry experiment (A cm^{-2})
ΔG	free energy change (kJ mol^{-1})
D	diffusion coefficient (m^2 s^{-1})
E_e^0	formal electrode potential for the couple O/R vs. a reference electrode (V)
E_{CELL}^e	reversible (equilibrium) difference potential of the cell reaction (V)
E_C^e	equilibrium cathode potential vs. a reference electrode (V)
E_A^e	equilibrium anode potential vs. a reference electrode (V)
E	experimental electrode potential vs. a reference electrode (V)
ΔE^*	electrode potential difference corrected with IR drop (V)
$erfc$	complementary error function
ϕ_0	current density at $t = 0$ s. Data from chronoamperometry experiment (A cm^{-2})
I	current (A)
IR_{CELL}	ohmic potential drop in the cell (inter-electrode gap) (Ω)
IR_{CIRC}	ohmic potential in the electrical circuit (Ω)
j	current density (A cm^{-2})

$\vec{j}$	partial cathodic current density for (A cm^{-2})
$\overleftarrow{j}$	partial anodic current density for (A cm^{-2})
j_0	exchange current density (A cm^{-2})
$\vec{k}$	rate constant for the cathodic reaction (m s^{-1})
$\overleftarrow{k}$	rate constant for the anodic reaction (m s^{-1})
$\vec{k}_0$	rate constants for electron transfer when the potential is zero versus a defined reference electrode; cathodic reaction (m s^{-1})
$\overleftarrow{k}_0$	rate constants for electron transfer when the potential is zero versus a defined reference electrode; anodic reaction (m s^{-1})
K	is a proportionality constant depending on electrode material and environment
n	number of electrons involved in an electrode process (dimensionless) or a parameter ranging between 1.4 and 2.0 in ALT tests
η_C	cathodic overpotential (V)
η_A	anodic overpotential (V)
η	overpotential (V)
T	temperature (K)
t	time from beginning of experiment (h) or (s)
α_C	cathodic transfer coefficient (dimensionless)
α_A	anodic transfer coefficient (dimensionless)
O / R	oxidising / reducing species
R	gas constant (J K^{-1} mol^{-1})
SL	service life (h)
ALT	accelerated life test
NOR	normal plant operating conditions
CV	cyclic voltammetry
LSV	linear sweep voltammetry

CA	chronoamperometry
SEM	scanning electron microscopy
EDS	energy dispersive X-ray spectroscopy

Chapter 1 Introduction and literature survey

This chapter provides the following information:

- Background to this study
- Review of the literature on coated titanium anodes
- The aims and scope of the present study
- A theoretical background on thermodynamics and kinetics of electrode processes with a discussion of the electrochemical techniques used, in order to facilitate interpretation of the results presented in a later chapter.

1.1 Background to this study

Traditionally, chromic acid is produced by the reaction of sodium dichromate with concentrated sulphuric acid. In a process recently developed, the conversion is made by electrolysis from sodium dichromate in a divided electrolytic cell as shown in Figure 1.1.

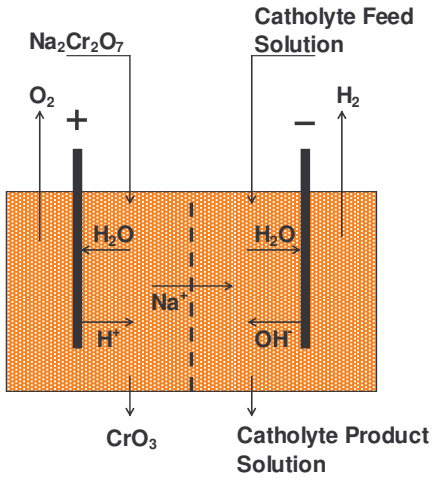


Figure 1.1 Electrolytic production of chromic acid

For this electrolytic process route, the cell reactions are as follows:

Anode:

$$H_2O \rightarrow 2H^+ + \tfrac{1}{2}O_2^{\uparrow} + 2e^- \qquad E_e^0 = 1.225\ V \qquad 1.1$$

Cathode:

$$2H_2O + 2e^- \rightarrow H_2^{\uparrow} + 2OH^- \qquad E_e^0 = -0.828\ V \qquad 1.2$$

The overall electrochemical process involves oxidation and reduction of water with O_2(g) and H_2(g) being by products of the chromic acid production. Details related to conversion of dichromate to chromic acid are not included due to proprietary restrictions.

Reaction (1.1), the oxygen evolution reaction (OER), is one of the most important anodic reactions in electrochemical engineering coupled with the cathodic systems occurring in aqueous solutions such as water electrolysis, metal electrowinning, electrosynthesis, etc. It operates at high overpotential in many electrochemical processes, so that the economics of the entire process is often governed by that reaction. Moreover, OER generally creates very aggressive corrosion conditions for the electrode material. This is particularly true in acid solutions, where these conditions are enhanced. (Hrussanova et al., 2004) Following the successful use of coated titanium anodes in the chlor-alkali industry, similar anodes have been proposed as alternatives for the various lead alloys currently used.

The recently developed anodes consist of precious metal oxide coatings on a high grade titanium metal substrate. Titanium is used because of its excellent chemical resistance as well as its ability to passivate when made anodic. The titanium can be in any form; sheet, mesh, rod, etc. The precious metal oxide is an electrocatalyst, that is, it minimizes the overvoltage at which oxygen evolves at its surface. The electrocatalytic

coating contains a precious metal oxide plus one or more non-noble metal oxide. The metals are chosen so that they form a mixed crystal lattice with the precious metal. This stabilizes the precious metal and minimizes its wear rate. (Malkin, 1982)

Oxides such as IrO_2, PtO_x, SnO_2, Co_3O_4 and Ta_2O_5, and some oxide mixtures have been used to improve anodic stability and increase service life. An oxide anode with a mixture of IrO_2 as the active component and Ta_2O_5 as the inert component has long been of great interest, due to its excellent performance in the electrochemical oxygen evolution environment. (Xu and Scantlebury, 2003)

Since its discovery in 1960s, by Beer (Xueming et al., 2005), the classical RuO_2 -TiO_2 coated titanium anode has proved to be unstable for OER due to serious corrosion of the RuO_2 active component in the oxide mixture. A significant decrease in electrode performance is also observed for the IrO_2 coated titanium. This deactivation is noticed on irregular and largely unpredictable time intervals without obvious links of this lifespan to the origin of manufacture, process operation, etc.

The cost of these electrodes and the down-time required for the replacement is a significant contributor to the profitability of the plant. In addition, during deactivation there is an increase in the voltage applied to the cell. This is directly related to the energy consumed in the electrolysis section.

In this study, the electrode degradation will be investigated using the oxygen evolution reaction as the model reaction in typical plant solution conditions using accelerated life tests, while the change of electrocatalytical properties will be monitored by chronoamperometric and voltammetric methods. These electrochemical characteristics are measured using commercially prepared samples. Once suitable

procedures have been developed and validated, these will be implemented on a sample of an industrial expanded mesh electrode.

1.2 Review of the literature on coated titanium anodes

Investigations of electroactivity, stability and service life of oxide coatings, such as Ta_2O_5/IrO_2, have been carried out, and their applications, anode modification and degradation mechanism were discussed by many workers. (Xu and Scantlebury, 2003) Anodes consisting of a titanium substrate with Ta_2O_5/IrO_2 coatings have been successfully tested for OER in sulphate solutions. However, to the best of our knowledge, no previous investigation has been done in chromic electrolytes. The electrode performance is found to be dependent on operating conditions as well as the nature and concentration of the electrolyte, temperature and current density. (Martelli et al. 1994)

An extensive search of an oxygen evolution electrocatalyst has been performed in the laboratory by Comninellis since the late 1980s (Chen et al., 2003). A great number of binary oxide mixtures were examined. It was found that IrO_2-Ta_2O_5 was the best pair among various combinations. The optimum molar ratio of IrO_2 to Ta_2O_5 is 70:30, below which the electrode stability decreases rapidly. The service life of Ti/IrO_2-Ta_2O_5 (with 70 mol % IrO_2) was estimated to be from 5 to 10 years based on an accelerated electrolysis test performed in 0.5 M H_2SO_4 at a current density of 2 A cm^{-2}. (Mraz et al., 2003)

Titanium coated anodes have been studied widely and intensively in the field of electrocatalysis. Otogawa et al. (1998) studied the effect of the microstructure of IrO_2-based anodes on electrocatalytic properties and found that the surface structure affected significantly the electrocatalytic activity. Oliveira-Sousa et al. (2000) also proved that the preparation method influenced the morphological and electrochemical properties of Ti/IrO_2-coated electrodes. Hu et al. (2002) proposed a degradation

mechanism for a long service life during electrolysis in sulphuric acid. Xu and Scantlebury (2003) characterized physically and electrochemically titanium electrodes used in cathodic protection. Da Silva et al. (2004) recently reported on details of the surface, kinetic and electrocatalytic properties of Ti/(IrO_2+Ta_2O_5) electrodes, prepared using controlled cooling rate, for simultaneous oxygen evolution and ozone production processes. Their study showed that these processes depend on both electrode coating composition and the nature of supporting electrolyte.

1.3 Aims and scope of the present study

The aims of this project are:

- to develop an accelerated life test (ALT) to establish the mechanisms by which the tantalum–iridium oxide coatings on titanium substrates (plate and mesh) fail;
- to apply various electrochemical techniques to measure the activity of the electrode surface before and during ALT.

This dissertation contains four chapters. The first chapter provides the aims of the investigation, historical development and current state of the literature on coated titanium anodes, and the theoretical background of thermodynamics, kinetics and electrochemical techniques used in this study.

In Chapter 2 general experimental procedures employed to perform accelerated life test and electrochemical tests are described.

Chapter 3 contains the presentation and the discussion of the data collected and analysed in this study.

In Chapter 4 the main conclusions of this study are summarised, a procedure for rapid evaluation of anode performance is proposed, and some recommendations for further research are made.

1.4 Theoretical background

1.4.1 Electrochemical thermodynamics

An electrode process is a heterogeneous chemical reaction, which occurs via the transfer of charge, usually electrons, across the interface between an electrode and an electrolyte.

$$O + ne^{-} \quad R \qquad 1.3$$

The minimum components required for an electrochemical reaction to take place are an anode at which oxidation of species occurs, a cathode at which reduction occurs, ionic contact between the electrodes via an electrolyte and electronic contact between them, i.e. an external electrical circuit. (Walsh, 1993)

For electrolysis to occur, energy must be supplied by applying a potential across the electrodes. The magnitude of the essential equilibrium cell potential E^{e}_{CELL} may be calculated from Gibbs function:

$$\Delta G = -nFE^{e}_{CELL} \qquad 1.4$$

where ΔG is the change in Gibbs function, n is the number of electrons involved in the reaction, F is the Faraday constant and E^{e}_{CELL} is the reversible (equilibrium) difference potential of the cell reaction.

By convention, the reversible cell potential is defined as the difference between the equilibrium potentials of the cathode and the anode:

$$E^e_{CELL} = E^e_C - E^e_A \qquad 1.5$$

where the equilibrium cathode and anode potentials may be obtain from the Nernst equation,

$$E_e = E^0_e + \frac{2.3RT}{nF}\log\frac{c_O}{c_R} \qquad 1.6$$

where E^0_e is the formal potential for the redox reaction in the solution under standard conditions, n is the number of electrons involved in electrode reaction, R is gas constant, T is the temperature, c_O and c_R respectively concentrations of both species O and R. More correctly, these thermodynamic equations should be written in terms of ratios of activities. (Pletcher, 1991)

The equilibrium potential E_e can only be measured by comparing it to the potential of another redox couple. The standard hydrogen electrode (SHE) is used as the reference basis for the redox couples. A standard equilibrium potential of 0.0 V is assigned to SHE when it is used as reference electrode. The standard hydrogen electrode is not the only one reference electrode used in electrochemistry. The standard calomel electrode (SCE) has a standard equilibrium potential of 0.242 V vs. SHE at 298 K. The silver – silver chloride electrode at 298 K and 1 M KCl has 0.222 V with respect to the SHE. (Hamann et al., 1998)

The application of the equilibrium cell potential would, however, not enable reactions to occur. It is essential to apply overpotentials to each electrode to enhance the rate of the electron transfer processes and also to supply a potential to drive the current through the electrolyte solutions. Overall, the cell voltage, which is applied between the two electrodes to allow the current, I is given by (Walsh, 1993)

$$E_{CELL} = E^{e}_{CELL} + \eta_C + \eta_A + IR_{CELL} + IR_{CIRC} \quad 1.7$$

where η_C and η_A are respectively the cathodic and anodic overpotential terms, IR_{CELL} includes ohmic voltage drop in the inter-electrode gap and IR_{CIRC} is the ohmic voltage in the electrical circuit. E^{e}_{CELL} is the thermodynamic decomposition potential determined by the difference potential at equilibrium between cathode and anode.

1.4.2 Pourbaix diagrams

The use of an electrochemical equilibrium diagram for studying aqueous electrode processes is of great importance. It enables the determination whether (i) a solid system is in a region of immunity where the tendency of corrosion is nil, (ii) in a region where the tendency of corrosion is high, or (iii) in a region where the tendency for corrosion may still exist but where there is a tendency for a protective or passive film to form. Those diagrams are found by plotting electrode potential against pH measurements. Such diagrams are called Pourbaix diagrams. They are based on thermodynamics, and indicate the stable phase for given conditions but say nothing about rates of reactions. (Pourbaix, 1974)

These diagrams are constructed considering the metal (M), metal ion (M^{n+}), oxide and hydroxide equilibrium and Gibbs function data for the formation of the ions concerned. For reactions involving charge transfer, the equilibrium potentials are calculated from the Nernst equation (1.6) and equation (1.4).

Thick solid lines represent the phase boundaries of the solid phase oxides. Diagonal dashed lines (a) and (b) in such as Figure 1.2, represent the equilibrium potentials of the hydrogen and oxygen evolution reactions, respectively, in the aqueous solutions. Between the lines (a) and (b) water

is stable, below the line (a) water decomposes with evolution of hydrogen, and above line (b) water decomposes with evolution of oxygen.

a. Stability of CrO_3

Potential-pH diagram for the chromium - water system are presented in Figure 1.2.

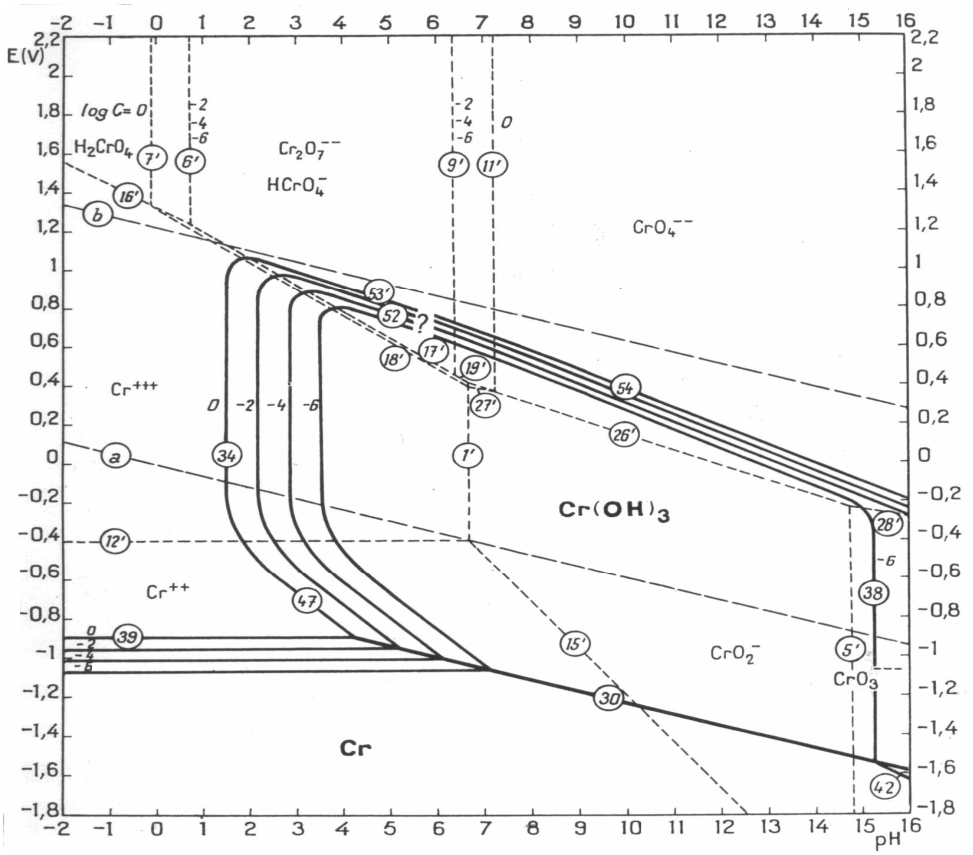


Figure 1.2 Representative potential-pH equilibrium diagram for the chromium-water system, chloride free, at 25º C. Labels 0, -2, -4 and –6 are the log of soluble ion activity for the indicated lines. (Pourbaix, 1974)

The diagram illustrates that chromium acts as a base metal in acid solutions. It dissolves as either Cr^{2+} or Cr^{3+}, through either O_2 reduction or H^+ reduction. In neutral and alkaline solutions it tends to become covered with a passive a layer of Cr_2O_3.

At high potential, above line (b), the chromium dissolves in acid solution to give hexavalent species, mainly, $HCrO_4^-$ and $Cr_2O_7^{2-}$. It can be deduced from Figure 1.2 that at high potential and low pH, H_2CrO_4, $Cr_2O_7^{2-}$ and $HCrO_4^-$ are present in solution during the electrolysis in chrome medium and chromium (VI) species are very stable and cannot be oxidize at the anode.

b. Stability of IrO_2

Figure 1.3 represents the conditions of thermodynamic equilibrium of the system iridium-water, at 25º C.

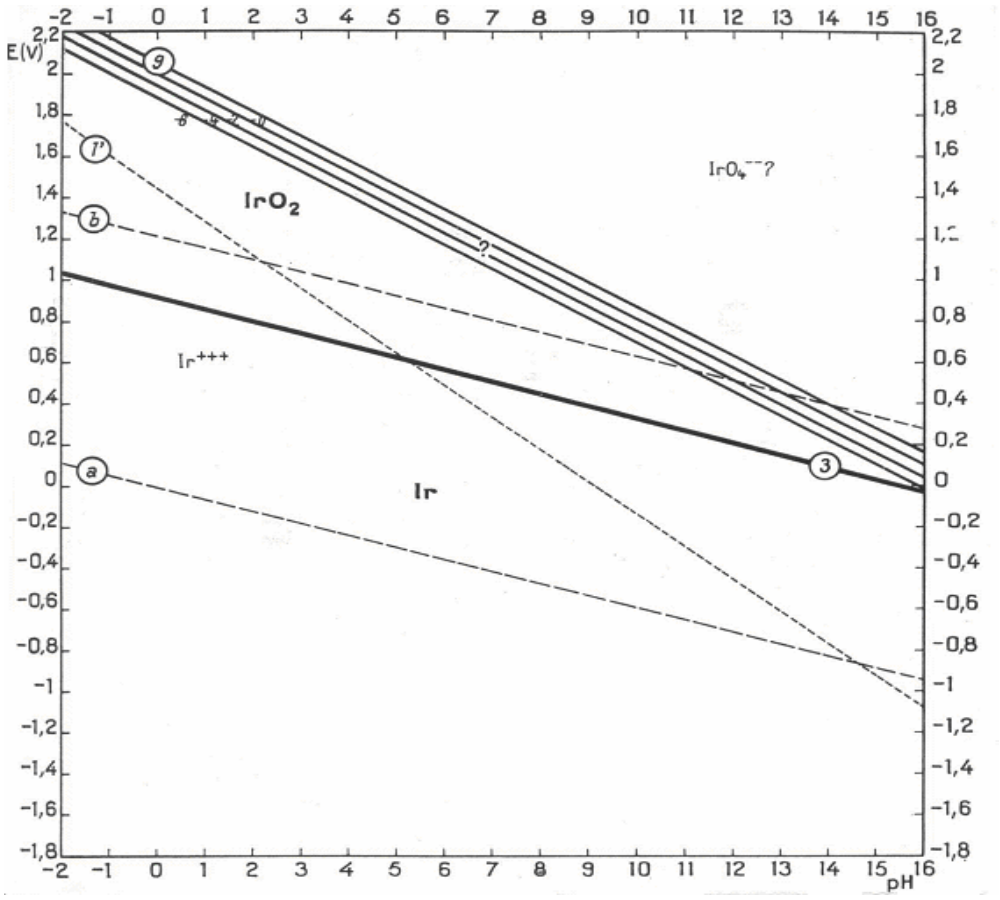


Figure 1.3 Potential-pH equilibrium diagram for the system iridium-water, at 25º C. (Pourbaix, 1974)

According to Figure 1.3, IrO_2 should be insoluble in acid solutions and should be soluble in alkaline solutions. But at low pH and high potential, it might be soluble and form iridates (IrO_4^{2-}) according to the following reaction:

$$IrO_2 + 2H_2O \rightarrow IrO_4^{2-} + 4H^+ + 2e^- \qquad 1.8$$

c. Stability of Ta_2O_5

The Pourbaix diagram (Pourbaix, 1974) for the system tantalum-water at 25 ºC shows the predominance stability for Ta_2O_5 in the high potential region and at very low pH. It means that Ta_2O_5 is a substance, which is thermodynamically stable in the presence of water and also acid.

d. Stability and corrosion of Ti

Titanium is not a noble metal. In actual fact its domain of thermodynamic stability in water lies well below the latter. If this metal is used at high electrode potential, a passivating film of oxide is formed on its surface. This covering protects the metal from further deterioration.

The potential–pH diagram for the system titanium-water (Pourbaix, 1974) shows that the domain of stability of TiO_2 covers the domain of stability of water. The oxide is very stable.

1.4.3 Butler-Volmer Equation

Electrode reactions, as heterogeneous processes, are generally not simple and involve a number of steps, which can occur consecutively or simultaneously. These steps generally involve three processes: a mass transport process of the reactant from the bulk solution to the interface, a surface reaction at the electrode, and a mass transport process of the product from the interface to the bulk solution. See Figure 1.4.

$$O_{bulk} \xrightarrow{mass\_transport} O_{electrode}$$

$$O_{electrode} \xrightarrow{electron\_transfer} R_{electrode}$$

$$R_{electrode} \xrightarrow{mass\_transport} R_{bulk}$$

Figure 1.4 Steps involved in the overall electrode process, $O + ne^- \rightarrow R$ where O and R are solution phase species.

The rate of the overall process will be determined by the rate determining step of these three steps.

An electrochemically controlled reaction is one in which the rate determining step involves the transfer of charge across the electrode – solution interface – see second process in Figure 1.4. For an electrochemical reaction (Equation 1.3), the partial cathodic and anodic current densities at each potential are given by (Pletcher, 1991):

$$-\vec{j} = nF\vec{k}c_O \qquad 1.9$$

$$\overleftarrow{j} = nF\overleftarrow{k}c_R \qquad 1.4$$

where $\vec{j}$ and $\overleftarrow{j}$ are current densities for the reduction and oxidation reactions respectively, $\vec{k}$ and $\overleftarrow{k}$ are electrochemical rate constants of reduction and oxidation where the reaction orders are assumed to be one with respect for both the oxidation and the reduction, c_O and c_R the concentration of species.

It is found empirically that the rate constants of heterogeneous electron transfer $\vec{k}$ and $\overleftarrow{k}$ are strongly dependent upon the applied potential. Assuming an exponential variation with potential (always found experimentally), leads to the relationship between the current density and the electrode potential:

$$j = \overleftarrow{j} + \vec{j} \tag{1.11}$$

$$j = nF\overleftarrow{k}_0 c_R \exp\left(\frac{\alpha_A nFE}{RT}\right) - nF\vec{k}_0 c_O \exp\left(\frac{-\alpha_C nFE}{RT}\right) \tag{1.12}$$

The constants $\vec{k}_0$ and $\overleftarrow{k}_0$ are defined as the rate constants for electron transfer when the potential is zero versus a defined reference electrode, and have no fundamental significance due to their arbitrary nature. E is the experimental electrode potential.

α_A and α_C are constants known as the anodic and cathodic transfer coefficients, which sum to one, $\alpha_A + \alpha_C = 1$, for a simple electrode reaction and commonly the transfer coefficients both have value close to 0.5. The transfer coefficients are also called Tafel constants and are important kinetic parameters of electrode processes.

By defining the overpotential as:

$$\eta = E - E_e \tag{1.13}$$

where E_e is given by Nernst equation (Equation 1.6).

By recalling that the partial anodic and cathodic current densities at the equilibrium potential are equal and known as the exchange current density, Equation 1.12 at the equilibrium potential leads to:

$$j_0 = nF\overleftarrow{k}_0 c_R \exp\left(\frac{\alpha_A nFE_e}{RT}\right) = -nF\vec{k}_0 c_O \exp\left(\frac{-\alpha_C nFE_e}{RT}\right) \tag{1.14}$$

By making substitution of equation (1.13) into (1.12) and using the equalities of Equation 1.14, it can be shown that:

$$j = j_0\left[\exp\left(\frac{\alpha_A nF\eta}{RT}\right) - \exp\left(\frac{-\alpha_C nF\eta}{RT}\right)\right] \tag{1.15}$$

where j_0 is the exchange current density.

Equation 1.15 is known as the Butler–Volmer equation which describes the relationship between the current density through an electrode and the potential difference across the electrode–solution interface. For a given reaction, i.e. a known n value, at constant temperature T, the j vs. η characteristics will depend upon the exchange current density, j_0 and the transfer coefficients for anodic and cathodic processes (α_A and α_C).

For positive values of η the first exponential term in equation (1.15) is greater than unity, while the second is less than unity – the net current density is positive, in other words anodic. For $\eta < 0$, the net current density is of negative sign, or cathodic. The situation at equilibrium ($\eta = 0$) is a dynamic one, the oxidation and reduction reactions are occurring at equal rates given by j_0. Three limiting forms of equation (1.15) may be derived:

When $\eta \gg 0$: $$j \gg \vec{j} = -j_0 \exp\left(\frac{-\alpha_C nF\eta}{RT}\right)$$

or $$\log - j = \log j_0 - \frac{\alpha_C nF\eta}{RT} \qquad 1.16$$

$\eta \gg 0$ $$j \gg \overleftarrow{j} = j_0 \exp\left(\frac{\alpha_A nF\eta}{RT}\right)$$

or $$\log j = \log j_0 + \frac{\alpha_A nF\eta}{RT} \qquad 1.17$$

when $\eta \approx 0$ $$j = j_0 \frac{nF\eta}{RT} \qquad 1.18$$

Equations (1.16) and (1.17) are known as the Tafel equations. It can be seen that, at both positive and negative overpotentials, there will be a linear relation between $\log|j|$ and η. The Tafel equations provide a useful method for determination of the kinetic parameters α_C, α_A and j_0 from a

set of charge transfer controlled j vs. η data, as illustrated by the "Tafel plots" in Figure 1.5

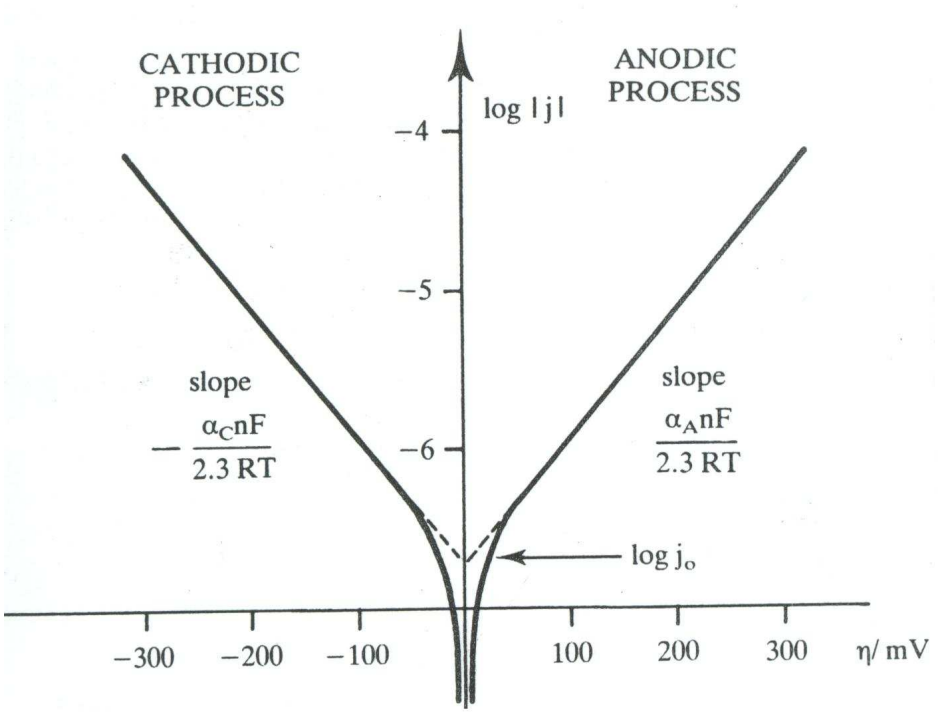


Figure 1.5 Semilog plot of j vs. η data to obtain kinetic parameters, Tafel slopes and exchange current density j_0.

Tafel slopes are given respectively by:

$$\frac{-\alpha_C nF}{2.3RT} \quad \text{and} \quad \frac{\alpha_A nF}{2.3RT} \qquad 1.19$$

For a reaction where $n=1$ and $\alpha_A = \alpha_C = 0.5$, the slopes will be both 1/120 mV or 120 mV decade^{-1}. The importance of the Tafel slope is that it contains information relating to the mechanism of the overall electrochemical reaction.

a. Exchange current densities

In the absence of any current, a dynamic equilibrium will exist where the partial cathodic and partial anodic current densities are equal in magnitude but opposite in sign. The magnitude of the partial current densities at equilibrium is known as the exchange current density, j_0 :

$$j_0 = \vec{j} = \overleftarrow{j} \qquad 1.20$$

This important kinetic parameter is a measure of the degree of electron transfer activity at the equilibrium potential. It is a measure of the electrocatalytic properties of the electrode for a given reaction and it is often very dependent upon the electrode material. A high value of the exchange current density leads to a significant current density at low overpotentials as illustrated in Figure 1.6. Reactions with large exchange current densities (i.e. typically > 10^{-7} A cm^{-2}) are generally termed reversible electrochemical reactions, and those with low values for j_0 (i.e. < 10^{-8} A cm^{-2}) are called irreversible electrochemical reactions. (Paul, 1983)

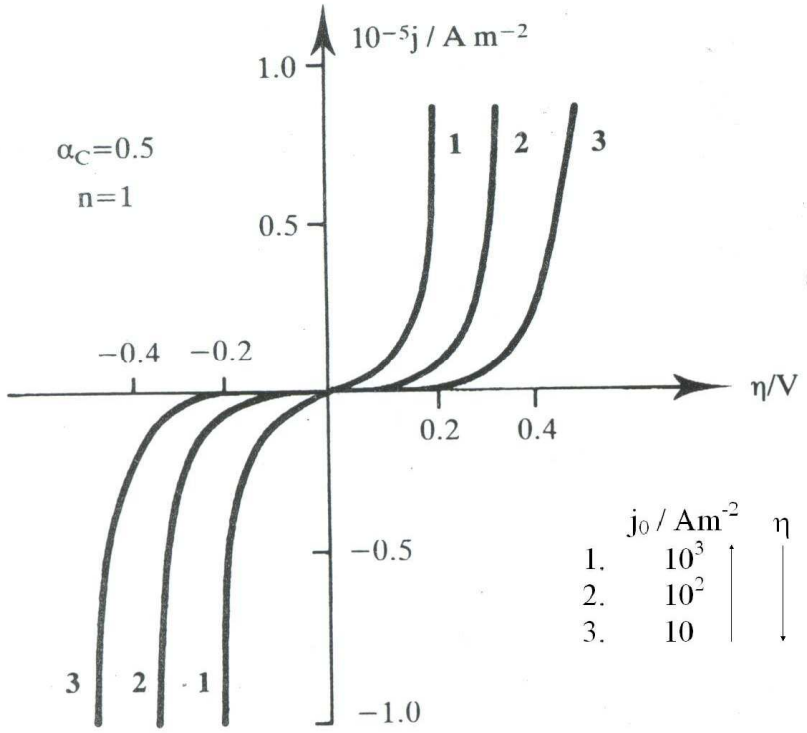


Figure 1.6 The influence of the exchange current density on the j-η response when $\alpha_A = \alpha_C = 0.5$

The exchange current density may be indirectly obtained by Tafel extrapolation, derived from the Butler - Volmer equation.

1.4.4 Performance of electrode material Ti/IrO_2-Ta_2O_5 for oxygen evolution reaction

a. General properties

The selection of the appropriate anode material is of great importance for successful electrochemical processes. Walsh (1993) gives a useful general guideline in the choice of electrode material as shown in Table 1.1

Table 1.1 General properties an of electrode material

1. High physical stability
2. High chemical stability
3. High electrical conductivity
4. Ease of fabrication into a suitable physical form
5. Suitable electrocatalytic properties
6. Long lifetime
7. Non-polluting and non-contaminating
8. Low cost
9 Safe
10. Readily available

Among all these characteristics, for a technological application, electrode stability, service life and electrochemical activity are always of main concern.

b. Coating for oxygen evolution reaction

Dimensionally stable anodes (DSA) use conductive platinum group metal (PGM) oxides as electrocatalysts on a titanium substrate. RuO_2 is known to be the most attractive electrocatalyst because it has exhibited excellent activity for both Cl_2 and O_2 evolution. (Chen et al. 2005) But the electrode anodes with RuO_2-TiO_2 coatings have a limited service life in the case of oxygen evolution due to the corrosion of active component (RuO_2).

In principle, many other catalysts could be used. Many papers (i.e. Martelli et al., 1994) describe the properties of various combinations between PGM oxides (RuO_2, IrO_2, PtO_x) - the catalysts, and valve metal oxides (TiO_2, ZrO_2, Ta_2O_5) – the stabilizers, applied as coating on the substrates

of different substrate metals (Ti, Zr, Ta, Nb). Stable ternary electrocatalyst like IrO_2 - Sb_2O_5 – SnO_2, RuO_2- Sb_2O_5 – SnO_2 for oxygen evolution have been successfully developed showing a better service life under harsh operating conditions. (Xueming et al., 2005)

An analysis of the behaviour of various coatings, applied on Ti substrate, that confirms the best coating for oxygen evolution in acidic solutions is: Ti / IrO_2 – Ta_2O_5 based on the concept of anodic efficiency and stability. (Martelli et al., 1994) These authors and others demonstrated electrocatalytic properties and electrode stability for O_2 evolution only in sulphate and alkaline medium.

c. Oxygen evolution reaction at Ti/IrO_2-Ta_2O_5

Many researchers have studied coated titanium anodes for oxygen evolution in the past decade. (Hu et al., 2004). In acid media the following reaction scheme was proposed as the mechanism for oxygen evolution:

$$S + H_2O \rightarrow S - OH_{ads} + H^+ + e^- \qquad 1.21$$

$$S - OH_{ads} \rightarrow S - O_{ads} + H^+ + e^- \qquad 1.22$$

$$S - O_{ads} \rightarrow S + \tfrac{1}{2} O_2^{\uparrow} \qquad 1.23$$

where S stands for active sites on the oxide surface, and $S - OH_{ads}$, $S - O_{ads}$ are two adsorption intermediates. This mechanism predicts the following Tafel slopes: 120 mV decade^{-1} if step (1.21) is the rate determining step, 40 mV decade^{-1} for step (1.22) and 30 mV decade^{-1} for step (1.23). (Hu et al., 2004) The rate determining step depends on the strength of the adsorption intermediates, which in turn is governed by the composition of the oxide layer.

Another model proposed for oxygen evolution reaction could be through dissolution of IrO_2. (Kulandaisamy et al., 1997) Starting from $Ir(OH)_3$, a deprotonation step leads to the formation of $IrO(OH)_2$ with Ir in the tetravalent state. After another two deprotonation steps, IrO_3 is formed, with Ir in the hexavalent state, where oxygen is split off. Simultaneously uptake of one water molecule leads back to tetravalent iridium as the starting position for the cycle.

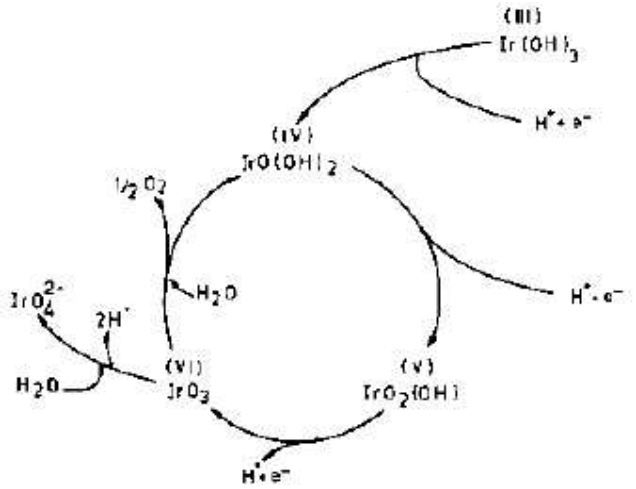


Figure 1.7 Model for oxygen evolution and dissolution of IrO_2

d. Brief description of deactivation mechanisms of Ti/IrO_2-Ta_2O_5

The degradation of an electrode material depends on three major operating conditions: the current density, electrolyte composition and temperature. Martelli et al. (1994) has demonstrated the deactivation mechanisms of oxygen evolving anodes by looking at how these parameters influence degradation. A little change in one of these parameters affects the reproducibility of the process significantly.

They classified the deactivation mechanism on Ti/IrO_2-Ta_2O_5 into five classes which are not to be considered as rigidly separated, namely: metal base passivation, coating consumption, coating detachment, mechanical damage and a mixed mechanism.

Passivation

Passivation is the most frequent deactivation mechanism associated with operations at high current densities (> 10 A cm^{-2}). This behaviour is attributed to the formation of an insulating layer of TiO_2 at the interface between the metallic base and the active coating.

It is characterised by a sudden increase of electrode potential that reaches very high values, signifying a large electrical resistance.

Coating consumption

Coating consumption probably occurs as a result of chemical consumption and/or electrochemical corrosion.

The chemical consumption occurs via interactions with electrolyte components or impurities contained therein. For instance, Hardee (Martelli, 1994) indicated that phosphates or chromates could react preferentially with the tantalum component. Organic impurities may react with PGM's, forming stable complexes. In general, all substances able to promote the consumption of at least one component of the coating, changing the surface ratio, will promote the mixed deactivation mechanism of consumption and passivation.

The electrochemical consumption is an oxidation and dissolution of noble oxide at high potentials reached by the electrode. For a coating containing IrO_2, dissolution via electrochemical dissolution is possible – see reaction 1.8. It was reported that at sufficiently high potentials [higher than 2.0 V vs. normal hydrogen electrode], the formation of IrO_4^{2-} is promoted. It also has been pointed out that during its life, the electrode material for oxygen evolution rarely reaches these high potentials. (Martelli et al., 1994)

Coating detachment

Detachment is promoted by all those factors able to weaken the bonding between the metal base and the coating like chemical attack of base metal by acidic electrolyte or electrolyte containing F^- ions. In general, the bonding between the coating particles is usually very good. In spite of this, erosion is possible, mainly because the metal mixed oxide coating is porous and the gas evolution at the surface is large and can induce the detachment of some of coating particles that are weakly bonded to the substrate.

Mechanical damage

Mechanical damage is a trivial cause of deactivation. This can destroy a good coating in a few seconds.

Mixed mechanisms

In practice it is most likely that two or more of the above mechanisms result in deactivation of the anode.

1.4.5 Electrochemical techniques for assessing service life and electroactivity of coated titanium anodes

a. Introduction

Several techniques exist to discern and characterize coated titanium anodes. These include accelerated life tests, cyclic voltammetry, linear sweep voltammetry, chronoamperometry and alternating current impedance spectroscopy.

In most electrochemical techniques, there are three electrodes – the working electrode (WE), the reference electrode (RE) and the counter (or auxiliary) electrode (CE). Three electrodes are connected to a potentiostat

(galvanostat), an instrument which controls the potential (current) of the working electrode and measures the resulting current (potential).

In this work, four types of techniques were used, namely, cyclic voltammetry, linear sweep voltammetry, chronoamperometry and accelerated life test. These techniques will be described in the following sections

b. Accelerated life test (ALT)

Accelerated life test is just a standard electrolysis where current density is fixed and the cell voltage is recorded during the test. In order to accelerate the deactivation, the electrolyte concentration, the temperature, or the current density are increased. Operating in this way, a particular deactivation mechanism is forced. Anode deactivation is indicated when cell voltage rises steeply at constant current density.

A typical response for the last named is shown in Figure 1.8 in which an extended zone with slight potential variation is observed, followed by a swift rise to higher potential. The time for the voltage to rise to 10 V defines the failure time. This value is the time required for a total removal of the electroactive surface coating. (Pilla et al., 1997)

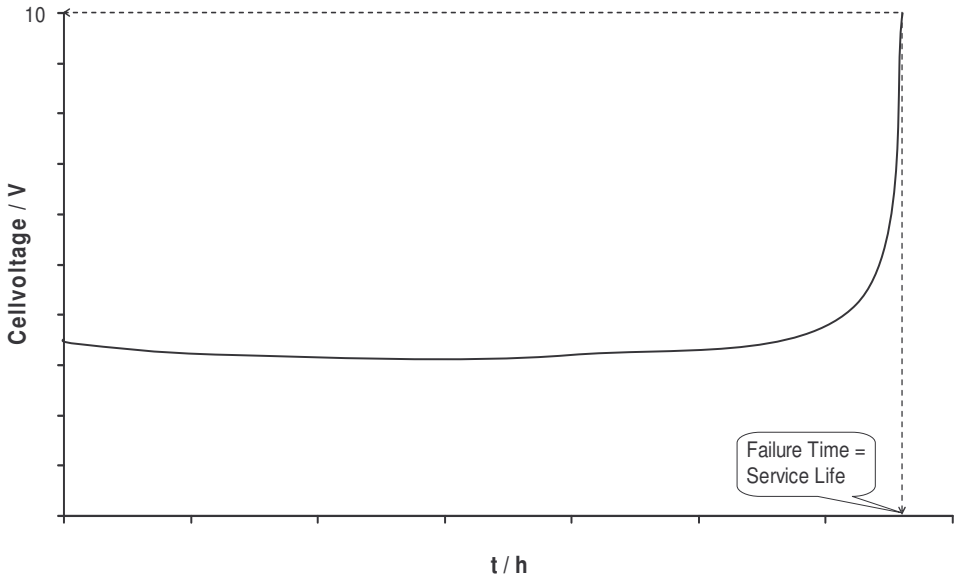


Figure 1.8 General time dependence of electrode potential in the accelerated life test. The failure time or service life equals to the time when the anode potential reaches 10 V.

Many approaches can be followed for analysing the profile of electrode potential as a function of electrolysis time in order to predict the service life of an electrode material from accelerated testing. In this work, we only present one of them.

Chen et al. (2005) reporting the work of Hine and Malkin propose an empirical relationship between the electrode service life (SL) and the current density (j) as follows:

$$SL_{ALT} = \frac{K}{j_{ALT}^{n}} \qquad 1.24$$

and

$$SL_{NOR} = \frac{K}{j_{NOR}^{n}} \qquad 1.25$$

where SL_{ALT} is the service life in hours as measured by the ALT, j_{ALT} is the current density in Acm^{-2} in the ALT test, SL_{NOR} is the service life in hours as expected in normal operating conditions, j_{NOR} is the current density in A cm^{-2} in normal plant conditions, n is a parameter ranging between 1.4 and 2.0, K is a proportionality constant depending on electrode material and environment.

By dividing Equation (1.25) by Equation (1.24) leads to

$$\frac{SL_{NOR}}{SL_{ALT}} = \frac{j_{ALT}^{n}}{j_{NOR}^{n}} \qquad \Rightarrow \qquad SL_{NOR} = SL_{ALT} \times \left(\frac{j_{ALT}}{j_{NOR}} \right)^{n} \qquad 1.26$$

Given accelerated life test conditions and the service life experimentally found, we can predict the service life of the electrode under normal operating conditions using an average $n = 1.7$ or a service life between 2 limits $n = 1.4$ and $n = 2.0$.

c. Cyclic voltammetry (CV)

In CV, a cyclic linear potential sweep is imposed on a working electrode. A current plot (voltammogram) is obtained by measuring the current at the working electrode during the potential sweep. The primary event is the oxidation or reduction of chemical species at an electrode.

The shape of CV provides an electrochemical spectrum giving possible evidence of intermediate species, of surface redox transitions or of phase formations. In addition, voltammetric curves are very sensitive to whatever small modification can occur in the structure of the surface. Voltammetric curves can also provide, besides voltammetric charges, ΔE_p values, i.e. the potential difference between couples of anodic and cathodic peaks as shown in Figure 1.9. A high value of ΔE_p normally indicates irreversibility for reactions of dissolved species; in the case of redox reactions of oxide

surface sites, ΔE_p is to be understood as a consequence of the growth of an insulating layer below the catalyst coating, which increases the ohmic drop. (Trassatti, 1990)

A typical cyclic voltammogram for a reversible process is shown in Figure 1.9.

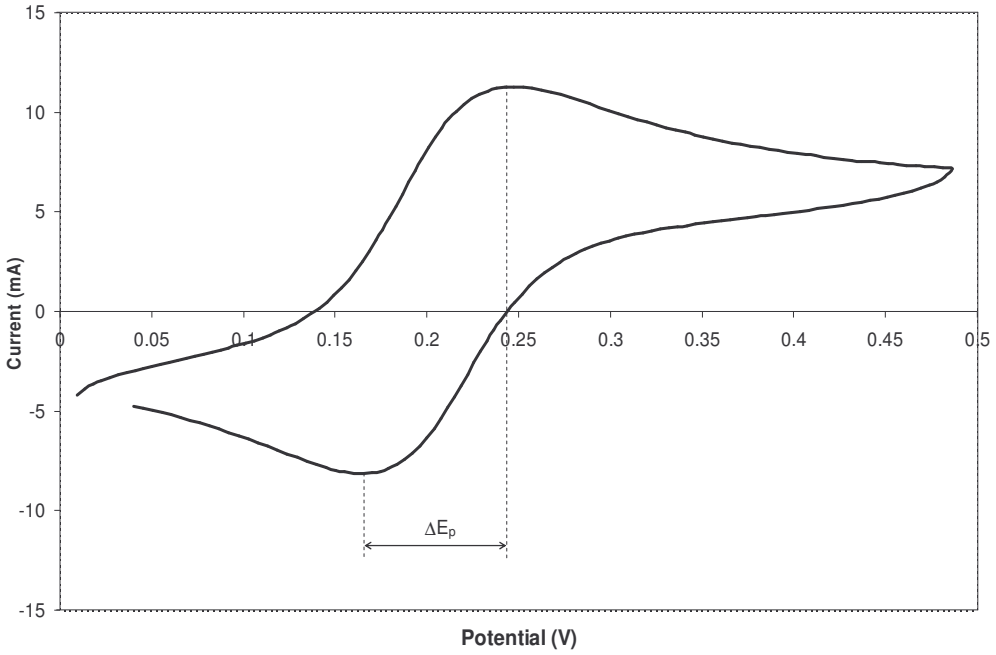


Figure 1.9 CV of 50 mM $K_4Fe(CN)_6$ in 2 M KNO_3 (pH 3.0). Scan rate 20 mV s^{-1} in the range 0.0–0.5 V versus an Ag/AgCl (1 M KNO_3) as reference electrode. Working electrode: plate IrO_2–Ta_2O_5 coated titanium anode; geometrical area = 2.0 cm^2.

In this work, CV was used to investigate the electrocatalytic activity of electrodes by evaluating the current density at a constant potential. The current density at constant potential depends on both electronic and geometric factors. (Xu et al., 2003)

d. Linear scan voltammetry (LSV)

In CV, a cyclic linear potential sweep is imposed on a working electrode. A voltammogram is obtained by measuring the current at the working electrode during the potential sweep. The same principle is employed in LSV, except for the fact the linear potential sweep is not cyclic. In other words, the LSV curve will consist of a forward sweep only, compared to a forward and reverse sweep observed for CV.

In this work, LSV was mainly used to perform slow potential sweep experiments. The resulting $j-E$ plots were used in an attempt to obtain kinetic parameters using Tafel analysis.

e. Chronoamperometry (CA)

Chronoamperometry is defined as a potential step experiment. In this experiment, the potential of the working electrode is suddenly (effectively instantaneously) stepped from an initial potential where no current passes (i.e. no chemical change occurs at the surface) to the final potential where the electrode reaction of interest takes place. In chronoamperometry, the current versus time response is recorded subsequent to the potential step.

Let us consider the effect of a single potential step on the reaction $O + ne^- \rightarrow R$. The potential will be stepped from a value where no current flows, to a potential into one of three regions (a) the diffusion controlled region at high overpotentials (b) the region of mixed control (c) the Tafel region at low overpotential when electron transfer is the slow step as shown in the Figure 1.10.

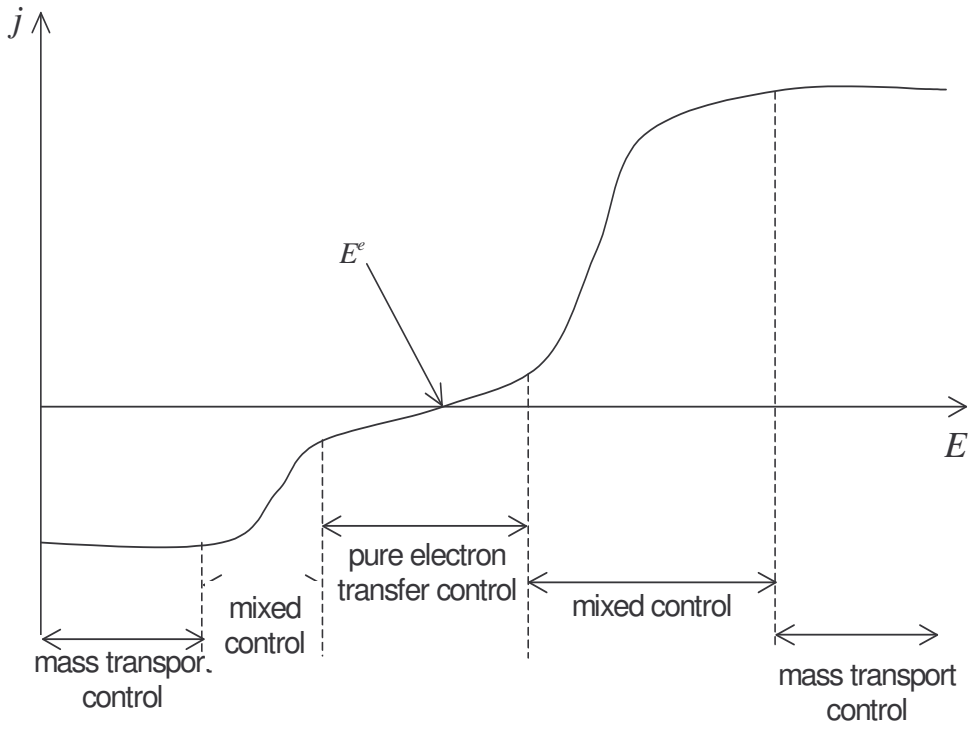


Figure 1.10 Current density–potential response for an irreversible electrode reaction. (Pletcher, 1991)

Depending on the potential step perturbation, the dependence of current density on time at constant applied potential can be summarised as follows: (Pletcher, 1991):

a) The potential step falls into the region of diffusion control: the $j-t$ transient is found by solving Fick's diffusion equation. The mathematics leads to the well-known Cottrell equation:

$$j = \frac{nFD^{1/2}c_R}{\pi^{1/2}t^{1/2}} \qquad 1.27$$

where D = diffusion coefficient (m^2 s^{-1}) and c_R = concentration of the reactive species in the bulk solution (mol m^{-3}).

It provides a test that the potential used for the experiments is, indeed, in the diffusion controlled region; a plot of j vs. $t^{-½}$ should be linear or, alternatively $jt^{-½}$ is a constant.

b) For a potential step into the mixed controlled region: the chronoamperometric response is given by

$$j = nF\vec{k}c_R \exp\left(\frac{\vec{k}^2 t}{D}\right) erfc\left(\frac{\vec{k}t^{½}}{D^{½}}\right) \qquad 1.28$$

where $erfc$ is the complementary error function, $\vec{k}$ is the rate constant for oxidation at the applied potential.

c) If the potential is stepped into the Tafel (electron transfer) region: the j – t response is independent of time variation.

Presentation of these equations for various values of step potential is shown in Figure 1.11.

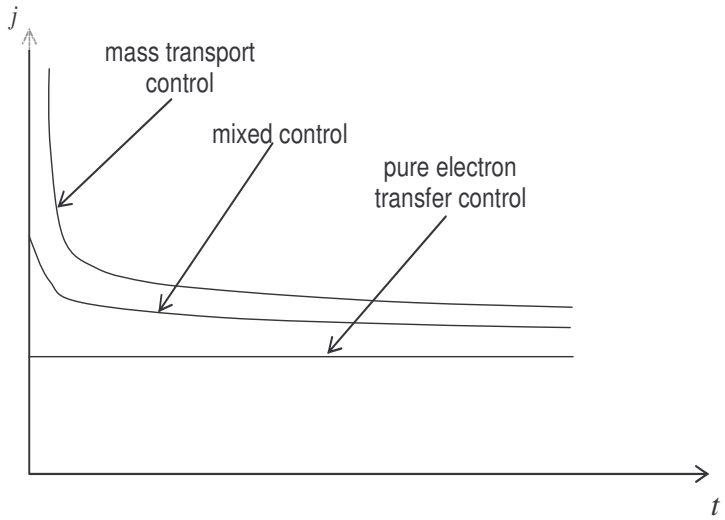


Figure 1.11 Current density versus time responses for potential step experiments with the potential regions under (a) diffusion control (b) mixed control and (c) electron transfer control

For experiments described in this dissertation, chronoamperometry was used to have a rapid measure of the electrocatalytic activity of the electrode material with time and to calculate the electrochemical active surface area of industrial expanded mesh electrodes.

Chapter 2 Experimental procedures

This chapter provides the following information related to experiments described in the dissertation:

- A description of instrumentation, electrodes, reagents and solutions used to carry out the experimental part.
- The procedure used to perform the accelerated life test (ALT);
- Procedures used to monitor the change on the sample electrode by electrochemical measurements;
- Details about physical tests used.

2.1 Equipment, electrodes and reagents

The instrumentation, electrodes, equipment, reagents and solutions used to carry out the analytical procedures are listed below.

2.1.1 Electroanalytical equipment

An Autolab/PGSTAT30 connected to a 663 VA stand via IME 663 interface to obtain a three-electrode cell configuration with potentiostatic control was used. For application requiring more than 1 ampere output current, a booster BSTR10A was also used.

The control of the equipment, real time monitoring of experiments and data acquisition were accomplished by use of GPES 4.9 software installed on a personal computer.

The electrochemical cell consisted of 400 ml water-jacketed glass vessel which was thermostatted to within 0.1 ºC by a constant temperature water bath / circulator. The reaction cell was fitted with a PVC cover with five

openings, through which the various electrodes and the Dosimat pipe (to control electrolyte level) could be inserted.

2.1.2 Preparation of electrodes

The sample of an anode coated with IrO_2-Ta_2O_5, (5 cm x 1 cm x 0,1 cm) was supplied by NMT Electrodes (Pty) and was used as working electrode. The substrate titanium used was ASTM grade 1. The formulation of the coating was:

- Inner layer: 20/80 wt % IrO_2-Ta_2O_5; 10 g/m^2, followed by
- Outer layer: 80/20 wt % IrO_2-Ta_2O_5; 20 g/m^2.

The sample was welded on a titanium rod, as illustrated in Figure 2.1. The geometrical working area was 1,0 cm x 1,0 cm x 2 (both sides) = 2,00 cm^2.

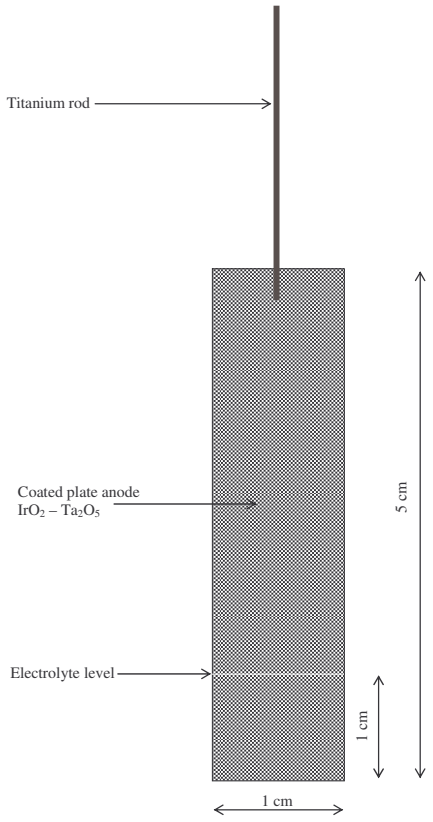


Figure 2.1 Sample of titanium anode coated with IrO_2-Ta_2O_5

All electrode potentials for electrochemical measurements were read against an Ag/AgCl as reference electrode containing the base electrolyte (1 M KNO_3) (0.23 V vs. SHE). The salt bridge was slightly bent towards working electrode to minimise ohmic drop due to uncompensated solution resistance.

Two large stainless steel plates with area 20 cm^2 were positioned parallel to the opposite faces of the sample anode. The stainless steel used was of a high grade to prevent corrosion from the electrolyte.

A divided cell was not used meaning that the anolyte was not separated from the catholyte. So gases were not preventing from mixing.

2.1.3 Description of reagents and solutions

A description of the reagents and solutions used for all experiments is provided in this section.

a. Reagents

- Chromic acid, CrO_3, MM = 99.99 g mol^{-1}, supplied by sponsoring company.
- Sodium dichromate crystals, $Na_2Cr_2O_7$, MM = 298 g mol^{-1}, Chrome International S.A.
- Potassium chloride, KCl, MM = 74.55 g mol^{-1}, Analytical reagent (AR) grade; (Saarchem).
- Potassium nitrate, KNO_3, MM = 101.11 g mol^{-1}, Guaranteed reagent (GR) grade; (Merck)
- Nitric acid, HNO_3, 65 %, MM = 63.01 g mol^{-1}, AR grade (Saarchem)
- Potassium ferrocyanide, $K_4Fe(CN)_6$, MM = 442.41 g mol^{-1}, Guaranteed reagent (GR) grade; (Merck).

b. Solutions

In order to meet operational conditions in the electrolytic production of chromic acid, all tests were made in an electrolyte composed of CrO_3 and $Na_2Cr_2O_7$ according to **Table 2.1**. For instance, electrolyte solution 1, a mass of 480.78 g CrO_3 and 661.25 g $Na_2Cr_2O_7.2H_2O$ was weighed out. A volume of 500 ml de-ionised water was added to the mixture of crystals. This was followed by stirring and warming at 60º C until complete dissolution of mixture crystals. The solution was diluted to a volume 1000 ml with de-ionised water. The same procedure was followed to prepare electrolyte solution 2.

Table 2.1 Composition of electrolyte solution 1 and 2 used during the experimental investigation

Electrolyte solution	Density ($g.cm^{-3}$)	CrO_3 (%)	$Na_2Cr_2O_7.2H_2O$ (%)	Concentration (M)	
				$H_2Cr_2O_7$	$Na_2Cr_2O_7$
1	1.72	27.92	38.40	2.40	2.22
2	1.75	34.63	34.40	3.02	2.02

2.2 Accelerated Life Test

The ALT is generally used to evaluate the stability/service life of the mixed metal oxide electrodes because the oxide anode can have a very long service life under the normal conditions (0.3 A cm^{-2}) of electrolysis in industry. The ALT was conducted under galvanostatic electrolysis at a current density of 1.2 A cm^{-2} in an electrolyte made of CrO_3 and $Na_2Cr_2O_7$. The cell voltage between a working electrode and an auxiliary electrode was recorded via computer interfaced to the experimental set-up. The time when the cell voltage reached 10 V was taken as the accelerated life of the oxide electrode.

The electrolysis was then run for a further 24 hours to ensure complete deactivation of the anode.

2.2.1 Laboratory set-up and schematic diagram

To get a better understanding of the setup, Figure 2.2 is included.

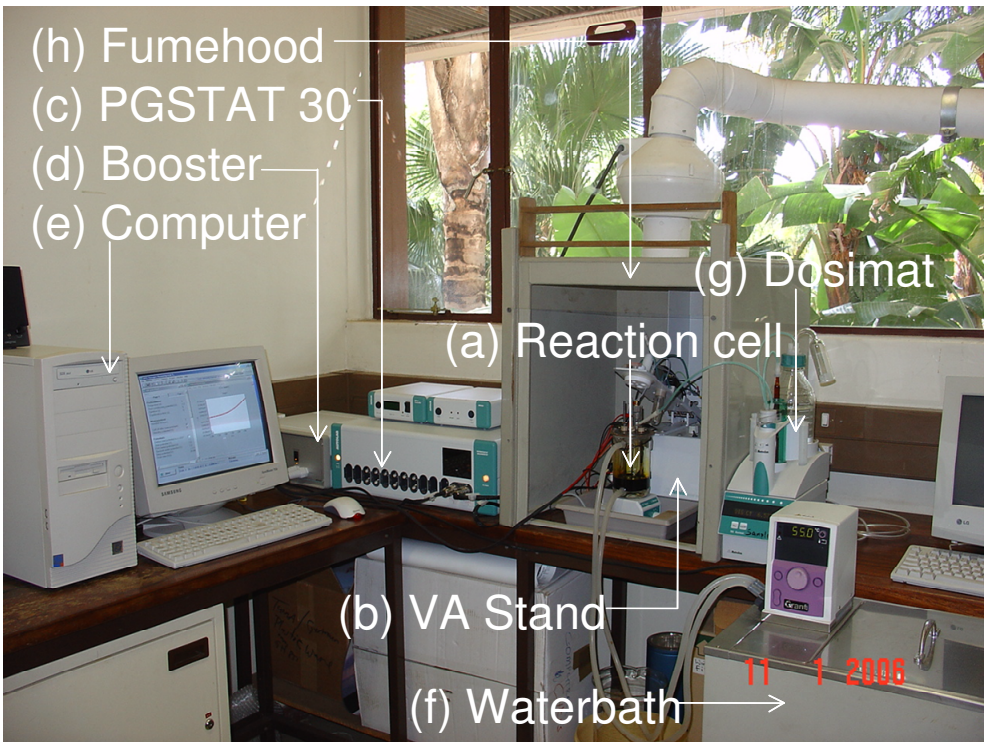


Figure 2.2 Photograph of laboratory set-up used for ALT

This set-up is illustrated in Figure 2.2.

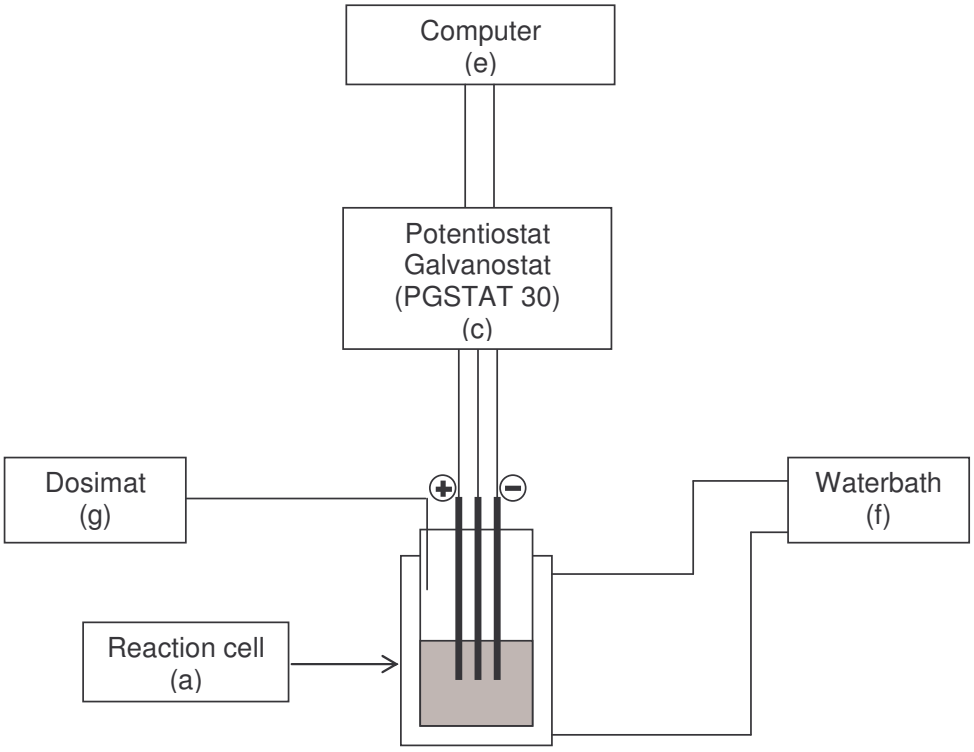


Figure 2.3 Circuit diagram for the ALT and electrochemical tests

2.2.2 General procedure

- A volume of 100 ml of electrolyte was placed into a clean reaction cell.
- The cell cover, in which the various electrodes and components were fitted, was lowered into the reaction cell in order to establish contact between the electrodes and the solution in the cell.
- The constant temperature water bath, already connected to the jacketed reaction cell was switched on. The temperature was fixed at 55,0 ± 1,0 ºC, and all experiments were conducted at this temperature. Sufficient time was allowed (approximately 1 hour) to ensure that the solution in the reaction vessel reached the temperature maintained by the water bath.

- For the ALT experiments, the technique chrono methods (interval time > 0.1s) potentiometry (galvanostat) identical to a standard electrolysis was selected via the instrument software Autolab GPES 4.9. The relevant information and settings required for the experiment were entered.

  In this case, a first conditioning current of 0.24 A was set few seconds while the cell voltage was measured in intervals of 60 seconds. A standby current of 2.4 A was used during 86400 seconds (i.e. 1 day).

- De-ionised water flowing from a Dosimat was added to compensate loss of water due to evaporation and saturated gas bubbles. Care was taken to keep constant level of electrolyte in the reaction cell. At the start of each run, the Dosimat was switched on and required rate of water addition was set.

- At the same time, the experiment commenced via the Autolab software. At the end of the 1-day experiment, the data were collected and saved in a file.

- After the electrolysis experiment, a volume of 50 ml was taken out for chemical analysis, labelled and stored.

- A 50 ml of fresh solution was added into the reaction vessel before a set of electrochemical tests was performed.

2.3 Electrochemical measurements

Electrochemical measurements involving Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV) and Chronoamperometry (CA) were used to monitor the surface properties of the oxide anodes.

All of the electrochemical measurements were carried out in a single compartment, taking two large stainless steel plates as auxiliary electrode (AE), and a silver silver chloride electrode (SSE) as a reference electrode.

The tests were made under the same conditions of temperature and concentrations as during the ALT.

2.4 Physical techniques

Surface morphology and elemental composition of the coating oxide film were analyzed through scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) using a JEOL 5800 LV, Japan. The operating voltage of electronic beam was 20 keV for EDS analysis and 10 keV for morphological observation.

These tests were performed for comparison purposes, on the fresh sample anode and after accelerated life tests, on the deactivated anode.

Chapter 3 RESULTS AND DISCUSSION

This chapter contains the presentation and discussion of data collected in this study.

a) The measurement of cell voltage as a function of time at constant current density in order to investigate the stability or service life of coated titanium anodes. (accelerated life test)

b) During the course of the above experiment, cyclic voltammetry, linear sweep voltammetry and chronoamperometry experiments were performed periodically on the anode.

c) At the end of each experiment, the anode was removed from the reaction cell and certain physical properties were investigated.

3.1 Accelerated life test (ALT)

The stability or service life of the coated titanium anodes was tested by an accelerated life test performed by applying a constant current of 1.2 A cm^{-2} at 55 ºC, in an electrolyte solution 2, then in electrolyte solution 1 on a coated titanium plate anode. Finally, the test was carried out in solution 1 on an industrial expanded mesh anode.

The ALT experiment was periodically interrupted to monitor the change on the surface electrode according to the protocol in section 2.2.2 and to collect electrochemical data.

During these ALT experiments, huge amounts of oxygen were evolved at the anode and hydrogen at the cathodes according to Equation 1.1 and 1.2. At beginning of each electrolysis experiment, the initial cell voltage was high but within a few minutes it had dropped, which can be attributed to a temporary state before reaching a steady state and the variation of

concentration due to the renewal of half of the electrolyte solution as indicated in Section 2.2.2. The cell voltage was then generally stable for long periods suggesting that the coated titanium anode is a good material for this process.

The detailed results are shown in Figures 3.1 to 3.3. From these curves, it can be seen that the cell voltage is not very smooth. These oscillations are a consequence of the way in which the level of electrolyte was manually controlled and are also due to interruptions when adding new electrolyte and performing electrochemical tests. Loss of electrolyte was due to the cell reaction as well as evaporation. That is why water from a Dosimat was supplied in an attempt to maintain a constant level. In addition during electrochemical experiments, the anode potential was at times raised by 1.5 V which could cause some temporary modification of the iridium oxide layer.

Figure 3.1 shows the evolution of the cell voltage as function of the electrolysis time on coated titanium plate with electrolyte solution 2.

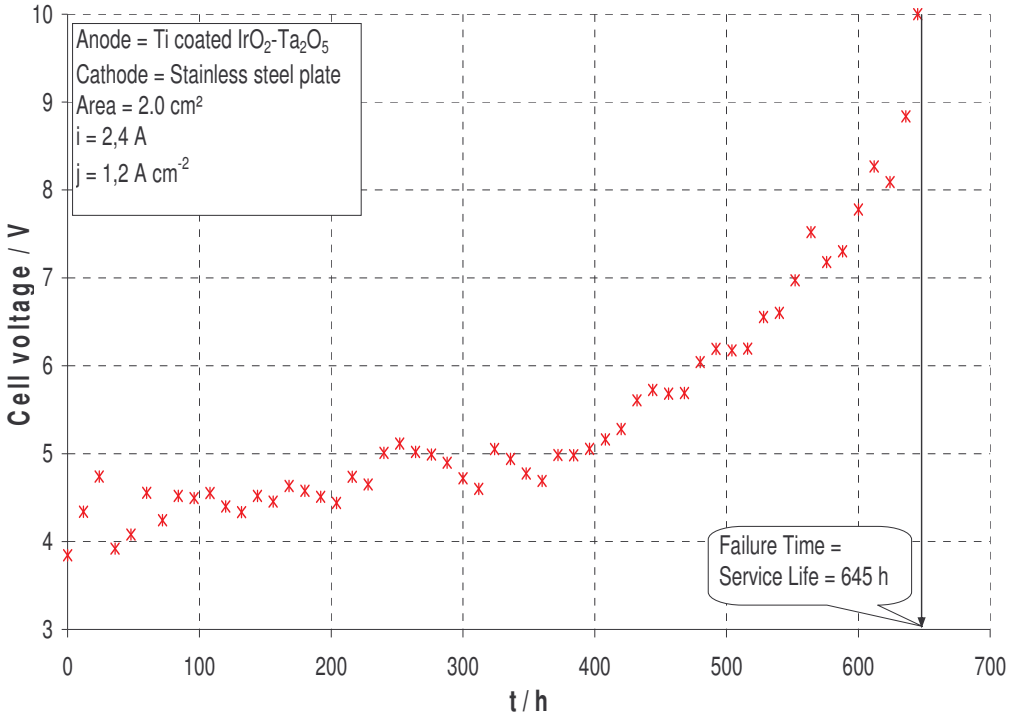


Figure 3.1 Cell voltage vs. electrolysis time during the ALT performed in electrolyte solution 2 at 55º C

It can be seen in Figure 3.1 that the cell voltage generally increases steadily with increasing time of electrolysis. Finally, an abrupt increase occurs which is likely related to coating consumption and base metal passivation. For the purposes of this study, the failure time will be regarded as that when the cell voltage reaches 10 V.

The variation in cell voltage versus time in the accelerated life test performed in electrolyte solution 1 on coated titanium anode is shown in Figure 3.2.

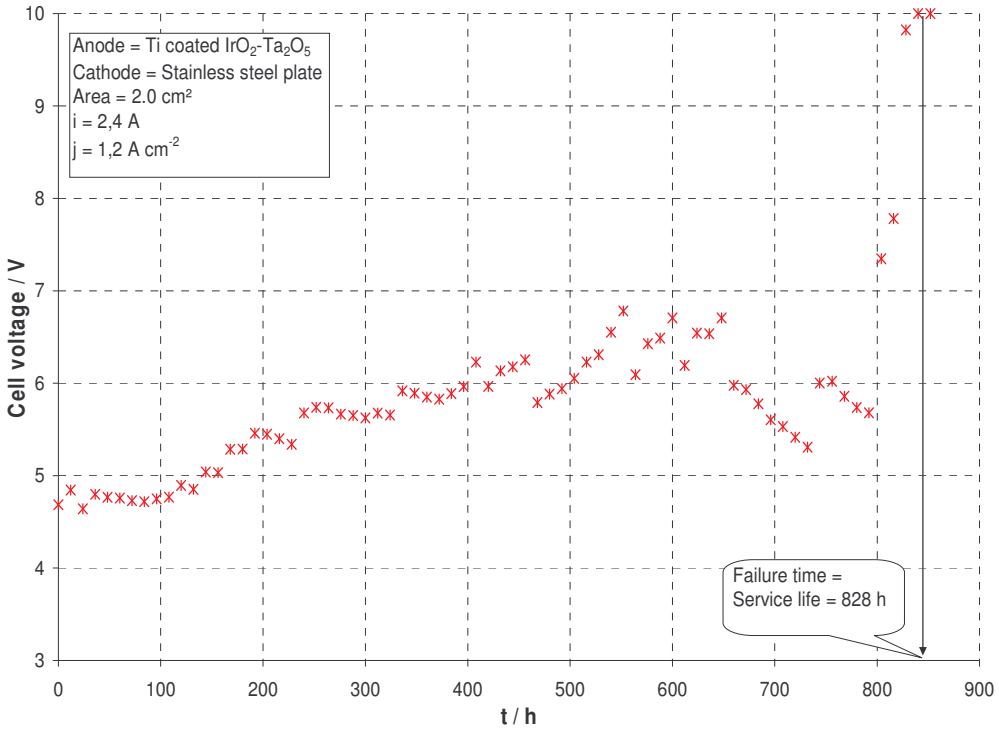


Figure 3.2 Cell voltage vs. electrolysis time during ALT performed in electrolyte solution 1 at 55º C

The comparison of the ALT performed under these two conditions shows reproducible behaviour of the anode. As expected, the anode placed in the higher chromic acid solution failed at an earlier time.

Figure 3.3 shows the experimental data of the cell voltage versus time during the life test performed on industrial expanded titanium mesh placed in electrolyte solution 1. The operating conditions were kept the same as in the two previous tests. Prior to the long polarization electrolysis, the working area of expanded titanium mesh was determined electrochemically by means of a chronoamperometric technique. More details, on how to find this electrochemical area was established are shown in Appendix A.

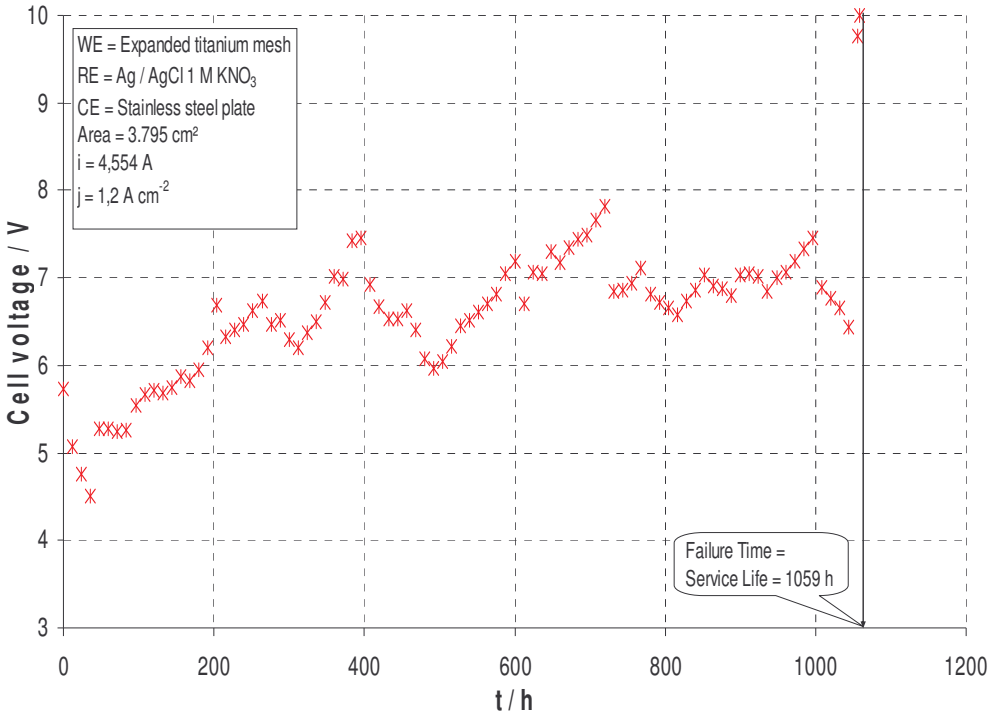


Figure 3.3 Cell voltage vs. electrolysis time during the ALT performed in electrolyte solution 1 at 55º C on expanded titanium mesh.

The results for the expanded titanium mesh in Figure 3.3 show essentially the same behaviour as for the plates.

3.2 Monitoring the change of the electrode surface during the ALT

3.2.1 Cyclic voltammetry (CV)

CV is a particular powerful technique for initial studies because the data are presented in a form which allows a rapid, qualitative interpretation without recourse to detailed calculation. That is why it was used in this study for detecting if any redox transitions control the surface state of electrode during electrolysis.

The results at different electrolysis time can be seen in Figure 3.4, 3.5 and 3.6.

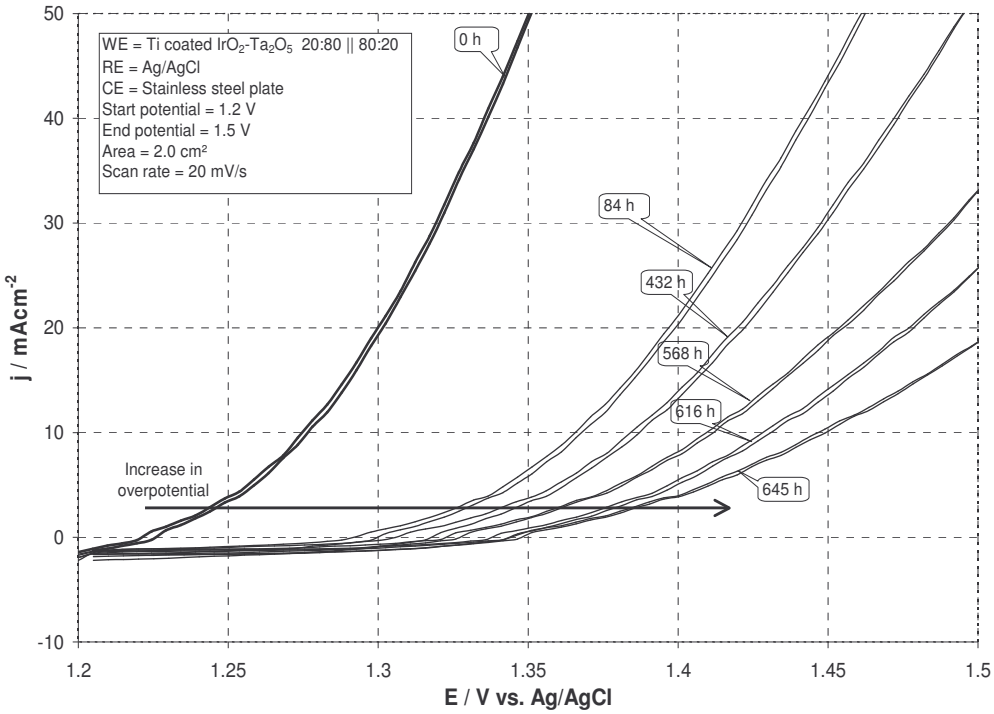


Figure 3.4 Change in the CV curves as a function of electrolysis time: Electrolyte solution 2; Scan rate = 20 mV s^{-1}; T = 55º C; Coated titanium plate anode

Figure 3.4 presents typical cyclic voltammograms, showing similar shape but lower current density with increasing electrolysis time. No current peaks appear except the oxygen evolution current. At the end of the ALT, the voltammetric curve shows a very small current for oxygen evolution.

In general, at the beginning of the electrolysis experiment (0 hour), the current density for oxygen evolution is very high which can be attributed to the high electrochemical activity of the surface due to its porous structure as observed on new electrode. After each electrolysis experiment, the voltammetric current density of the coated titanium anodes decreases

considerably with time. This decrease in the electroactivity indicates corrosion of the IrO_2 species and titanium substrate passivation.

The voltammograms shift to the right side means that the anode material becomes less active because as the experimental conditions (concentration, temperature, scan rate, potential range) were the same throughout the experiment, hence the change can be due only to anode material. This is consistent with theoretical aspects discussed in Section 1.4.3 (a), low overpotentials lead to high observable current density. In addition the shape of all voltammograms is the same suggesting that in the voltage range investigated [1.2 V – 1.5 V], no other electrochemical reactions occur except the oxygen evolution reaction.

Near the end of service life, the sudden and sharp increase in the cell voltage is interpreted on the CV spectra by very small shape of CV compared to the first at 0 hour electrolysis. That can be understood as being the result of accelerated corrosion and titanium substrate passivation. As the coating surface undergoes dissolution, this makes the titanium substrate more accessible to the electrolyte. Then passivation of the metal support is the main cause of electrode deactivation.

Figure 3.5 shows cyclic voltammograms recorded in electrolyte solution 1 at 55ºC on titanium plate coated with IrO_2-Ta_2O_5. The voltammetric curves are similar to the previous ones in higher solution concentration.

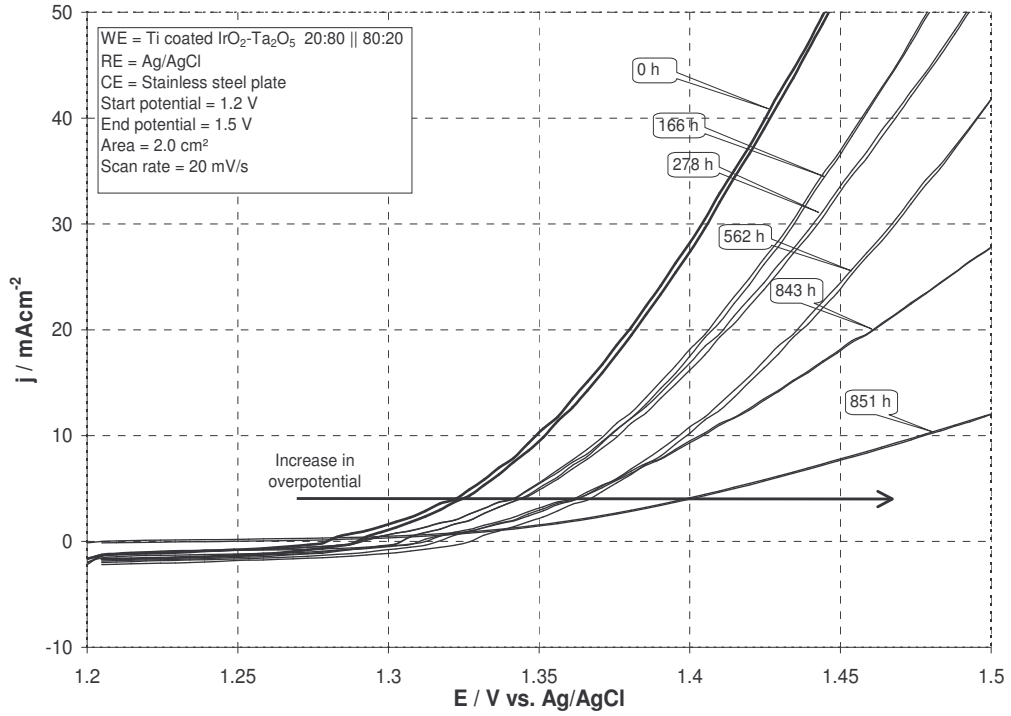


Figure 3.5 Change in the CV curves as a function of electrolysis time: Electrolyte solution 1; Scan rate = 20 mV s^{-1}; T = 55º C; Coated titanium plate anode

In Figure 3.6 curves represent the CV of the expanded mesh electrode in electrolyte solution 1 at 55ºC. A similar trend is also visible but the voltammograms at intermediate time (538 h, 842 h, and 999 h) seem to be mixed. This may be related to the accuracy of the measurements. In addition, the degradation of the anode material appears to stabilize during that period which is confirmed by another technique (chronoamperometry).

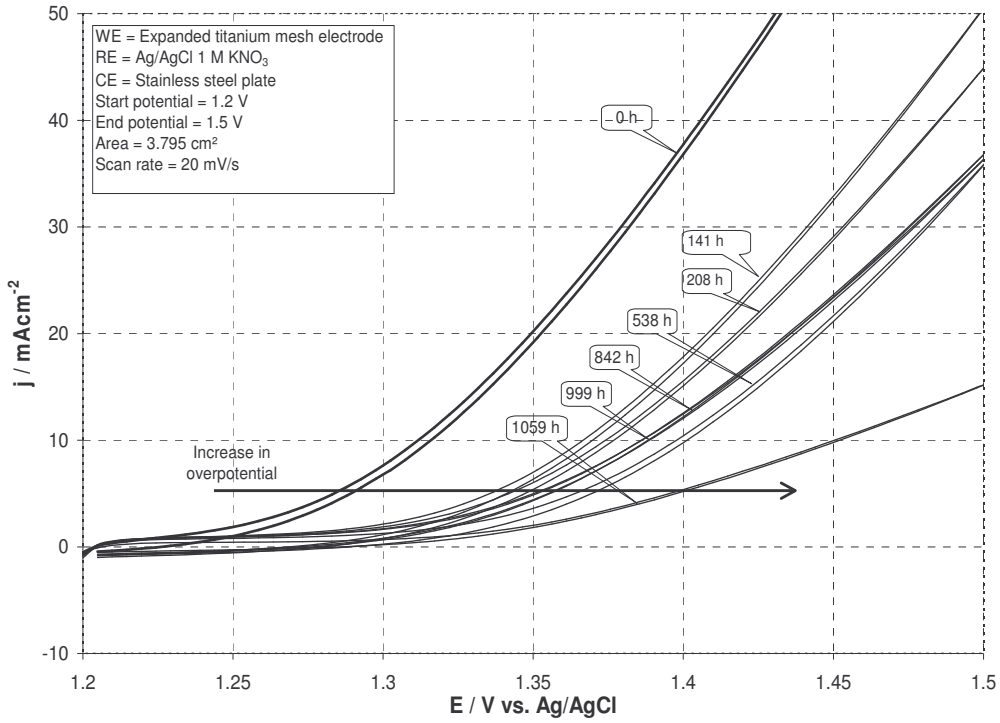


Figure 3.6 Change in the CV curves as a function of electrolysis time: Electrolyte solution 1; Scan rate = 20 mV s^{-1}; T = 55º C; Expanded titanium mesh

Even after deactivation of the oxide layer (a condition assumed after the potential cell reach 10 V, the voltammetric current density still presented evidence of oxygen evolution reaction, suggesting a residual IrO_2 content is still present in the oxide layer. For example, comparing the initial voltammetric current density (180 $mAcm^{-2}$) at 1.5 V with the current density at the end of the service life (20 $mAcm^{-2}$) in Figure 3.4, only 10 % of the electroactivity remained.

3.2.2 Linear sweep voltammetry (LSV)

During CV tests the cycle is reverse many times and that can lead to a modification of electrochemical surface properties. Therefore LSV at scan rate of 1 mV s^{-1} was used to perform these measurements in the range of oxygen evolution (1.2 V – 1.5 V).

In order to analyze the LSV spectra, current density for oxygen evolution at 1.5 V was considered without using kinetic parameters j_0 and Tafel slope (explanation can be found in Section 3.2.2 (a)).

The typical LSV curves recorded on electrolyte solution 2 (coated titanium plate anode) are shown in Figure 3.7.

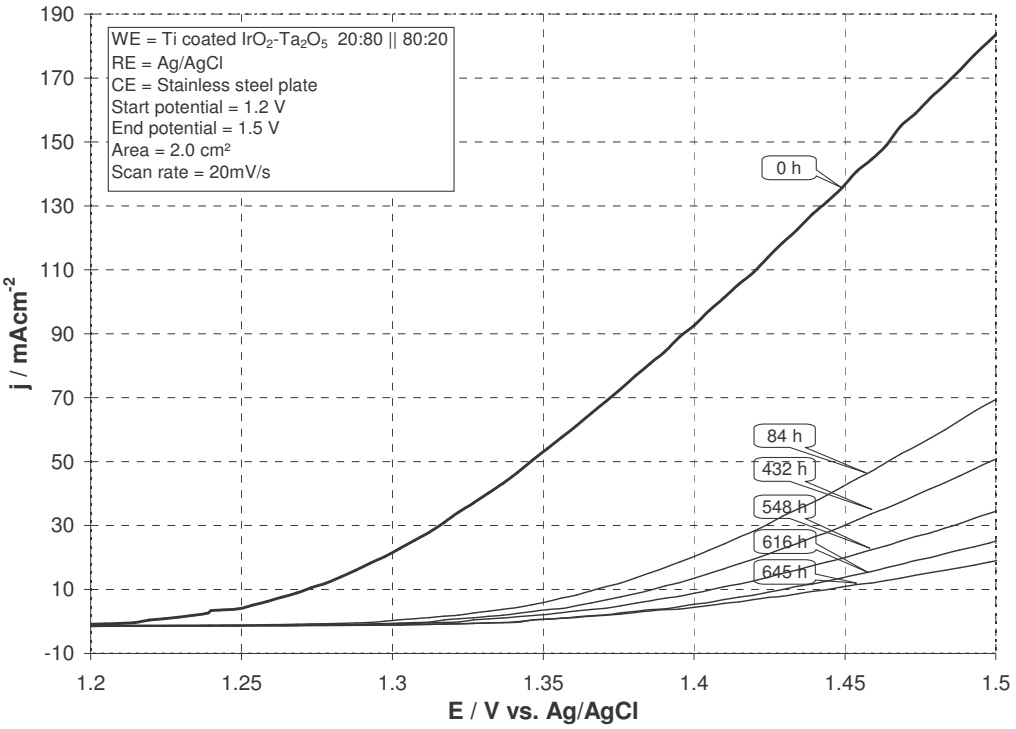
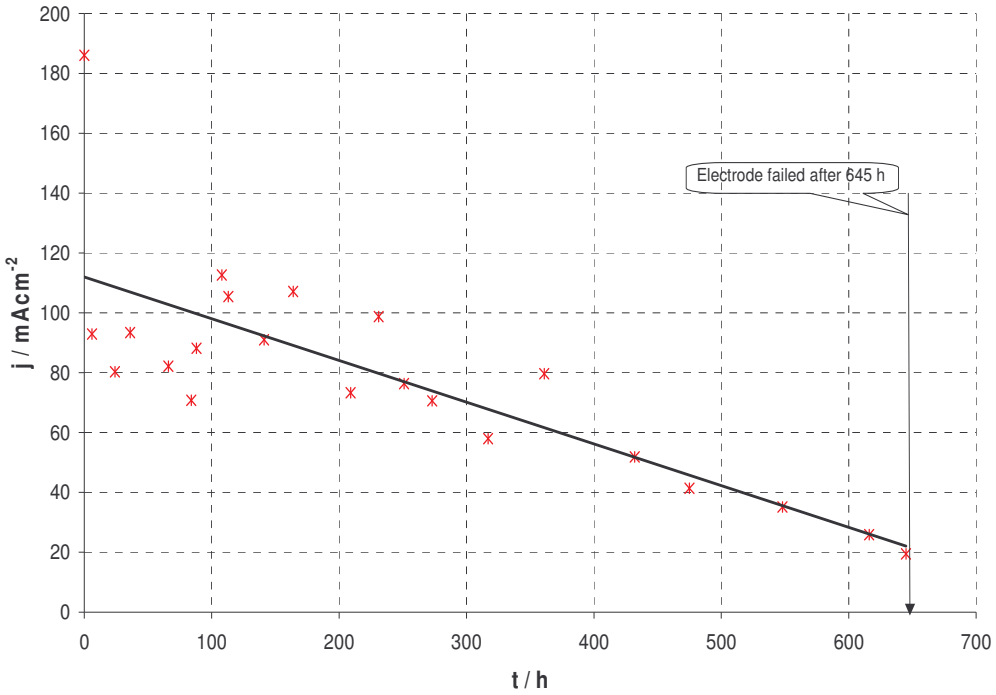


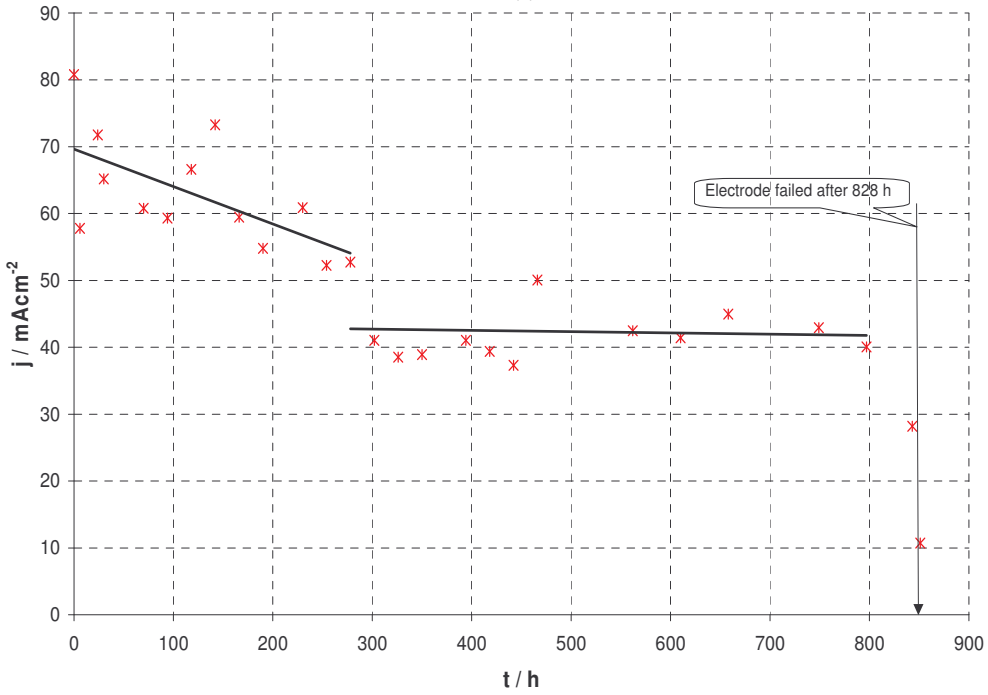
Figure 3.7 Change in the LSV curves as function of electrolysis time performed in electrolyte solution 2 at 55ºC; Coated titanium plate anode

The current density at 1.5 V has been used to evaluate the electroactivity for the anode material. The plot of current density versus electrolysis time in Figure 3.8 gives the evaluation of anode activity.

(a)


Electrode failed after 645 h
j / mAcm-2
t / h
0
20
40
60
80
100
120
140
160
180
200
0
100
200
300
400
500
600
700

(b)


Electrode failed after 828 h
j / mAcm-2
t / h
0
10
20
30
40
50
60
70
80
90
0
100
200
300
400
500
600
700
800
900

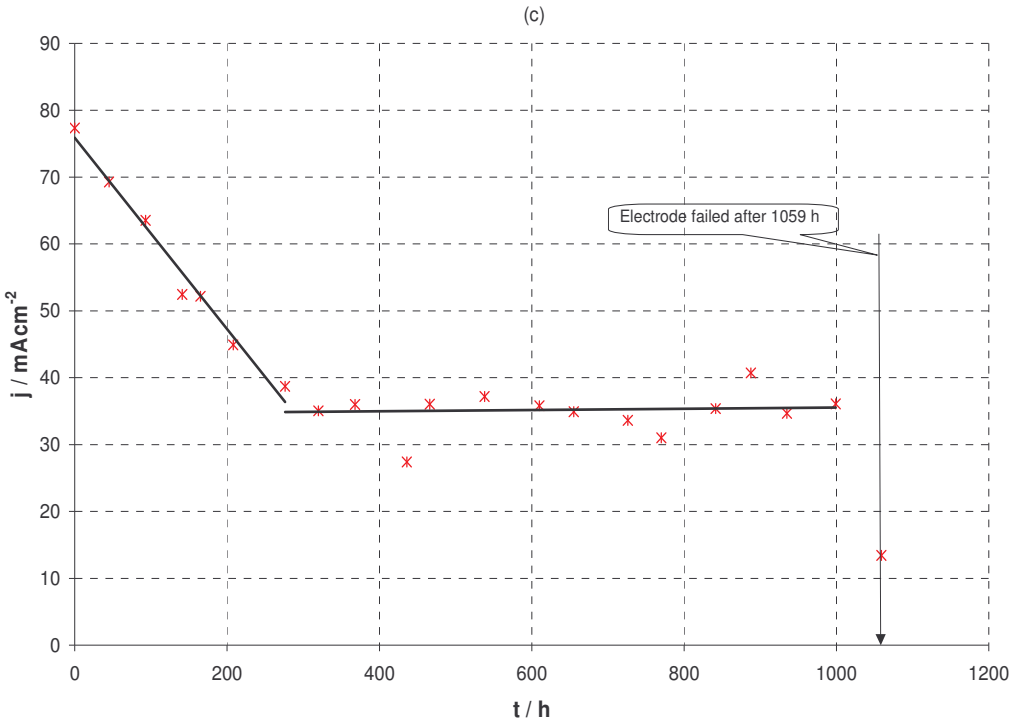


Figure 3.8 Dependence of current density at 1.5 V with electrolysis time. Data from linear sweep voltammetry for oxygen evolution reaction on

(a) coated titanium plate anode in electrolyte solution 2 at 55ºC

(b) coated titanium plate anode in electrolyte solution1 at 55ºC

(c) expanded titanium mesh in electrolyte solution1 at 55ºC.

From Figure 3.8 (a), (b) and (c), one can see that the current density for oxygen evolution reaction at constant potential (1.5 V) decreases with electrolysis time. It has a similar shape to that in Figure 3.11 (b) and (c) for the same solution (electrolyte solution 1) but different material anode. In electrolyte solution 2, in higher chromic acid concentration, the electroactivity for oxygen evolution represented by the current density linearly decreases (Figure 3.8 (a)). This result indicates that the dissolution rate of IrO_2 active component changes with concentration of the solution.

a. Exchange current density and Tafel line analysis

In Section 1.4.3 (a), it was shown how to find the kinetic parameters. Figure 3.9 displays typical polarization curves of IrO_2-Ta_2O_5 coated titanium in electrolyte solution 2 generated from Figure 3.7.

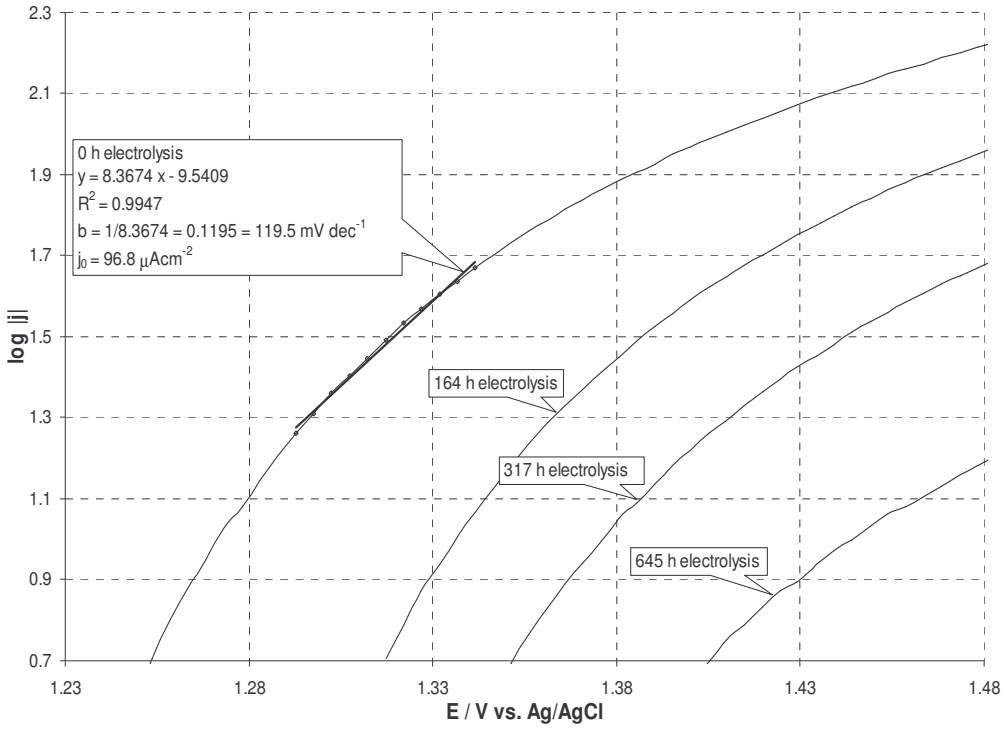


Figure 3.9 Tafel plot analysis derived from LSV data performed on coated titanium in electrolyte solution 2.

The semilogarithmic plots in Figure 3.9 don't show a well defined straight line where Tafel analysis might be applied. A correct estimation of the Tafel slopes is possible only if the linear Tafel region covers at least one decade in current. This poor Tafel region is partially due to the mass transport control of the kinetics (diffusion and convection of gas bubbles). That is why kinetic parameters are difficult to extract from this data. But a quick look at the first curve shows $j_0 = 96.8\,\mu$A cm^{-2} where a Tafel slope $b = 119.5$ mV decade^{-1} (theoretically expected) was identified among the

experimental points. More details how to determine the j_0 can be found in Appendix C (10). The j_0 value suggests that the oxygen evolution process is kinetically rapid and proceeds with one electron transfer according to the mechanism below proposed by Hu et al., (2004) (see Equation 1.21 which is reproduced below).

$$S + H_2O \rightarrow S - OH_{ads} + H^+ + e^-$$

where S stands for active site on the oxide surface and $S - OH_{ads}$ is an adsorption intermediate.

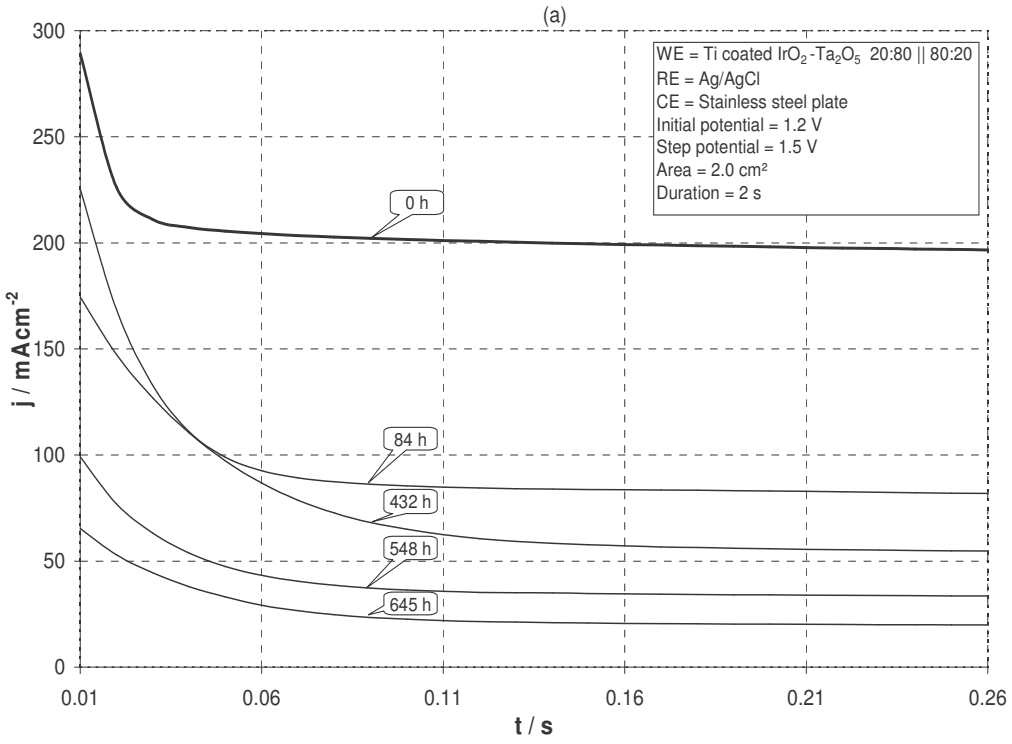
3.2.3 Chronoamperometric data at different electrolysis times

Chronoamperometric experiments were used for a rapid assessment of the anode activity since the potential is changed instantaneously from an initial potential (1.2 V) where there is no net oxygen evolution to the step potential (1.5 V) where oxygen is produced. Since the current is directly proportional to the rate of electrolysis, the current response to this potential step is a current due to the initial rate and is mainly controlled by the kinetics of the surface reaction and diffusionnal effects as discussed in Section 1.4.5 (e).

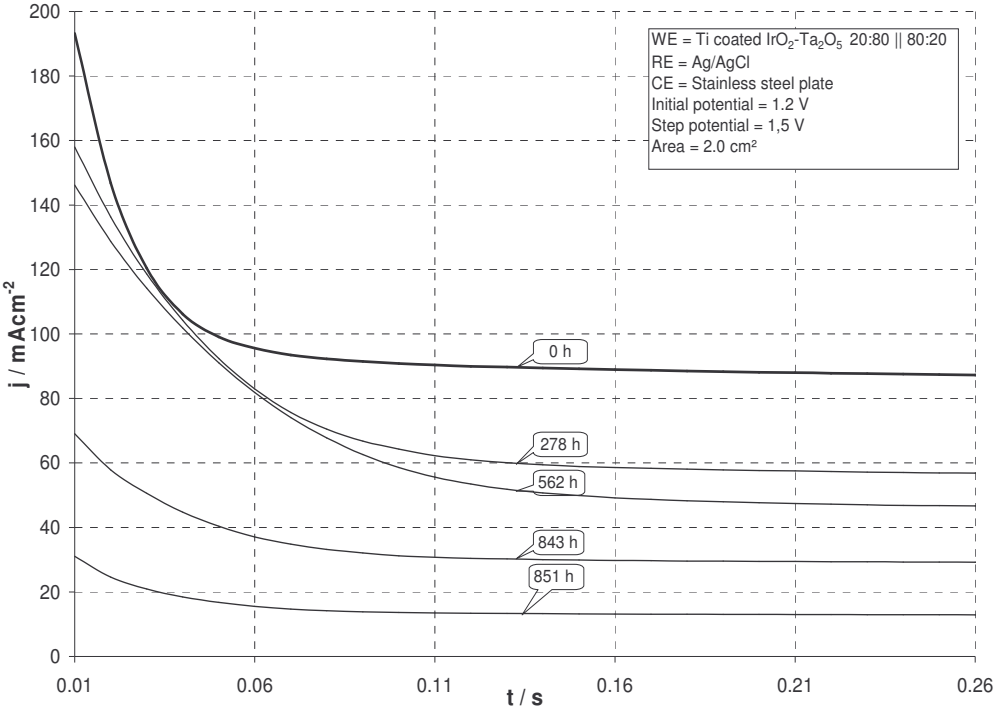
Depending on the potential perturbation, the current density–time ($j-t$) curve may be described by one of three equations (which are reproduced below):

- Diffusion control current: $j = \frac{nFD^{1/2}c_R}{\pi^{1/2}t^{1/2}}$ Cottrell equation
- Mixed controlled region: $j = nF\vec{k}c_R \exp\left(\frac{\vec{k}^2 t}{D}\right) erfc\left(\frac{\vec{k}t^{1/2}}{D^{1/2}}\right)$
- Tafel (electron transfer) region: the $j-t$ response is independent of time variation

Tests were performed at different electrolysis times and the results are shown in Figures 3.10 (a), (b) and (c). The electroactivities evaluated by chronoamperometric tests were done in the same solution mixtures on coated titanium plate anodes and expanded titanium meshes at 55º C. It is seen that significant differences are observed soon after the potential change is applied (at 10 ms). A fresh electrode shows a large current density, which becomes lower with time of use until it becomes almost completely deactivated at failure.



(b)


WE = Ti coated IrO_2-Ta_2O_5 20:80 || 80:20
RE = Ag/AgCl
CE = Stainless steel plate
Initial potential = 1.2 V
Step potential = 1,5 V
Area = 2.0 cm²
0 h
278 h
562 h
843 h
851 h
j / mAcm-2
t / s
200
180
160
140
120
100
80
60
40
20
0
0.01
0.06
0.11
0.16
0.21
0.26

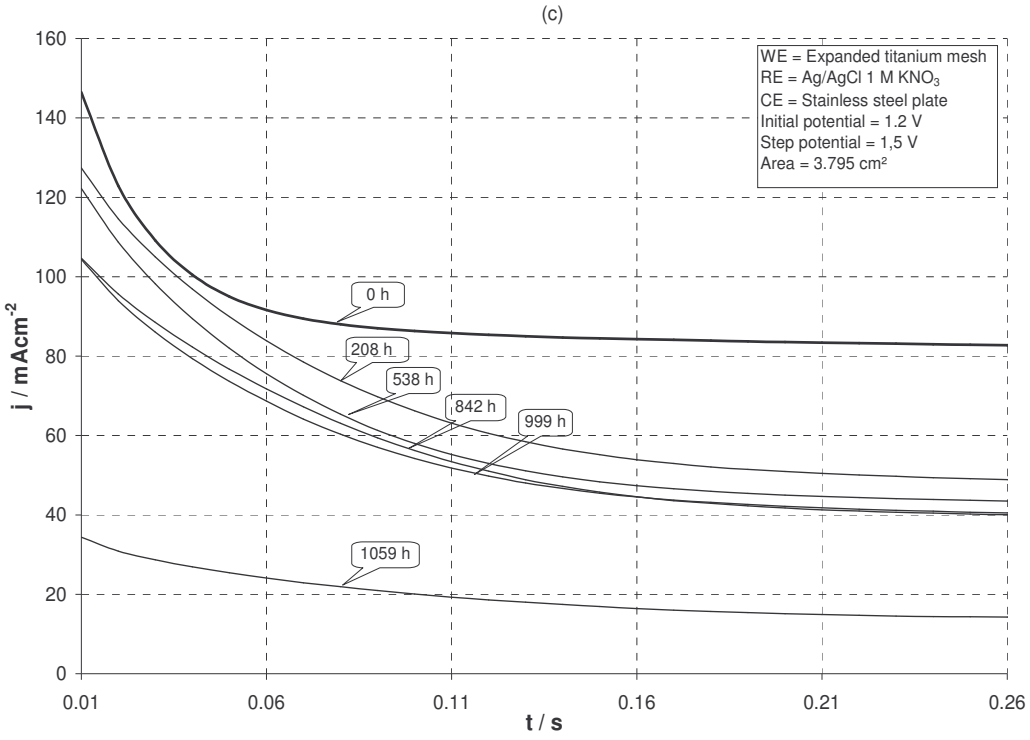


Figure 3.10 Change of current – time responses observed with electrolysis time in chronoamperometric tests performed on

(a) coated titanium plate anode in electrolyte solution 2 at 55ºC.

(b) coated titanium plate anode in electrolyte solution 1 at 55ºC.

(c) expanded titanium mesh in electrolyte solution 1 at 55ºC.

From the CV and LSV curves (Figures 3.5 to 3.7), it is clear that the step potential experiments were performed in a mixed controlled region (electron transfer + mass transport). The change in potential at the anode initiates a very rapid oxidation of all H_2O. Thereafter, the electron transfer is limited by diffusion of a reduced species from the bulk solution and convection of O_2 bubbles from the electrode surface. One can clearly see the fact that current densities at 1.5 V from LSV curves (Figure 3.7) agree with current densities from chronoamperometric measurements at infinite time (Figure 3.10 (a)). So there is a need to separate the electron transfer

from the mass transfer in order to assess the electroactivity of the anode material.

It may be possible to interpret the chronoamperometric data using Equation 3.1 which describes the response of a step potential in the mixed region. The use of this equation implies many assumptions:

- The potential step is quite a long way from the equilibrium potential, so the rate constant for reduction is small compared to $\overleftarrow{k}$, the rate constant for oxidation of H_2O;
- The oxygen evolution reaction proceeds with first order kinetics;
- For very short times, $\overleftarrow{k}^2 t/D \ll 1$, Equation 1.28 could be approximated by

$$j = nF\overleftarrow{k}c_R\left[1-\frac{2\overleftarrow{k}t^{1/2}}{\pi^{1/2}D^{1/2}}\right] \qquad 3.1$$

$$j = C_k - C_{k+d}t^{1/2} \qquad 3.2$$

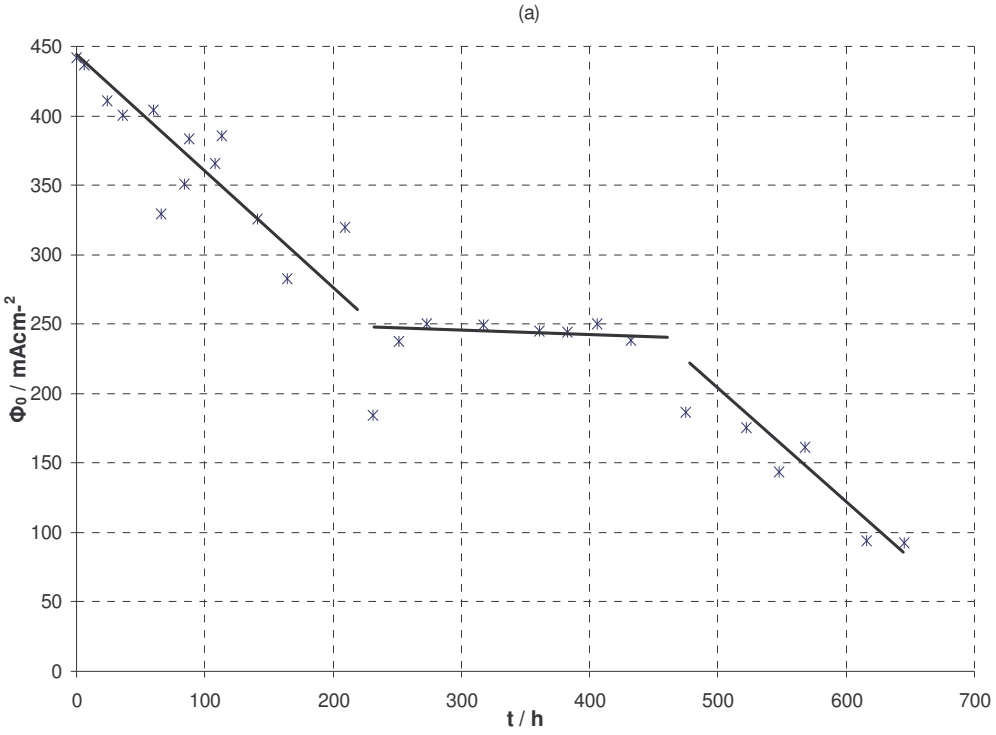
where C_k is a kinetic term and C_{k+d} contains both kinetic and diffusion terms.

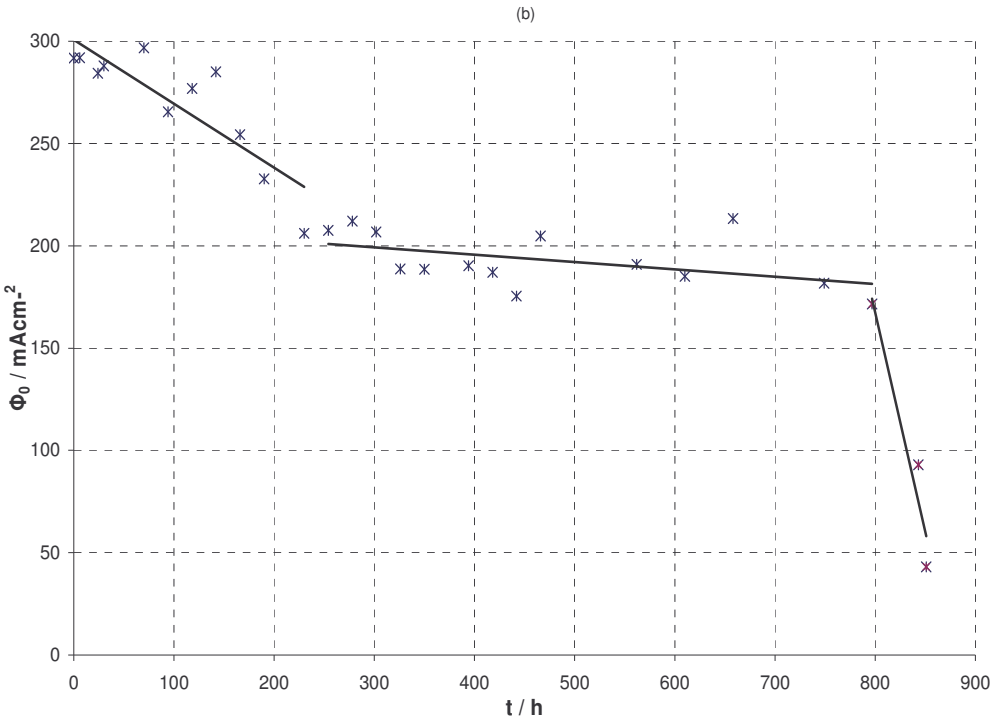
$$C_k = nF\overleftarrow{k}c_R = \phi_0 \qquad 3.3$$

$$C_{k+d} = \frac{2nF\overleftarrow{k}^2 c_R}{\pi^{1/2}D^{1/2}} \qquad 3.4$$

A plot of j against $t^{1/2}$ should be linear and hence can be extrapolated back to zero time to yield the value for j without diffusion. It may be seen that the current density at $t = 0$ is a measure of the electrochemical activity for the electrode material. When c_R the concentration of species in the bulk solution is well-known, the rate constant for oxidation $\overleftarrow{k}$ and the diffusion coefficient D may be obtained from (3.3) and (3.4).

Analysis of chronoamperometric data at different times using this new kinetic parameter ϕ_0 is shown in Figure 3.11 (a), (b) and (c). A decrease in electrode activity with electrolysis time is clearly observed in all these results.




(b)
300
250
200
150
100
50
0
Φ_0 / mAcm^{-2}
0
100
200
300
400
500
600
700
800
900
t / h

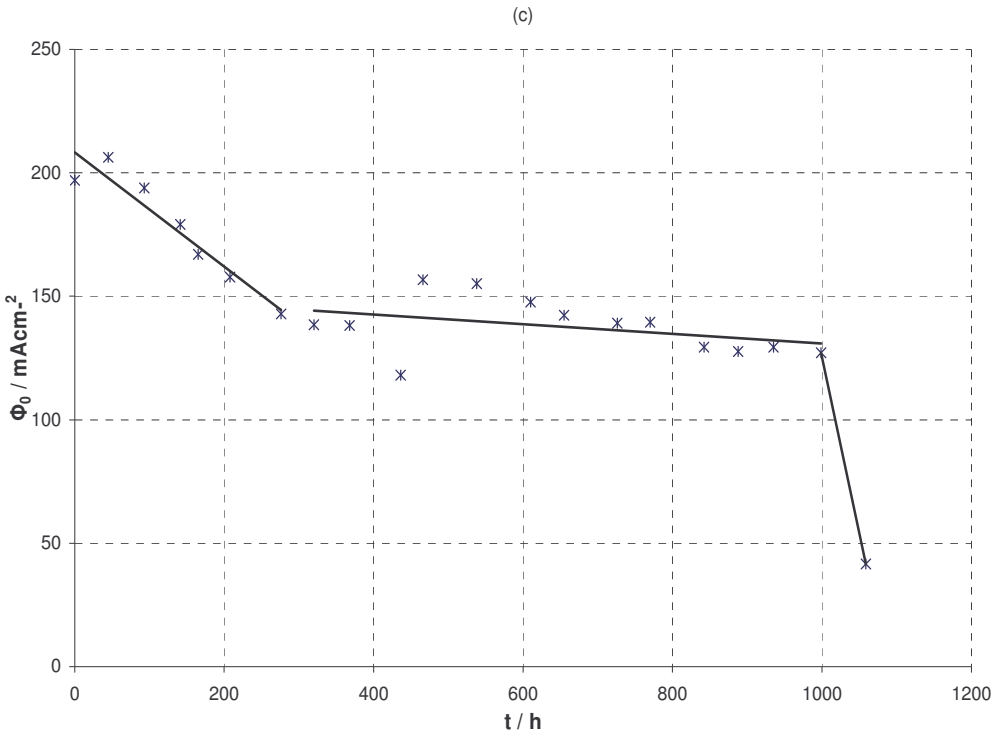


Figure 3.11 Variation in current density j at t = 0 s (ϕ_0) with electrolysis time. Data from chronoamperometry on

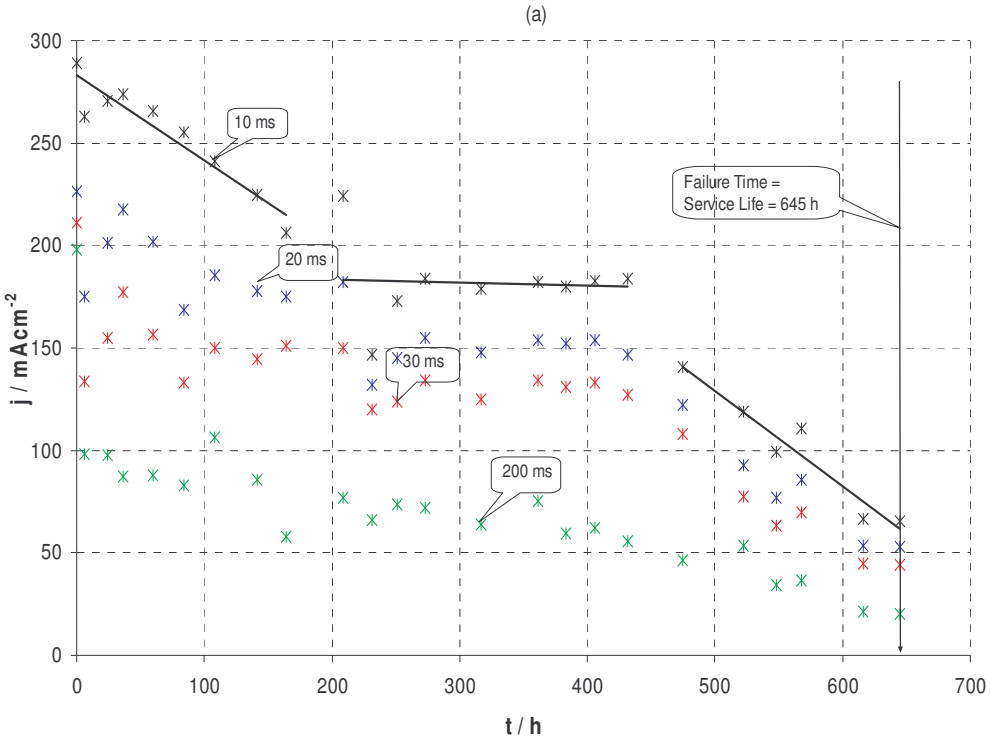
(a) coated titanium plate anode in electrolyte solution 2 at 55ºC.

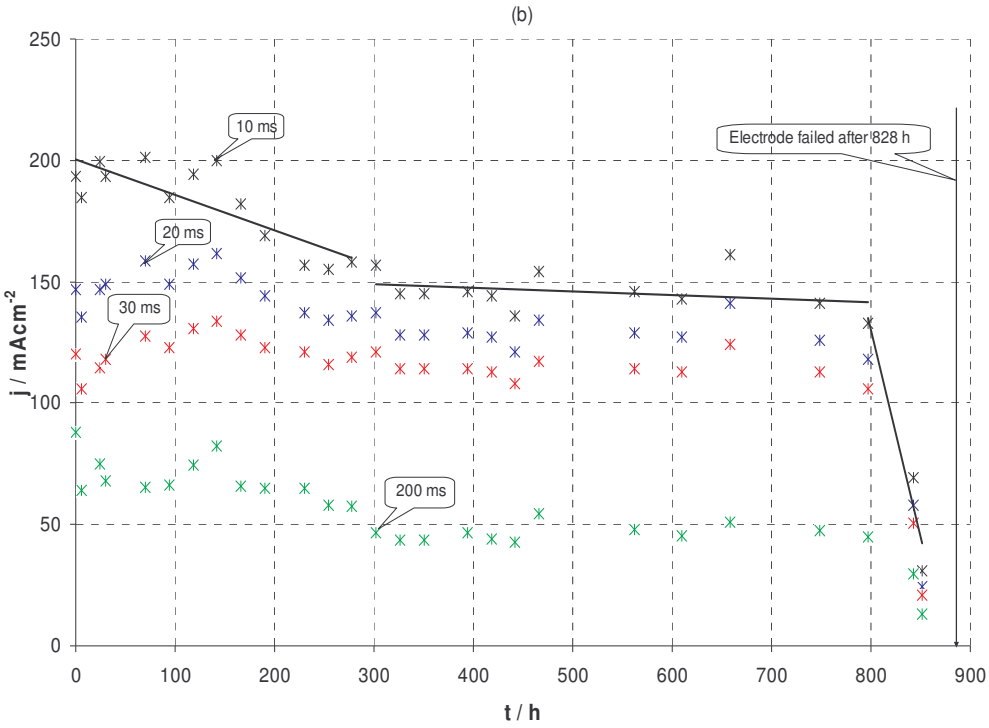
(b) coated titanium plate anode in electrolyte solution 1 at 55ºC.

(c) expanded titanium mesh in electrolyte solution 1 at 55ºC.

As noticed in Section 3.2.3, the current density at step potential = 1.5 V shows a initial zone where the electroactivity of the anode material decreases rapidly, then levels off and decreases significantly at the end. The initial decrease is explained in terms of large change in electrochemical surface area at the beginning for a fresh anode and dissolution of the active component at constant rate in the second zone. At the end of the service life, there is no significant electrocatalyst left as seen on the SEM images (i.e. Figure 3.19 (2)) and the formation of TiO_2 on the titanium substrate leads to a rapid drop in the current density.

The same results might be expected if one records only the current density at very short times (i.e. $t = 10$ ms or $t = 20$ ms) from chronoamperometric data, see Figure 3.12. The plot of current density at $t = 10$ ms fits perfectly with the variation of kinetic parameter, ϕ_0 and can be used for a rapid assessment of electrocatalytic activity.




(b)
250
200
150
100
50
0
j / mAcm-2
0
100
200
300
400
500
600
700
800
900
t / h
10 ms
20 ms
30 ms
200 ms
Electrode failed after 828 h

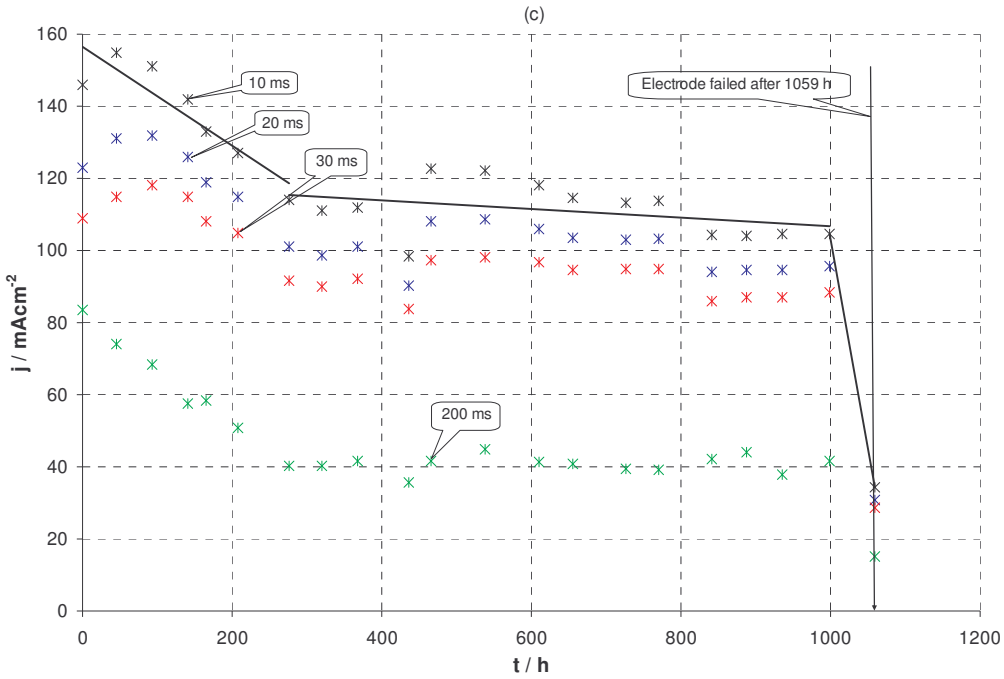


Figure 3.12 Variation in current density j at 1.5 V with electrolysis time. Data from chronoamperometry at 10 ms; 20 ms; 30 ms and 200 ms on

(a) coated titanium plate anode in electrolyte solution 2 at 55ºC.

(b) coated titanium plate anode in electrolyte solution 1 at 55ºC.

(c) expanded titanium mesh in electrolyte solution 1 at 55ºC.

A $j-t$ (electrolysis time) profiles are plotted for chronoamperometric data at $t=10$ ms , $t=20$ ms or $t=30$ ms and show the same trends represented by the kinetic parameter ϕ_0 in Figure 3.11. However, it is quite difficult to predict clearly chronoamperometric characteristics with anodization time from data at $t=200$ ms.

3.3 Surface morphology and coating composition

The images were obtained on five zones of the sample plate according to the diagram below:

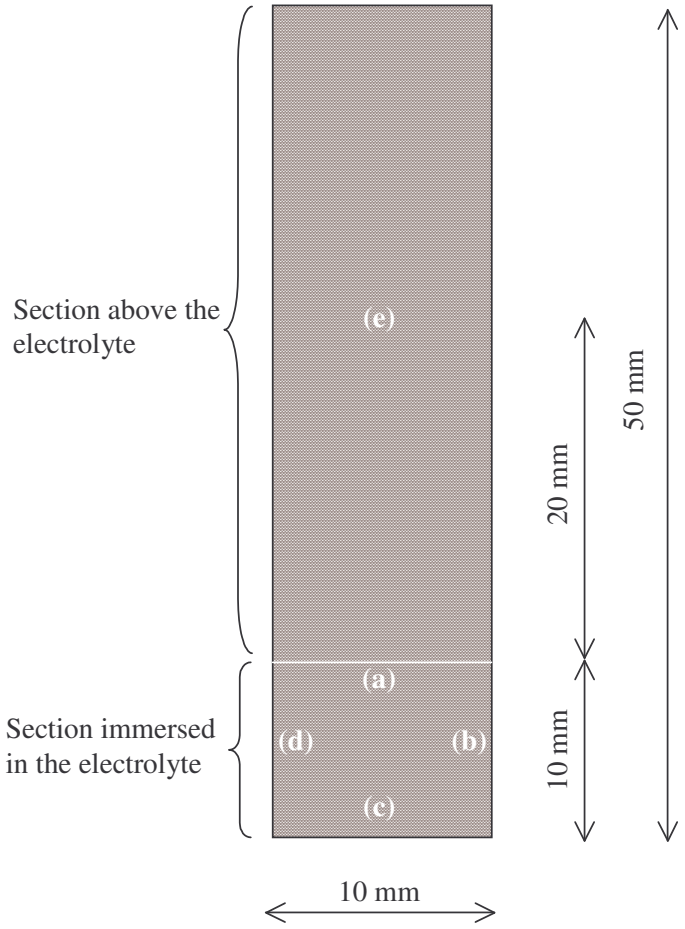


Figure 3.13 Places where SEM images and EDS elemental analysis were done. (a) corresponds to the top middle at 10 mm from the bottom of sample anode; (b) corresponds to the right edge at 5 mm from the bottom; (c) corresponds to the middle edge at the bottom; (d) corresponds to the left edge at 5 mm from the bottom; (e) corresponds to the top middle at 30 mm from the bottom.

On the unused sample anode, the surface is rough and porous with mud-cracked structure and well-defined grains. The edges of the fresh samples have many cracks and the structure is slightly more disordered whereas the morphology of the other surface is compact without major cracks.

On the deactivated sample anodes, part (a) which was not totally in contact with the electrolyte kept the same morphology as on the unused section part (e). The surface morphology of the parts fully exposed to the aggressive electrolyte (b), (c) and (d) shows a clear change with a net disappearance of roughness and cracks. A detachment of coating and formation of a new oxide film are observed in some areas. These results are in good agreement with previous work. (Xu and Scantlebury, 2003)

The loss of the porous part of the oxide layer can be attributed to a combination of erosion through the process of bubble formation during oxygen evolution coupled with electrodissolution of the electrocatalytic component. Pilla et al. (1997) noticed the same mechanism when studying anode deactivation in both sulphuric acid and chloride solutions.

Figures 3.14 to 3.18 show comparative SEM micrographs of the coated titanium plate anodes before and after the ALT in electrolyte solution 1.

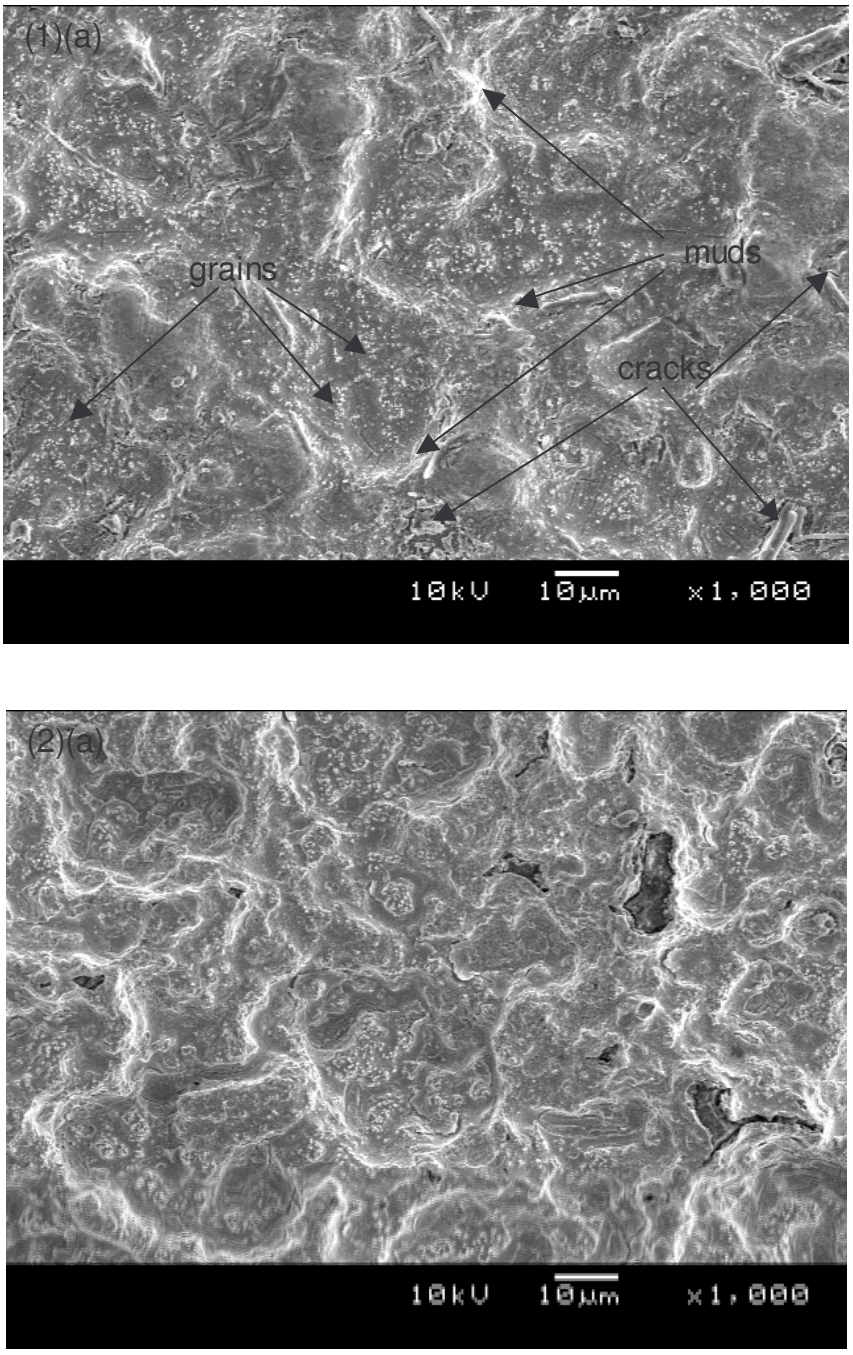


Figure 3.14 Comparison between SEM morphologies of IrO_2–Ta_2O_5 coated titanium anodes corresponding to the part (a) as seen in Figure 3.13. (1) fresh sample (2) after accelerated life test.

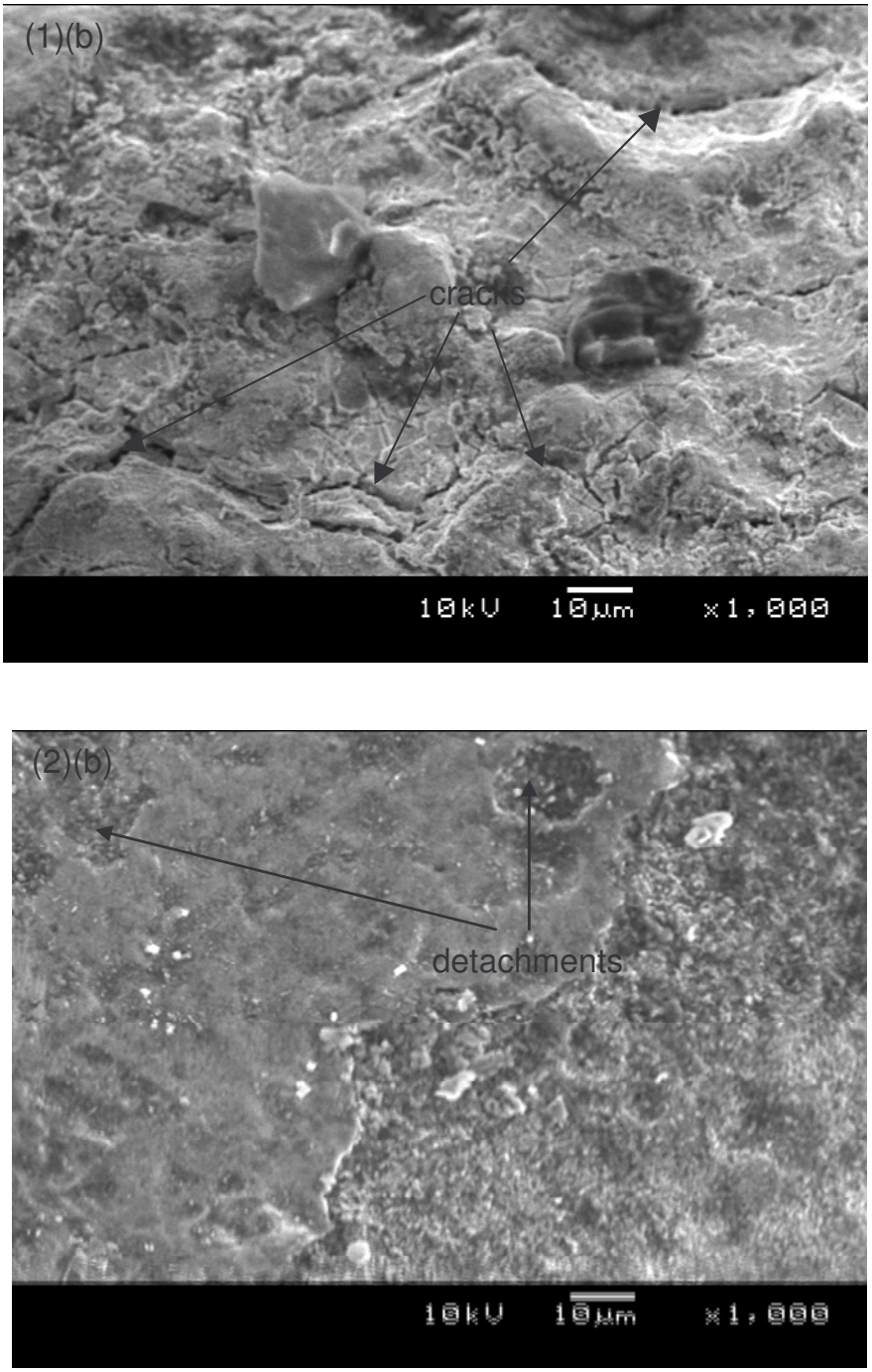


Figure 3.15 Comparison between SEM morphologies of IrO_2–Ta_2O_5 coated titanium anodes corresponding to the part (b) as seen in Figure 3.13. (1) fresh sample (2) after accelerated life test.

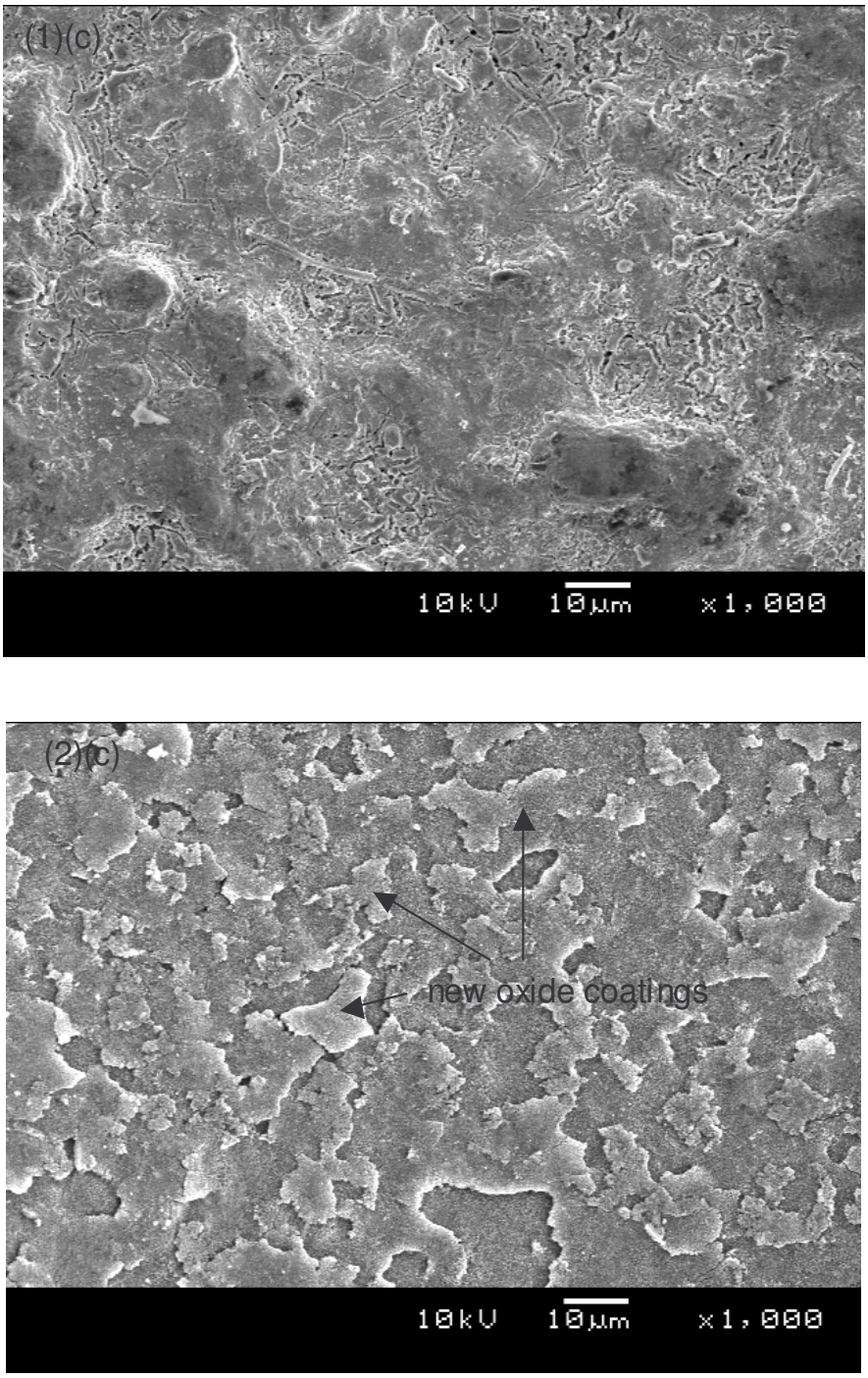


Figure 3.16 Comparison between SEM morphologies of IrO_2–Ta_2O_5 coated titanium anodes corresponding to the part (c) as seen in Figure 3.13. (1) fresh sample (2) after accelerated life test.

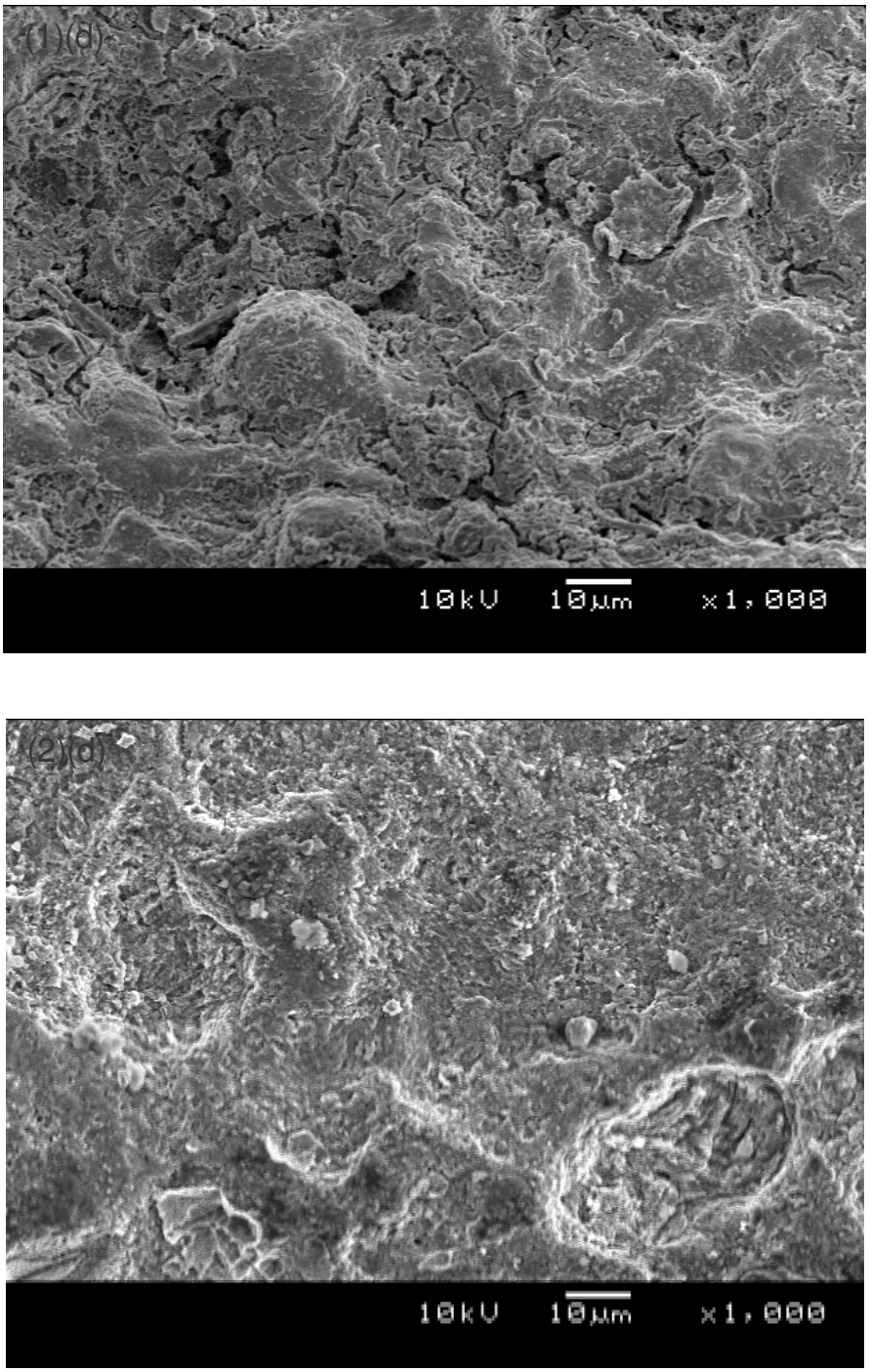


Figure 3.17 Comparison between SEM morphologies of IrO_2–Ta_2O_5 coated titanium anodes corresponding to the part (d) as seen in Figure 3.13. (1) fresh sample (2) after accelerated life test.

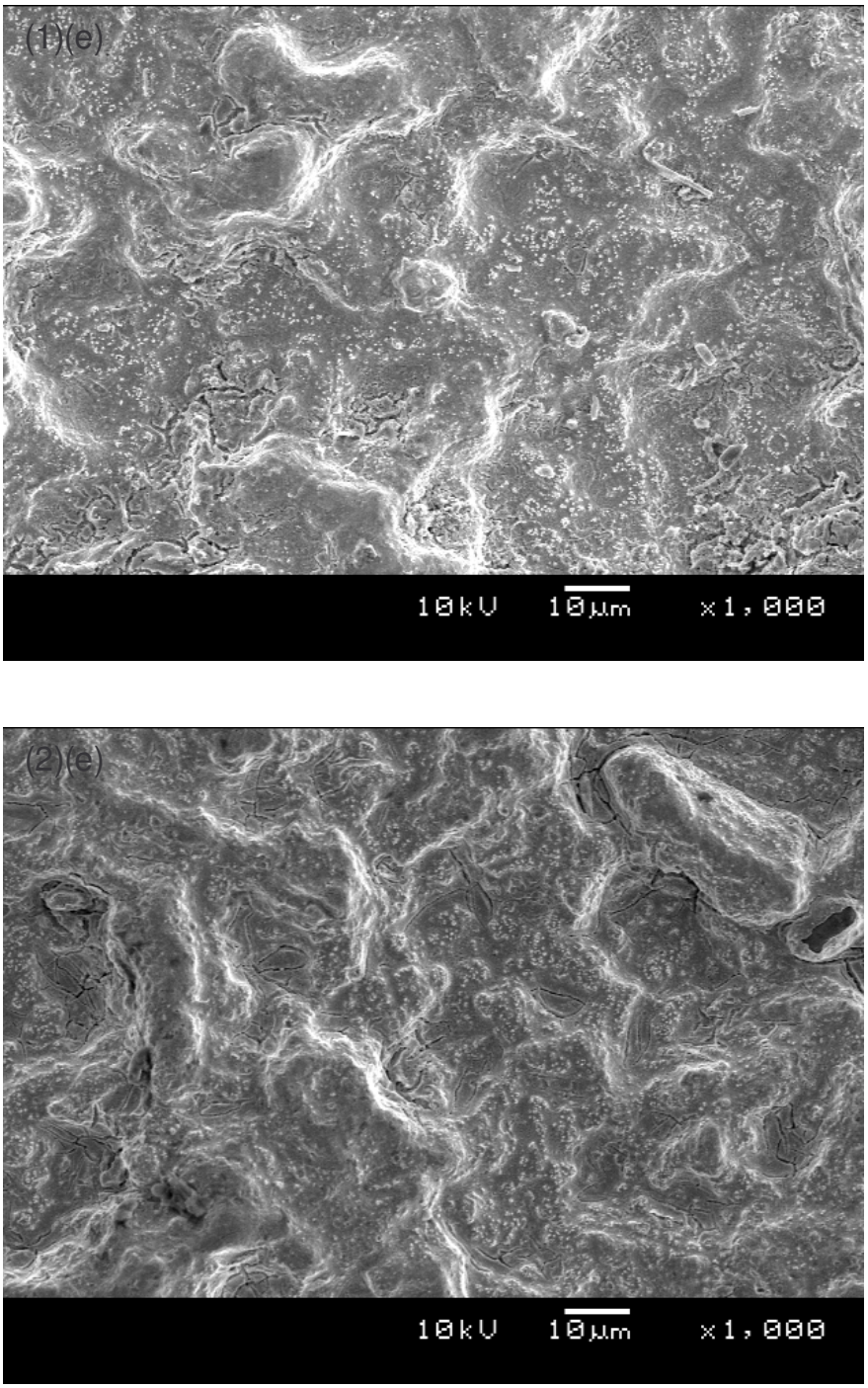


Figure 3.18 Comparison between SEM morphologies of IrO_2–Ta_2O_5 coated titanium anodes corresponding to the part (e) as seen in Figure 3.13. (1) fresh sample (2) after accelerated life test.

Energy dispersive X-ray spectroscopy (EDS) is usually used to measure the bulk element concentrations in a film. For this study, the test was only done for qualitative examination purposes. Three elements were examined: Ti, Ir and Ta. In addition C, Si, Na, Al, Cl… were detected in small proportion. For the unused anodes, Ti is probably coming from the titanium substrate, because of the maximum sampling depth of EDS ≈ 6 to 7 μm at 20 keV accelerating voltage. Other elements are impurities probably coming from the coating preparation method.

For the deactivated sample, the Ti detected is the substrate because the majority of coating is gone after the ALT experiment. Traces of Ir and Ta are observed due to some residual coating left at the end of the ALT experiment.

EDS analysis indicates that the surface composition is inhomogeneous before and after electrolysis as shown in Table 3.1. Two typical compositions can be seen in Figure 3.19. (More EDS - data are further presented in Appendix B).

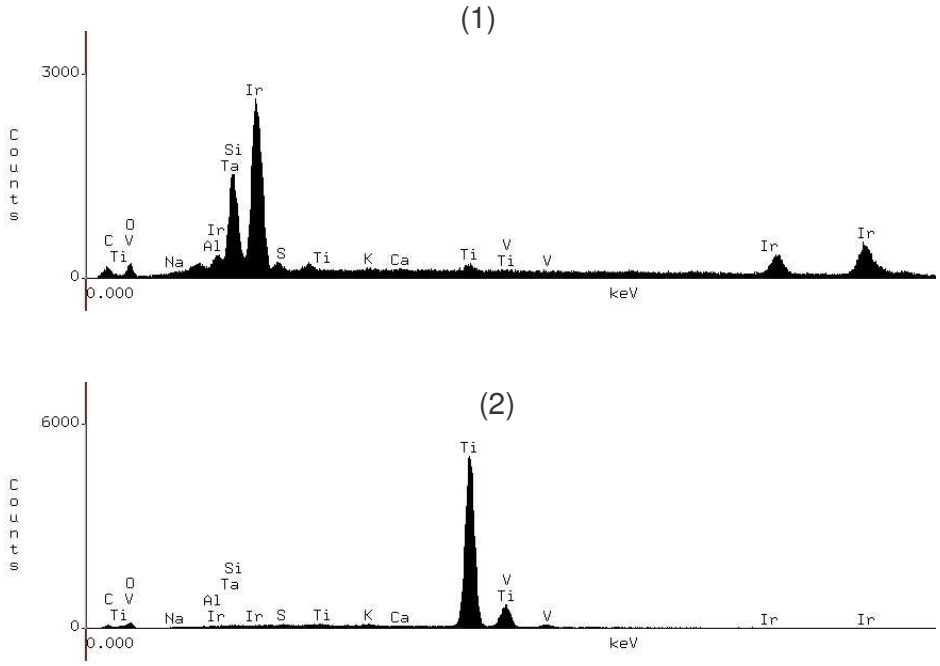


Figure 3.19 EDS spectra of the coated titanium anodes correspond to middle edge (c) at the bottom of sample anode: (1) before, and (2) after accelerated life test

Table 3.1 Quantitative analysis of the coated titanium on 5 representative zones: (1) before, and (2) after accelerated life test.

Elements	Ti (%)		Ir (%)		Ta (%)	
Places	(1)	(2)	(1)	(2)	(1)	(2)
(a)	0.98	3.86	66.33	73.88	26.37	20.34
(b)	1.14	94.80	64.32	0.00	26.49	0.22
(c)	1.26	95.03	64.44	0.00	28.50	1.10
(d)	1.47	96.77	64.33	0.00	28.16	0.47
(e)	0.77	1.29	65.52	77.86	27.50	17.50

From this table, zones (b), (c) and (d) where the anode was in contact with the electrolyte on the deactivated anode (2), compared to a fresh sample (1) shows the strong appearance of the titanium substrate and the almost complete removal of tantalum and iridium coating.

3.4 Prediction of anode life under normal plant conditions from ALT

Based on the analysis of Section 1.4.5 (b), the life of an anode in accelerated testing conditions can serve as a possible prediction of life in normal conditions at the plant according to Equation 1.26.

$$SL_{NOR} = SL_{ALT} \times \left(\frac{j_{ALT}}{j_{NOR}} \right)^{n}$$

Table 3.2 presents the service life between two limits $n = 1.4$ and $n = 2$. As $j_{ALT} = 1.2$ Acm^{-2} and $j_{NOR} = 0.3$ Acm^{-2}, the ratio $\frac{j_{ALT}}{j_{NOR}}$ will be 4 and then the service life in normal conditions will be 4^n times the life in accelerated conditions.

Table 3.2 Predicted service lives in normal conditions using the simple relationship between the service life and current density Equation 1.26 between $n = 1.4$ and $n = 2$.

ALT experimental operating conditions	j_{ALT} / A cm^{-2}	SL_{ALT} / hours	j_{NOR} / A cm^{-2}	SL_{NOR} / hours	
				Lower limit $n = 1.4$	Upper limit $n = 2$
Electrolyte solution 2 at 55ºC on titanium plate coated IrO_2 - Ta_2O_5 20:80 || 80:20	1.2	645	0.3	4492	10320
Electrolyte solution 1 at 55ºC on titanium plate coated IrO_2 - Ta_2O_5 20:80 || 80:20	1.2	828	0.3	5767	13248
Electrolyte solution 1 at 55ºC on expanded titanium mesh	1.2	1059	0.3	7375	16944

In normal operating conditions, the minimum service life found in the Table 3.2 is less than 1 year (8760 hours) and the maximum service life is less than 2 years (17520 hours) for the coated titanium plate and the expanded titanium mesh. A comparison of these values and service life of other titanium anodes is difficult because the service life depends not only on testing conditions but also on the coating loading and its properties.

Chapter 4 CONCLUSIONS AND SUGGESTIONS

4.1 Summary

The accelerated life tests performed on the coated titanium plates showed the coating failed earlier on the anode that was in the solution with the higher chromic acid concentration (i.e. Solution 2). Figures 3.1 and 3.2 indicate that the times for the cell voltages to reach 10 V for anodes in solutions 1 and 2 were 828 and 645 hours, respectively. The corresponding time for the expanded titanium mesh electrode in solution 1 was 1059 hours.

The higher chromic acid concentration probably increases the rate of chemical corrosion of the tantalum–iridium oxide layer, while the geometrical nature of a mesh provides additional adhesion for the coating. (A coated mesh anode is also the preferred shape in the chlor-alkali industry)

Cyclic voltammetry and linear sweep voltammetry did not provide any significant information other than to confirm that the oxygen evolution was the only electrochemical reaction occurring at the anode.

Chronoamperometry, on the other hand, proved to be a very useful technique for assessing the electrochemical activity of the anode surface. The main advantages are that it is a very rapid test and a parameter (ϕ_0) can be estimated from the data which is a fundamental kinetic parameter of the catalytic nature of the surface and the oxygen evolution reaction taking place on it.

Additional analysis by SEM and EDS before and after the accelerated life test confirmed that the deactivation was a result of corrosion of the IrO_2 followed by titanium substrate passivation.

4.2 Practical recommendation

It is recommended that chronoamperometry be employed for determining the activity of the tantalum–iridium oxide coating on a titanium substrate. Samples can be cut from a new anode or from one that has already been operating in a cell.

The surface area should first be determined electrochemically using the technique described in Appendix A. Then the electrocatalytical properties should be frequently measured by chronoamperometric methods. As accounting for the mixed electrochemical process does not provide additional information, analysis of chronoamperometric data with time at interval no more than 10 ms might be a quickest way for assessing the electroactivity.

From Figure 3.11, it would appear that a value of $\phi_0 = 120\,\text{mAcm}^{-2}$ would indicate that the coating is still sufficiently active. Furthermore, the time required to reach an operational electrochemical activity (steady state region) may be considered as a measure of electrode performance. It appears to be about 30 % of the service life. Moreover, the value of current density (chronoamperometric experiments) at which the electrode reaches the operational characteristics may be considered as a measure of electrode quality.

4.3 Suggestions for future work

ALT experiments should be done at a number different current densities in order to generalise the applicability of Equation 1.26 (reproduced below):

$$SL_{NOR} = SL_{ALT} \times \left(\frac{j_{ALT}}{j_{NOR}} \right)^n$$

In Chapter 3 (Section 3.1), it was noticed that the cell voltage measurements made during the long electrolysis were characterized by many up and downs due to the control of level of electrolyte; as a consequence the exposed electrode area varied in time. It is suggested that a strict control of the surface area during all electrochemical experiments must be applied.

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Appendix A

Electrochemical surface area determination

Since the electrode rates, especially current in this work, must be normalized to the unit exposed area, it is critical to know and control the area of exposure. Different methods have been proposed to find the surface area of solid electrodes and can be found in the IUPAC publication. (Trassatti et al., 1991)

In this dissertation, the electrochemical surface area of the expanded titanium mesh was determined by stepping the potential of the electrode to a value where the reduction or oxidation of a particular electroactive species used for the experiment is diffusion controlled. The Cottrell equation described in Chapter 1 (Section 1.4.5 (e) Equation 1.27) may then be used to calculate the electrochemical surface area. If the recorded current (i) is plotted against the inverse of the square root of the recorded time ($1/\sqrt{t}$), the slope of the linear plot can be solved for A.

a. Experimental design for the electrochemical surface area determination

A three-electrode electrochemical cell with potentiostatic control, identical to the experimental set-up described in Chapter 2 for the monitoring of change on the coated titanium anode was used to conduct the experiment described in this Section. For this experiment, Figures A1 and A2 below show how the sample of a mesh electrode was mounted for tests.

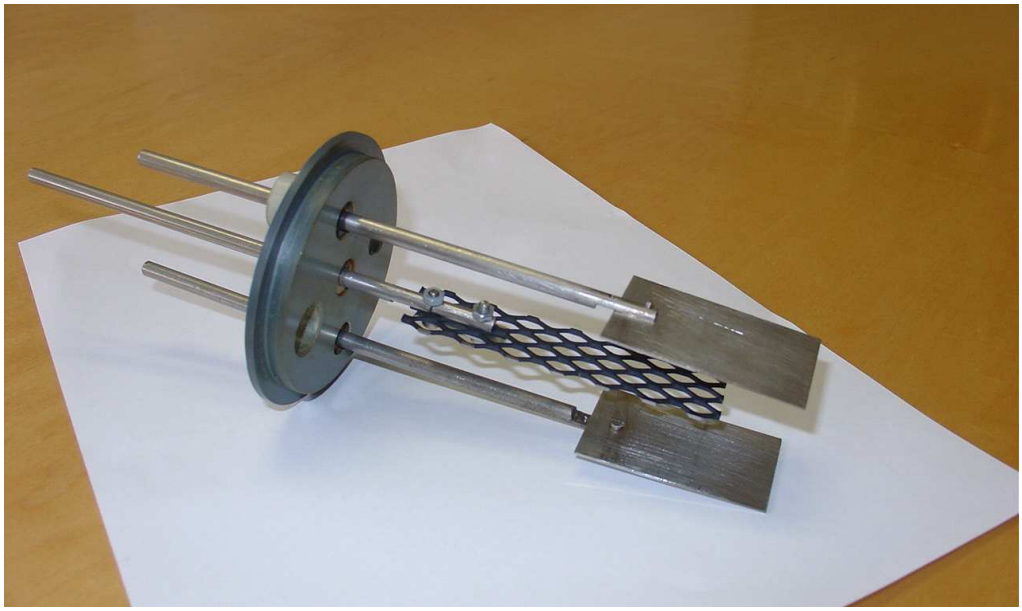


Figure A1 shows a vessel cover in PV with ports to mount the expended titanium mesh as anode, two stainless steel plates as cathode and the reference electrode.

Figure A2 shows a piece of expanded titanium mesh screwed up tight on a rod.

Information provided in Section 2.3 (Electrochemical measurements) also applies to experiments described in this Section. The only difference is that a 50 mM Potassium ferrocyanide, $K_4Fe(CN)_6$, was used as electroactive species in 2 M KNO_3 background. The pH of this solution was adjusted to 3 by drop wise addition of 0.5 M HNO_3.

b. Cyclic voltammetry

Prior to running the amperometric tests for the evaluation of electrochemical surface area, a cyclic voltammetry experiment was performed in order to identify the Redox couples as well as the potential range of diffusional transport control mode. A record $i-E$ plot for the forward and reverse scan is illustrated in Figure A3.

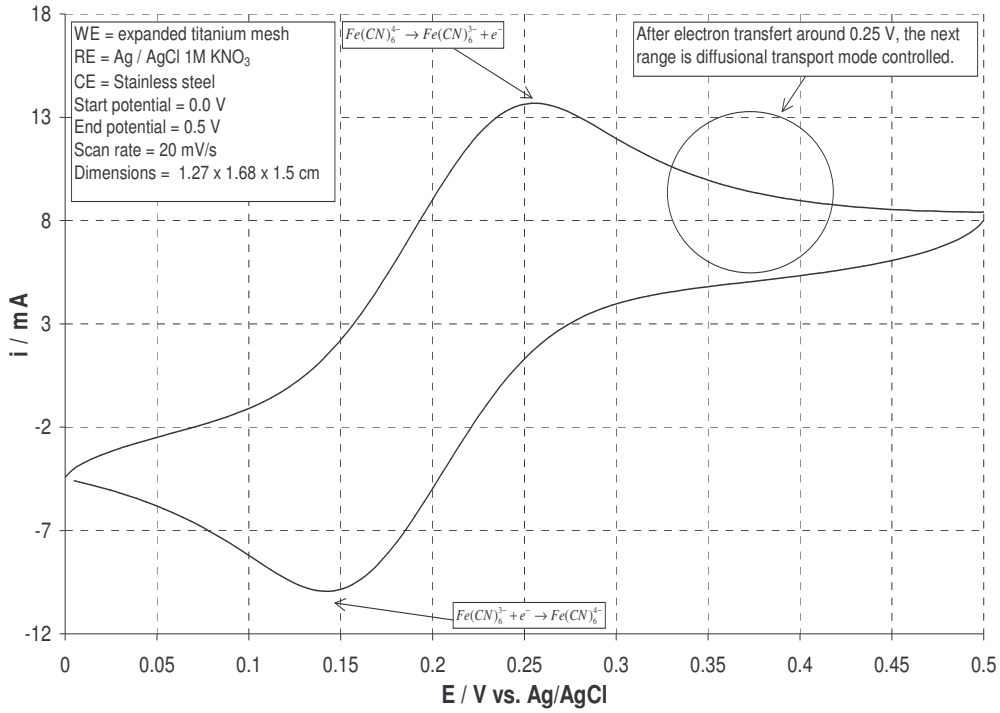


Figure A3 Cyclic voltammogram of 50 mM $K_4Fe(CN)_6$ in 2M KNO_3 (pH 3) solution at room temperature using an expanded titanium mesh as working electrode.

The ferricyanide/ferrocyanide couple was used to investigate the electrochemical surface area of expanded titanium anode. Cyclic voltammogram recorded for a 50 mM $K_4Fe(CN)_6$ solution using a potential scan rate of 20 mV sec $^{-1}$ is shown in Figure A3. It can be seen that the voltammogram shows a well formed anodic peak at $E = +0.254$ V and a cathodic peak at $E = +0.142$ V. This voltammogram when corrected with a $IR = 1.7 \times 0.01$ V has all the properties of a reversible redox couple. Moreover, analysis of the anodic peak current gives us a potential range where diffusion controls the process. That is why step potential of 0.4 V was chosen for the determination of electrochemical surface area.

c. Chronoamperometry

The electrochemical surface area of the expanded titanium mesh was determined by chronoamperometry by using the Cottrell Equation (see Equation 1.27) for a diffusion-controlled current. The results are presented graphically in Figures A4 and A5.

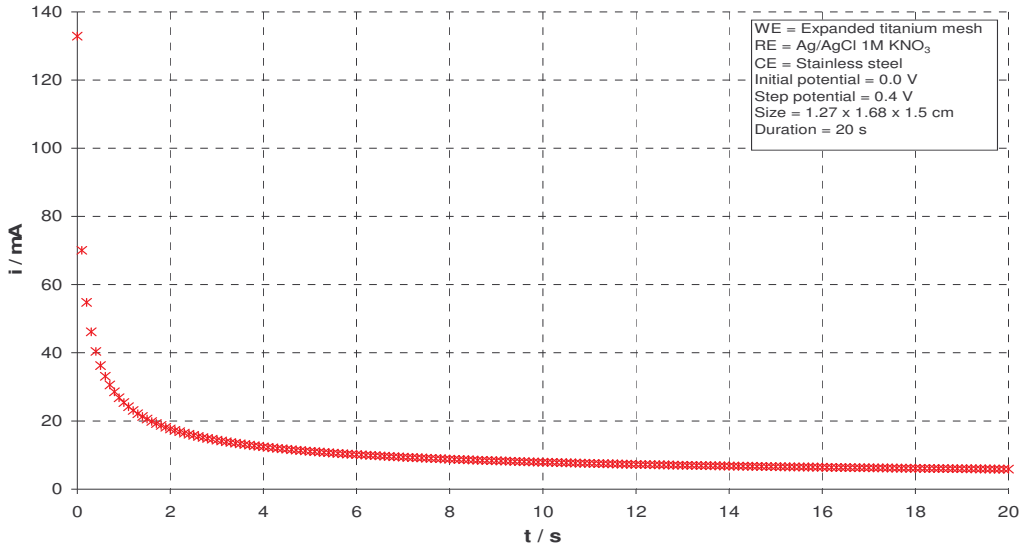


Figure A4 Chronoamperometric experiment involving a 50 mM $K_4Fe(CN)_6$ in 2M KNO_3 (pH 3) at room temperature used to establish the electrochemical surface area of an expanded titanium mesh.

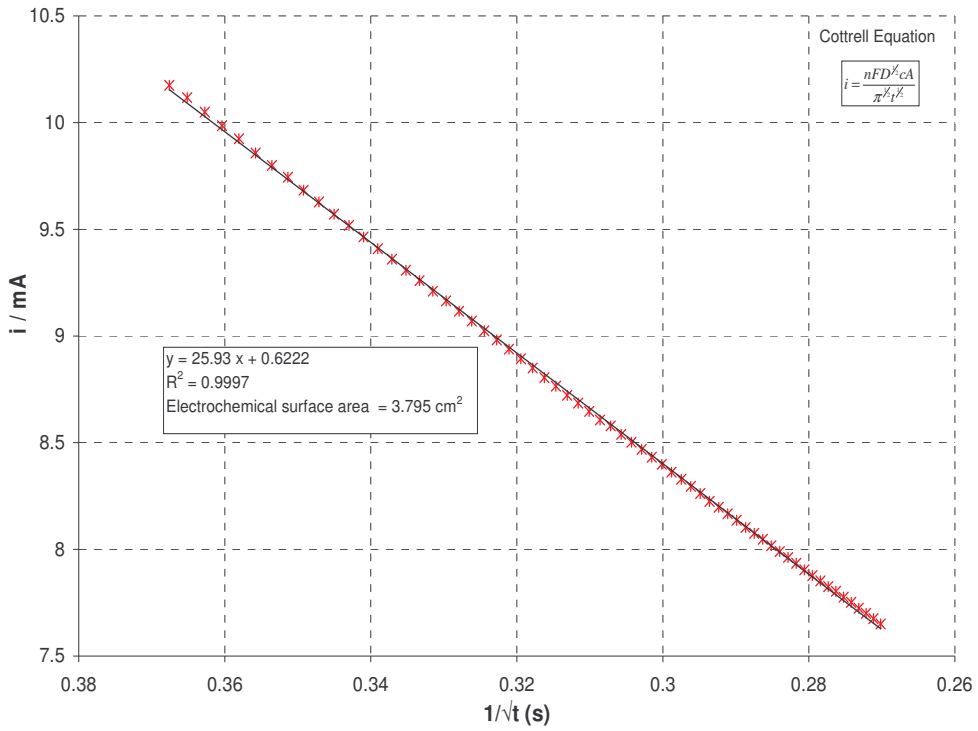


Figure A5 Plot used to calculate the electrochemical surface area of an expanded titanium mesh as working electrode via the Cottrell equation. Data obtained from Figure A4.

The Cottrell equation $i = \frac{nFD^{1/2}c_R A}{\pi^{1/2}t^{1/2}}$ can be rewritten as following:

$$i = slope\frac{1}{t^{1/2}}$$

where $slope = \frac{nFD^{1/2}c_R A}{\pi^{1/2}}$.

By solving the slope of the linear expression shown in Figure A5 for A, the electrochemical surface area of the working electrode will be:

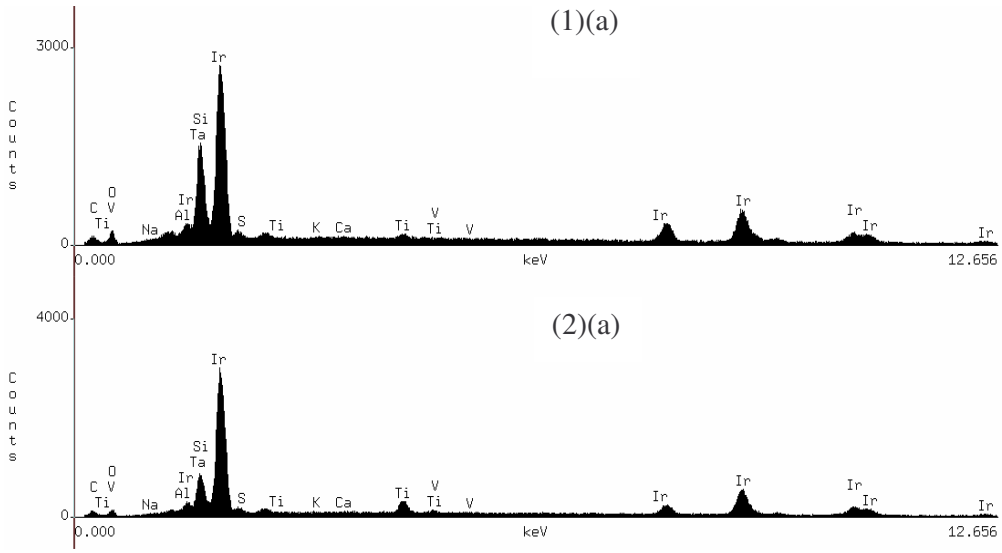
$$A = slope\frac{\pi^{1/2}}{nFD^{1/2}c_R}$$

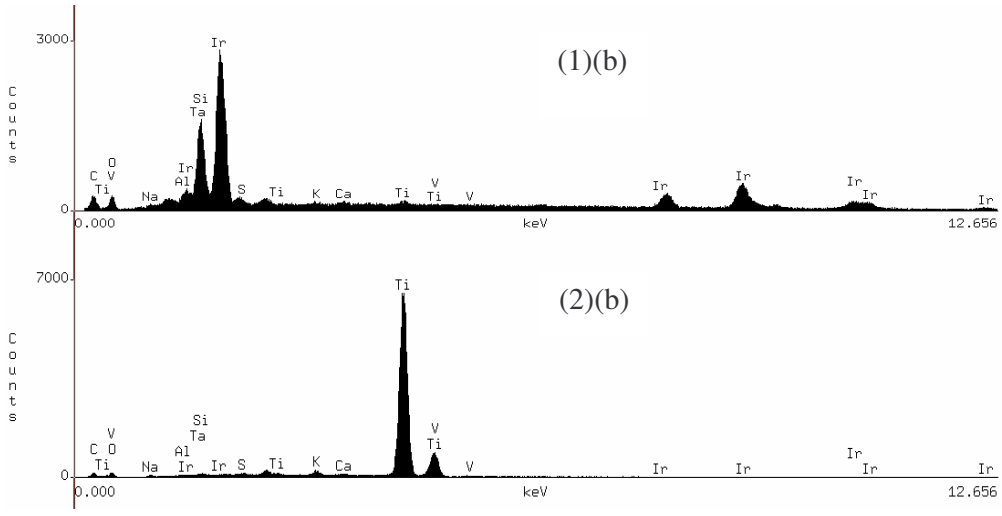
where $n = 1$ according to $Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^-$ equation; $F = 96485$ C mol^{-1}; $D = 6.3 \times 10^{-10}$ m^2 s^{-1}(Weast, 1978) and then concentration $c_R = 50$ mol m^{-3}.

An electrochemical surface area of 3.795 cm^2 was established from experiment and it compares well with to an estimated geometrical area of 3.918 cm^2. Hence the current densities reported in the accelerated life test and electrochemical measurement for the expanded titanium mesh were related to this electrochemical surface area exposed to the solution.

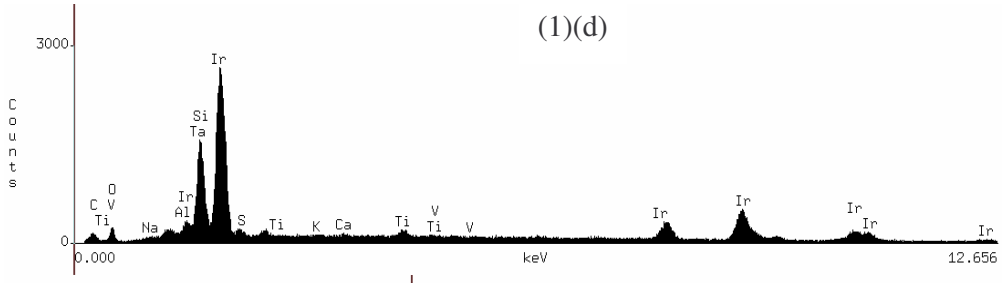
Appendix B

Additional EDS data on coated titanium anode before (1) and after (2) ALT in electrolyte solution 1





(1)(d)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Ti
O
V
Na
Al
Ir
Si
Ta
S
Ti
K
Ca
Ti
V
Ti
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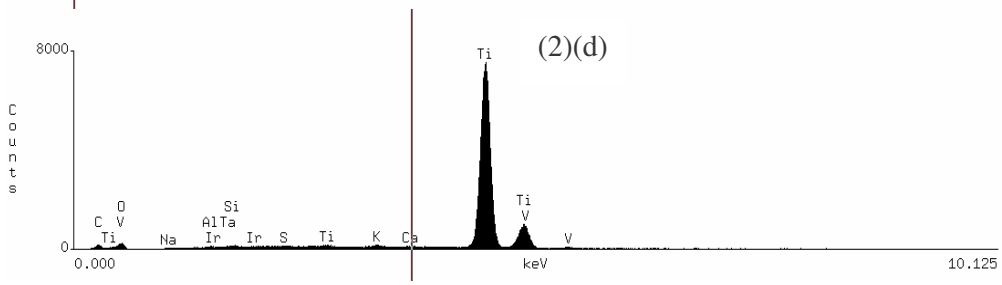
Ir
Ir
Ir
Ir
0.000
keV
12.656

(2)(d)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O
V
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Ir
Ir
S
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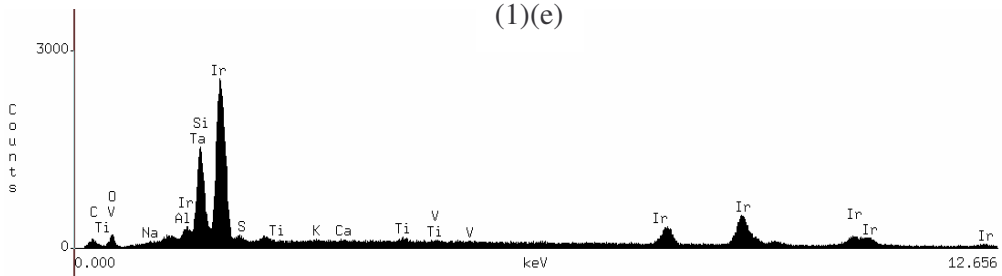
V
V
0.000
keV
10.125

(1)(e)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O
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K
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V
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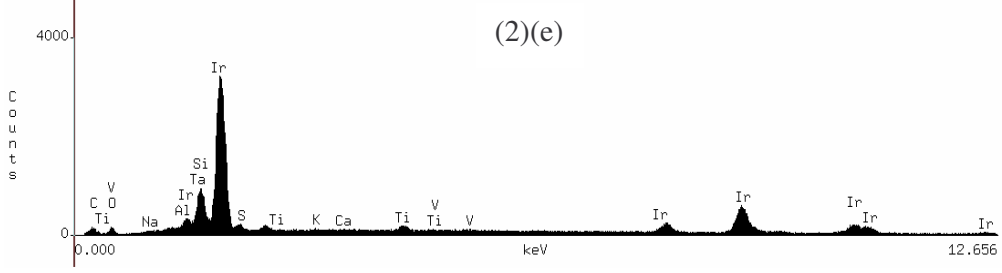
Ir
Ir
Ir
0.000
keV
12.656

(2)(e)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Ti
V
Ir
Ir
Ir
Ir
Ir
0.000
keV
12.656

Appendix C

1. ALT data in electrolyte solution 2 on plate anode

t / s	t / h	Cell voltage / V
0	0	3.845
43200	12	4.340
86400	24	4.739
129600	36	3.919
172800	48	4.079
216000	60	4.555
259200	72	4.243
302400	84	4.520
345600	96	4.496
388800	108	4.552
432000	120	4.399
475200	132	4.335
518400	144	4.520
561600	156	4.454
604800	168	4.633
648000	180	4.578
691200	192	4.510
734400	204	4.441
777600	216	4.736
820800	228	4.651
864000	240	5.011
907200	252	5.114
950400	264	5.020
993600	276	4.991
1036800	288	4.897
1080000	300	4.719
1123200	312	4.600
1166400	324	5.052
1209600	336	4.940
1252800	348	4.776
1296000	360	4.691
1339200	372	4.984
1382400	384	4.981
1425600	396	5.056
1468800	408	5.163
1512000	420	5.281
1555200	432	5.609
1598400	444	5.724
1641600	456	5.682
1684800	468	5.689
1728000	480	6.042
1771200	492	6.192
1814400	504	6.175
1857600	516	6.194
1900800	528	6.555

1944000	540	6.602
1987200	552	6.972
2030400	564	7.521
2073600	576	7.179
2116800	588	7.303
2160000	600	7.777
2203200	612	8.267
2246400	624	8.089
2289600	636	8.838
2322000	645	10.000

2. ALT data in electrolyte solution 1 on plate anode

t / s	t / h	Cell voltage / V
0	0	4.685
43200	12	4.845
86400	24	4.641
129600	36	4.798
172800	48	4.767
216000	60	4.758
259200	72	4.729
302400	84	4.720
345600	96	4.747
388800	108	4.769
432000	120	4.893
475200	132	4.852
518400	144	5.040
561600	156	5.031
604800	168	5.286
648000	180	5.287
691200	192	5.460
734400	204	5.448
777600	216	5.400
820800	228	5.340
864000	240	5.678
907200	252	5.739
950400	264	5.734
993600	276	5.666
1036800	288	5.651
1080000	300	5.626
1123200	312	5.677
1166400	324	5.656
1209600	336	5.917
1252800	348	5.893
1296000	360	5.850
1339200	372	5.828
1382400	384	5.888
1425600	396	5.963
1468800	408	6.229
1512000	420	5.966
1555200	432	6.134

1598400	444	6.180
1641600	456	6.253
1684800	468	5.790
1728000	480	5.884
1771200	492	5.943
1814400	504	6.052
1857600	516	6.228
1900800	528	6.309
1944000	540	6.552
1987200	552	6.782
2030400	564	6.090
2073600	576	6.428
2116800	588	6.490
2160000	600	6.707
2203200	612	6.190
2246400	624	6.543
2289600	636	6.534
2332800	648	6.706
2376000	660	5.980
2419200	672	5.930
2462400	684	5.779
2505600	696	5.605
2548800	708	5.531
2592000	720	5.415
2635200	732	5.309
2678400	744	6.003
2721600	756	6.022
2764800	768	5.860
2808000	780	5.738
2851200	792	5.681
2894400	804	7.348
2937600	816	7.781
2980800	828	9.824
3024000	840	10.000
3067200	852	10.000

3. ALT data in electrolyte solution 1 on expanded titanium mesh

t / s	t / h	Cell voltage / V
0	0	5.732
43200	12	5.075
86400	24	4.756
129600	36	4.511
172800	48	5.282
216000	60	5.280
259200	72	5.252
302400	84	5.264
345600	96	5.539
388800	108	5.665

432000	120	5.709
475200	132	5.685
518400	144	5.744
561600	156	5.869
604800	168	5.823
648000	180	5.948
691200	192	6.202
734400	204	6.693
777600	216	6.328
820800	228	6.401
864000	240	6.469
907200	252	6.618
950400	264	6.739
993600	276	6.470
1036800	288	6.512
1080000	300	6.295
1123200	312	6.208
1166400	324	6.369
1209600	336	6.501
1252800	348	6.719
1296000	360	7.010
1339200	372	6.983
1382400	384	7.422
1425600	396	7.452
1468800	408	6.920
1512000	420	6.667
1555200	432	6.528
1598400	444	6.524
1641600	456	6.618
1684800	468	6.410
1728000	480	6.075
1771200	492	5.970
1814400	504	6.042
1857600	516	6.210
1900800	528	6.453
1944000	540	6.508
1987200	552	6.609
2030400	564	6.701
2073600	576	6.812
2116800	588	7.047
2160000	600	7.198
2203200	612	6.700
2246400	624	7.066
2289600	636	7.055
2332800	648	7.303
2376000	660	7.183
2419200	672	7.347
2462400	684	7.440
2505600	696	7.496
2548800	708	7.668
2592000	720	7.813
2635200	732	6.843

2678400	744	6.860
2721600	756	6.941
2764800	768	7.114
2808000	780	6.814
2851200	792	6.719
2894400	804	6.652
2937600	816	6.585
2980800	828	6.738
3024000	840	6.858
3067200	852	7.039
3110400	864	6.909
3153600	876	6.883
3196800	888	6.801
3240000	900	7.027
3283200	912	7.057
3326400	924	7.012
3369600	936	6.841
3412800	948	7.008
3456000	960	7.059
3499200	972	7.183
3542400	984	7.339
3585600	996	7.462
3628800	1008	6.887
3672000	1020	6.760
3715200	1032	6.652
3758400	1044	6.437
3801600	1056	9.772
3812580	1059.05	10.000

4. CV data in electrolyte solution 2 on plate anode

E / V	j / mAcm^{-2} at 0 hours	j / mAcm^{-2} at 84 hours	j / mAcm^{-2} at 432 hours	j / mAcm^{-2} at 568 hours	j / mAcm^{-2} at 616 hours	j / mAcm^{-2} at 645 hours
1.200	-1.434	-1.633	-2.228	-1.724	-1.923	-1.953
1.205	-1.099	-1.328	-1.480	-1.404	-1.526	-1.587
1.210	-0.793	-1.221	-1.266	-1.297	-1.389	-1.480
1.215	-0.580	-1.160	-1.175	-1.251	-1.328	-1.419
1.219	-0.275	-1.129	-1.129	-1.221	-1.297	-1.389
1.224	0.549	-1.114	-1.099	-1.205	-1.266	-1.358
1.229	1.007	-1.068	-1.083	-1.175	-1.236	-1.343
1.234	1.587	-1.038	-1.068	-1.175	-1.221	-1.312
1.239	2.075	-1.007	-1.038	-1.160	-1.221	-1.328
1.244	2.869	-0.946	-1.022	-1.144	-1.190	-1.297
1.249	3.693	-0.900	-0.961	-1.129	-1.190	-1.282
1.254	4.349	-0.854	-0.916	-1.099	-1.175	-1.266
1.259	5.508	-0.778	-0.870	-1.099	-1.160	-1.266
1.263	6.729	-0.732	-0.824	-1.068	-1.160	-1.251
1.268	7.828	-0.671	-0.793	-1.038	-1.144	-1.221
1.273	9.506	-0.610	-0.732	-0.977	-1.129	-1.205
1.278	11.139	-0.504	-0.687	-0.931	-1.114	-1.190

1.283	12.680	-0.397	-0.626	-0.854	-1.068	-1.160
1.288	14.618	-0.259	-0.534	-0.809	-1.038	-1.144
1.293	16.678	0.061	-0.412	-0.732	-0.977	-1.099
1.298	18.997	0.504	-0.290	-0.671	-0.870	-1.068
1.302	21.149	0.809	-0.015	-0.580	-0.824	-0.992
1.307	23.483	1.099	0.488	-0.427	-0.763	-0.916
1.312	26.245	1.480	0.793	-0.320	-0.687	-0.839
1.317	28.778	1.892	1.038	-0.214	-0.610	-0.748
1.322	31.738	2.365	1.419	0.412	-0.504	-0.671
1.327	34.851	2.899	1.846	0.656	-0.366	-0.565
1.332	37.643	3.555	2.243	0.946	-0.229	-0.458
1.337	40.924	3.937	2.823	1.251	0.366	-0.336
1.342	44.006	4.822	3.387	1.663	0.626	-0.229
1.346	47.363	5.737	3.830	1.938	0.916	0.320
1.351	50.766	6.714	4.440	2.457	1.205	0.610
1.356	54.260	7.721	5.310	2.945	1.602	0.916
1.361	57.800	8.789	6.134	3.525	1.923	1.099
1.366	61.493	10.056	7.217	3.860	2.365	1.450
1.371	65.689	11.505	8.011	4.456	2.869	1.801
1.376	69.336	12.695	9.277	5.203	3.387	2.029
1.381	73.242	14.236	10.513	5.875	3.799	2.487
1.385	77.118	15.793	11.642	6.775	4.196	2.899
1.390	81.253	17.578	12.863	7.645	4.913	3.372
1.395	85.144	19.440	14.343	8.377	5.692	3.769
1.400	89.264	21.194	15.717	9.430	6.363	3.967
1.405	93.292	23.193	17.471	10.391	7.202	4.547
1.410	97.641	25.192	19.119	11.475	7.813	5.112
1.415	101.761	27.252	20.538	12.253	8.743	5.768
1.420	106.079	29.297	22.369	13.489	9.674	6.317
1.425	110.474	31.662	24.048	14.618	10.651	6.958
1.429	114.807	34.119	25.925	15.686	11.566	7.645
1.434	119.278	36.240	27.664	17.059	12.299	8.118
1.439	123.612	38.788	29.602	18.387	13.428	8.835
1.444	128.418	41.092	31.754	19.501	14.496	9.644
1.449	132.721	43.549	33.905	20.752	15.549	10.315
1.454	137.039	46.143	35.706	22.125	16.632	11.108
1.459	141.693	48.813	37.903	23.422	17.746	11.673
1.464	146.088	51.331	39.978	24.872	19.089	12.390
1.469	150.650	54.062	42.114	26.321	19.974	13.214
1.473	155.365	56.732	44.189	27.542	21.271	13.962
1.478	160.156	59.433	46.478	29.053	22.461	14.847
1.483	164.749	62.180	48.752	30.502	23.575	15.594
1.488	169.418	65.369	50.873	32.211	24.933	16.525
1.493	174.408	68.100	53.177	33.707	26.245	17.441
1.498	178.879	70.816	50.797	32.089	24.841	18.250
1.503	183.502	73.868	48.569	30.319	23.438	19.150
1.498	178.726	70.633	46.112	28.809	22.232	18.188
1.493	174.042	67.780	43.808	27.328	20.935	17.288
1.488	169.159	65.018	41.687	25.925	19.592	16.357
1.483	164.414	61.752	39.368	24.460	18.646	15.503
1.478	159.882	58.899	37.231	23.193	17.471	14.633
1.473	155.808	56.183	35.156	21.667	16.220	13.718
1.469	151.199	53.375	33.203	20.355	15.183	12.939
1.464	146.408	50.720	31.006	19.257	13.947	12.100

1.459	141.663	47.989	28.992	17.853	12.894	11.566
1.454	137.009	45.319	27.191	16.602	11.810	10.788
1.449	132.553	42.877	25.269	15.427	11.139	9.949
1.444	128.113	40.298	23.376	14.175	10.101	9.308
1.439	123.169	37.933	21.530	13.000	9.201	8.591
1.434	118.698	35.370	19.791	11.810	8.240	7.813
1.429	114.319	33.188	18.402	11.093	7.599	7.370
1.425	109.818	30.731	16.663	9.933	6.790	6.729
1.420	105.423	28.427	15.167	9.003	5.905	5.951
1.415	101.181	26.413	13.641	7.980	5.249	5.493
1.410	97.061	24.338	12.177	7.355	4.517	4.883
1.405	92.484	22.369	11.169	6.454	3.891	4.318
1.400	88.333	20.370	9.766	5.737	3.586	3.860
1.395	84.198	18.692	8.636	4.913	3.021	3.647
1.390	80.139	16.891	7.645	4.211	2.563	3.159
1.385	76.065	15.198	6.622	3.799	2.014	2.792
1.381	72.311	13.596	5.692	3.357	1.709	2.304
1.376	68.481	11.932	4.745	2.823	1.312	1.907
1.371	64.911	10.773	3.906	2.274	0.946	1.648
1.366	60.913	9.506	3.494	1.877	0.641	1.282
1.361	57.251	8.163	2.838	1.465	0.168	0.977
1.356	53.604	7.217	2.213	1.053	-0.290	0.732
1.351	50.201	6.073	1.785	0.809	-0.443	0.458
1.346	46.768	5.173	1.236	0.473	-0.610	-0.168
1.342	43.304	4.272	0.854	-0.168	-0.748	-0.336
1.337	40.115	3.754	0.443	-0.351	-0.885	-0.488
1.332	37.064	3.113	-0.244	-0.534	-1.022	-0.626
1.327	34.149	2.487	-0.473	-0.656	-1.129	-0.732
1.322	30.960	1.923	-0.687	-0.778	-1.190	-0.839
1.317	28.061	1.495	-0.839	-0.916	-1.251	-0.961
1.312	25.421	1.038	-1.053	-1.053	-1.312	-1.068
1.307	22.934	0.717	-1.190	-1.129	-1.358	-1.144
1.302	20.432	0.351	-1.282	-1.175	-1.419	-1.205
1.298	18.280	-0.275	-1.389	-1.236	-1.465	-1.266
1.293	15.945	-0.458	-1.465	-1.282	-1.511	-1.312
1.288	13.840	-0.626	-1.541	-1.312	-1.541	-1.358
1.283	11.948	-0.748	-1.602	-1.373	-1.572	-1.404
1.278	10.544	-0.854	-1.678	-1.419	-1.587	-1.450
1.273	8.835	-1.038	-1.709	-1.465	-1.617	-1.480
1.268	7.568	-1.114	-1.770	-1.495	-1.633	-1.511
1.263	6.134	-1.175	-1.801	-1.495	-1.648	-1.526
1.259	4.959	-1.251	-1.862	-1.526	-1.663	-1.556
1.254	3.906	-1.282	-1.938	-1.541	-1.694	-1.587
1.249	3.311	-1.343	-1.999	-1.556	-1.694	-1.602
1.244	2.472	-1.373	-2.045	-1.587	-1.724	-1.633
1.239	1.816	-1.419	-2.075	-1.602	-1.740	-1.648
1.234	1.160	-1.465	-2.121	-1.617	-1.770	-1.648
1.229	0.656	-1.495	-2.151	-1.633	-1.801	-1.678
1.224	-0.244	-1.511	-2.213	-1.663	-1.846	-1.709
1.219	-0.565	-1.556	-2.269	-1.688	-1.839	-1.732
1.215	-0.809	-1.556	-2.319	-1.710	-1.860	-1.755
1.210	-1.083	-1.587	-2.368	-1.732	-1.881	-1.777
1.205	-1.282	-1.617	-2.417	-1.754	-1.902	-1.800

5. CV data in electrolyte solution 1 on plate anode

E / V	j / mAcm^{-2} at 0 hours	j / mAcm^{-2} at 166 hours	j / mAcm^{-2} at 278 hours	j / mAcm^{-2} at 562 hours	j / mAcm^{-2} at 843 hours	j / mAcm^{-2} at 851 hours
1.200	-1.633	-1.678	-2.029	-2.197	-1.953	-0.132
1.205	-1.328	-1.205	-1.343	-1.373	-1.556	0.003
1.210	-1.221	-1.099	-1.175	-1.175	-1.434	0.055
1.215	-1.160	-1.022	-1.114	-1.099	-1.358	0.086
1.219	-1.114	-0.977	-1.068	-1.038	-1.328	0.109
1.224	-1.083	-0.916	-1.022	-0.992	-1.312	0.126
1.229	-1.053	-0.870	-0.961	-0.931	-1.297	0.142
1.234	-0.992	-0.854	-0.931	-0.931	-1.266	0.157
1.239	-0.900	-0.824	-0.885	-0.885	-1.236	0.172
1.240	-0.854	-0.809	-0.854	-0.885	-1.221	0.187
1.249	-0.778	-0.778	-0.824	-0.839	-1.190	0.202
1.254	-0.732	-0.748	-0.793	-0.824	-1.160	0.219
1.259	-0.656	-0.702	-0.748	-0.809	-1.129	0.236
1.263	-0.565	-0.671	-0.702	-0.793	-1.099	0.255
1.268	-0.443	-0.626	-0.626	-0.778	-1.053	0.276
1.273	-0.320	-0.549	-0.565	-0.748	-1.007	0.299
1.278	-0.153	-0.458	-0.473	-0.702	-0.916	0.325
1.283	0.443	-0.366	-0.366	-0.656	-0.824	0.355
1.288	0.748	-0.275	-0.275	-0.610	-0.748	0.388
1.293	1.007	0.107	0.214	-0.549	-0.671	0.426
1.298	1.419	0.488	0.504	-0.458	-0.565	0.470
1.302	1.846	0.778	0.793	-0.366	-0.412	0.520
1.307	2.289	0.992	1.022	-0.259	-0.290	0.578
1.312	2.884	1.343	1.373	-0.015	0.214	0.644
1.317	3.586	1.740	1.770	0.504	0.565	0.720
1.322	3.983	2.014	2.029	0.763	0.885	0.807
1.327	4.913	2.609	2.594	0.977	1.144	0.907
1.332	5.844	3.128	3.113	1.297	1.526	1.019
1.337	6.958	3.723	3.693	1.663	1.877	1.145
1.342	7.889	4.059	3.998	1.938	2.289	1.286
1.346	9.277	4.913	4.837	2.411	2.808	1.442
1.351	10.651	5.798	5.692	2.899	3.281	1.613
1.356	11.795	6.760	6.516	3.479	3.738	1.801
1.361	13.489	7.706	7.477	3.860	3.983	2.003
1.366	15.076	8.728	8.286	4.456	4.669	2.221
1.371	16.708	9.811	9.445	5.234	5.310	2.454
1.376	18.570	11.185	10.605	5.936	5.875	2.699
1.381	20.248	12.192	11.642	6.882	6.668	2.960
1.385	22.232	13.611	12.741	7.751	7.370	3.235
1.390	24.170	15.106	14.069	8.728	7.843	3.520
1.395	26.306	16.586	15.488	9.735	8.713	3.819
1.400	28.275	18.188	16.891	10.849	9.521	4.126
1.405	30.457	19.577	18.433	11.765	10.269	4.448
1.410	32.898	21.378	19.623	13.031	11.139	4.778
1.415	35.080	23.148	21.347	14.297	11.719	5.119

1.420	37.292	24.841	22.919	15.579	12.558	5.470
1.425	39.764	26.718	24.445	17.044	13.474	5.826
1.429	42.282	28.412	26.154	18.478	14.282	6.184
1.434	44.571	30.365	27.649	19.592	15.228	6.558
1.439	46.997	32.562	29.373	21.164	16.068	6.938
1.444	49.698	34.683	31.189	22.659	17.044	7.326
1.449	52.200	36.530	33.173	24.139	17.960	7.718
1.454	55.054	38.666	35.065	25.726	18.982	8.104
1.459	57.709	40.771	36.819	27.283	19.608	8.502
1.464	60.318	42.892	38.834	28.824	20.599	8.914
1.469	63.187	44.968	40.588	30.502	21.530	9.323
1.473	65.994	47.394	42.542	32.349	22.568	9.735
1.478	68.420	49.744	44.296	34.134	23.453	10.152
1.483	71.213	51.849	46.310	35.599	24.475	10.562
1.488	74.066	54.459	48.325	37.338	25.436	10.995
1.493	76.645	56.686	50.430	39.124	26.489	11.429
1.498	79.575	58.945	52.246	40.970	27.374	11.845
1.503	82.230	61.310	54.245	42.816	28.336	12.280
1.498	79.361	58.792	52.063	40.894	27.328	11.790
1.493	76.340	56.564	50.110	39.001	26.428	11.305
1.488	73.624	54.153	47.974	37.125	25.391	10.909
1.483	70.526	51.666	45.914	35.248	24.399	10.446
1.478	67.932	49.423	43.976	33.676	23.392	10.048
1.473	65.292	47.073	42.084	31.891	22.446	9.595
1.469	62.302	44.815	40.070	30.060	21.454	9.163
1.464	59.555	42.694	38.208	28.366	20.493	8.765
1.459	56.808	40.512	36.224	26.901	19.547	8.354
1.454	54.153	38.315	34.592	25.284	18.814	7.965
1.449	51.498	36.133	32.654	23.514	17.807	7.591
1.444	48.904	34.195	30.609	22.064	16.922	7.188
1.439	46.387	32.104	28.809	20.523	15.945	6.808
1.434	43.793	29.861	27.222	19.287	15.121	6.444
1.429	41.397	27.878	25.436	17.715	14.160	6.064
1.425	38.986	26.169	23.773	16.373	13.321	5.701
1.420	36.606	24.231	22.247	15.045	12.405	5.341
1.415	34.393	22.507	20.599	13.657	11.658	4.991
1.410	32.043	20.691	19.302	12.375	10.986	4.651
1.405	29.602	19.272	17.639	11.475	10.101	4.335
1.400	27.405	17.548	16.235	10.269	9.354	4.013
1.395	25.406	15.884	14.847	9.201	8.560	3.706
1.390	23.361	14.465	13.535	8.072	7.767	3.406
1.385	21.439	12.970	12.146	7.309	7.202	3.123
1.381	19.501	11.673	11.185	6.348	6.454	2.849
1.376	17.700	10.559	9.857	5.539	5.783	2.589
1.371	15.915	9.293	8.804	4.700	5.081	2.344
1.366	14.252	8.026	7.767	3.906	4.440	2.113
1.361	12.665	7.202	6.882	3.525	3.876	1.897
1.356	11.383	6.104	5.890	2.899	3.616	1.692
1.351	9.827	5.295	5.081	2.319	3.067	1.504
1.346	8.575	4.395	4.288	1.862	2.609	1.331

1.342	7.507	3.799	3.784	1.404	2.014	1.173
1.337	6.332	3.265	3.235	0.977	1.740	1.029
1.332	5.325	2.655	2.655	0.595	1.312	0.899
1.327	4.333	2.014	1.984	-0.031	0.931	0.783
1.322	3.738	1.663	1.648	-0.351	0.595	0.679
1.317	2.991	1.175	1.160	-0.565	0.061	0.587
1.312	2.365	0.854	0.839	-0.732	-0.351	0.505
1.307	1.831	0.488	0.443	-0.900	-0.549	0.433
1.302	1.312	-0.229	-0.259	-1.068	-0.702	0.370
1.298	0.885	-0.397	-0.443	-1.175	-0.839	0.314
1.293	0.458	-0.595	-0.626	-1.282	-1.022	0.266
1.288	-0.229	-0.732	-0.763	-1.373	-1.144	0.222
1.283	-0.427	-0.854	-0.931	-1.465	-1.221	0.185
1.278	-0.641	-1.007	-1.099	-1.541	-1.312	0.151
1.273	-0.793	-1.129	-1.175	-1.587	-1.389	0.121
1.268	-0.961	-1.190	-1.251	-1.633	-1.465	0.094
1.263	-1.083	-1.251	-1.343	-1.678	-1.526	0.070
1.259	-1.175	-1.297	-1.419	-1.740	-1.572	0.050
1.254	-1.266	-1.358	-1.480	-1.770	-1.617	0.030
1.249	-1.328	-1.404	-1.526	-1.816	-1.648	0.011
1.244	-1.373	-1.450	-1.572	-1.877	-1.678	-0.006
1.239	-1.434	-1.480	-1.617	-1.938	-1.724	-0.022
1.234	-1.480	-1.526	-1.648	-1.984	-1.755	-0.037
1.229	-1.526	-1.556	-1.694	-2.029	-1.801	-0.051
1.224	-1.572	-1.572	-1.724	-2.060	-1.816	-0.065
1.219	-1.587	-1.602	-1.740	-2.090	-1.846	-0.079
1.215	-1.617	-1.633	-1.785	-2.121	-1.907	-0.093
1.210	-1.633	-1.648	-1.816	-2.151	-1.938	-0.107
1.205	-1.663	-1.663	-1.862	-2.182	-1.984	-0.121

6. CV data in electrolyte solution 1 on expanded titanium mesh

E / V	j / mAcm^{-2} at 0 hours	j / mAcm^{-2} at 141 hours	j / mAcm^{-2} at 208 hours	j / mAcm^{-2} at 538 hours	j / mAcm^{-2} at 842 hours	j / mAcm^{-2} at 999 hours	j / mAcm^{-2} at 999 hours
1.200	-0.519	-0.799	-1.040	-0.754	-0.719	-0.831	-0.552
1.205	0.086	0.198	0.051	0.096	0.156	0.125	-0.097
1.210	0.340	0.536	0.469	0.391	0.469	0.487	0.128
1.215	0.518	0.686	0.660	0.522	0.610	0.650	0.250
1.219	0.672	0.768	0.761	0.590	0.685	0.740	0.319
1.224	0.820	0.820	0.820	0.635	0.732	0.791	0.358
1.229	0.976	0.863	0.862	0.665	0.768	0.830	0.383
1.234	1.146	0.900	0.894	0.697	0.799	0.859	0.397
1.239	1.335	0.936	0.924	0.727	0.829	0.887	0.408
1.240	1.550	0.971	0.951	0.746	0.858	0.912	0.416
1.249	1.799	1.010	0.982	0.778	0.890	0.938	0.425
1.254	2.087	1.055	1.015	0.808	0.925	0.967	0.434

1.259	2.417	1.106	1.054	0.836	0.965	1.000	0.445
1.263	2.797	1.164	1.099	0.875	1.010	1.037	0.457
1.268	3.232	1.233	1.152	0.919	1.061	1.080	0.472
1.273	3.725	1.313	1.216	0.975	1.123	1.133	0.489
1.278	4.282	1.411	1.294	1.039	1.196	1.191	0.510
1.283	4.905	1.525	1.383	1.114	1.278	1.261	0.536
1.288	5.595	1.664	1.495	1.202	1.377	1.346	0.568
1.293	6.358	1.827	1.628	1.305	1.493	1.448	0.605
1.298	7.191	2.019	1.785	1.430	1.627	1.568	0.650
1.302	8.089	2.245	1.970	1.575	1.781	1.707	0.704
1.307	9.071	2.510	2.190	1.745	1.963	1.874	0.769
1.312	10.111	2.816	2.446	1.944	2.172	2.069	0.845
1.317	11.219	3.171	2.742	2.178	2.410	2.297	0.936
1.322	12.387	3.573	3.082	2.445	2.681	2.558	1.042
1.327	13.614	4.033	3.470	2.751	2.987	2.857	1.166
1.332	14.901	4.547	3.911	3.098	3.332	3.198	1.308
1.337	16.252	5.122	4.401	3.490	3.717	3.579	1.470
1.342	17.659	5.755	4.945	3.921	4.139	4.011	1.653
1.346	19.107	6.452	5.546	4.408	4.607	4.482	1.857
1.351	20.610	7.212	6.202	4.941	5.116	5.002	2.083
1.356	22.162	8.031	6.914	5.525	5.670	5.570	2.331
1.361	23.747	8.918	7.677	6.155	6.265	6.180	2.599
1.366	25.371	9.860	8.497	6.833	6.904	6.834	2.888
1.371	27.052	10.862	9.380	7.557	7.583	7.539	3.197
1.376	28.765	11.917	10.305	8.333	8.305	8.280	3.523
1.381	30.502	13.020	11.277	9.164	9.073	9.070	3.867
1.385	32.279	14.161	12.298	10.031	9.870	9.899	4.226
1.390	34.088	15.351	13.357	10.944	10.706	10.753	4.598
1.395	35.930	16.590	14.459	11.897	11.581	11.651	4.982
1.400	37.795	17.860	15.601	12.887	12.486	12.574	5.381
1.405	39.677	19.163	16.783	13.912	13.421	13.526	5.791
1.410	41.599	20.522	17.997	14.973	14.394	14.531	6.211
1.415	43.545	21.913	19.251	16.083	15.391	15.552	6.639
1.420	45.507	23.337	20.530	17.209	16.429	16.598	7.077
1.425	47.493	24.800	21.841	18.375	17.474	17.659	7.520
1.429	49.520	26.296	23.176	19.565	18.560	18.761	7.971
1.434	51.538	27.816	24.543	20.795	19.670	19.879	8.432
1.439	53.597	29.360	25.934	22.050	20.795	21.029	8.890
1.444	55.655	30.936	27.341	23.328	21.945	22.179	9.361
1.449	57.738	32.544	28.789	24.639	23.111	23.385	9.852
1.454	59.845	34.176	30.244	25.966	24.293	24.599	10.338
1.459	61.960	35.825	31.716	27.317	25.500	25.805	10.834
1.464	64.091	37.498	33.211	28.708	26.730	27.052	11.322
1.469	66.238	39.178	34.723	30.115	27.976	28.314	11.838
1.473	68.393	40.907	36.259	31.539	29.231	29.593	12.341
1.478	70.548	42.620	37.803	33.002	30.493	30.879	12.848
1.483	72.744	44.373	39.371	34.490	31.788	32.182	13.365
1.488	74.923	46.134	40.964	35.978	33.083	33.501	13.872
1.493	77.142	47.919	42.564	37.506	34.410	34.852	14.418
1.498	79.322	49.713	44.172	39.034	35.737	36.171	14.949

1.503	81.388	51.514	45.796	40.553	37.071	37.522	15.488
1.498	79.129	49.640	44.132	38.969	35.680	36.139	14.901
1.493	76.837	47.799	42.475	37.401	34.313	34.764	14.346
1.488	74.593	45.973	40.859	35.873	32.978	33.413	13.807
1.483	72.333	44.156	39.243	34.353	31.635	32.070	13.260
1.478	70.106	42.379	37.642	32.866	30.317	30.783	12.732
1.473	67.903	40.618	36.074	31.394	29.030	29.472	12.217
1.469	65.675	38.881	34.514	29.947	27.743	28.161	11.704
1.464	63.504	37.152	32.978	28.523	26.473	26.875	11.179
1.459	61.333	35.447	31.442	27.116	25.226	25.628	10.686
1.454	59.186	33.782	29.955	25.749	24.020	24.398	10.171
1.449	57.063	32.126	28.459	24.390	22.806	23.176	9.684
1.444	54.940	30.502	27.003	23.063	21.616	21.969	9.203
1.439	52.833	28.893	25.564	21.760	20.458	20.787	8.729
1.434	50.766	27.333	24.165	20.490	19.308	19.629	8.247
1.429	48.691	25.781	22.774	19.243	18.198	18.496	7.779
1.425	46.665	24.269	21.423	18.021	17.112	17.370	7.334
1.420	44.671	22.798	20.096	16.839	16.035	16.276	6.884
1.415	42.684	21.358	18.801	15.697	15.005	15.223	6.436
1.410	40.698	19.943	17.547	14.571	13.992	14.193	6.009
1.405	38.768	18.576	16.324	13.494	13.028	13.188	5.600
1.400	36.862	17.249	15.126	12.457	12.080	12.218	5.198
1.395	34.989	15.954	13.976	11.454	11.160	11.281	4.798
1.390	33.123	14.708	12.866	10.489	10.283	10.373	4.412
1.385	31.298	13.510	11.793	9.570	9.434	9.499	4.039
1.381	29.504	12.368	10.761	8.688	8.625	8.661	3.688
1.376	27.759	11.269	9.775	7.862	7.848	7.864	3.341
1.371	26.038	10.215	8.838	7.069	7.112	7.104	3.014
1.366	24.358	9.216	7.946	6.325	6.415	6.385	2.702
1.361	22.717	8.269	7.105	5.628	5.759	5.703	2.413
1.356	21.133	7.386	6.314	4.981	5.147	5.073	2.132
1.351	19.581	6.551	5.576	4.382	4.567	4.481	1.871
1.346	18.101	5.779	4.887	3.833	4.037	3.932	1.628
1.342	16.646	5.065	4.250	3.320	3.543	3.425	1.402
1.337	15.247	4.406	3.668	2.856	3.087	2.959	1.198
1.332	13.912	3.805	3.131	2.433	2.668	2.540	1.012
1.327	12.644	3.258	2.646	2.056	2.289	2.154	0.841
1.322	11.424	2.765	2.210	1.718	1.948	1.810	0.689
1.317	10.277	2.326	1.819	1.415	1.640	1.499	0.552
1.312	9.179	1.932	1.467	1.145	1.362	1.224	0.431
1.307	8.150	1.584	1.159	0.911	1.116	0.980	0.333
1.302	7.200	1.278	0.885	0.703	0.896	0.764	0.239
1.298	6.375	1.011	0.646	0.522	0.701	0.573	0.158
1.293	5.551	0.775	0.435	0.363	0.529	0.405	0.085
1.288	4.792	0.569	0.250	0.223	0.375	0.260	0.022
1.283	4.104	0.393	0.092	0.107	0.241	0.143	-0.033
1.278	3.482	0.239	-0.037	0.005	0.134	0.032	-0.081
1.273	2.917	0.111	-0.159	-0.088	0.030	-0.068	-0.124
1.268	2.417	-0.005	-0.266	-0.165	-0.061	-0.154	-0.163
1.263	1.973	-0.107	-0.358	-0.241	-0.142	-0.232	-0.198

1.259	1.580	-0.195	-0.440	-0.302	-0.214	-0.301	-0.229
1.254	1.236	-0.274	-0.513	-0.359	-0.280	-0.361	-0.258
1.249	0.935	-0.345	-0.578	-0.410	-0.341	-0.418	-0.285
1.244	0.676	-0.406	-0.636	-0.456	-0.389	-0.468	-0.310
1.239	0.450	-0.462	-0.687	-0.495	-0.436	-0.515	-0.333
1.234	0.255	-0.514	-0.738	-0.533	-0.478	-0.558	-0.358
1.229	0.088	-0.561	-0.784	-0.570	-0.519	-0.600	-0.381
1.224	-0.050	-0.606	-0.828	-0.602	-0.557	-0.641	-0.406
1.219	-0.174	-0.647	-0.868	-0.632	-0.590	-0.677	-0.431
1.215	-0.283	-0.689	-0.911	-0.662	-0.623	-0.717	-0.458
1.210	-0.378	-0.730	-0.954	-0.690	-0.658	-0.757	-0.487
1.205	-0.458	-0.769	-0.994	-0.721	-0.691	-0.793	-0.519

7. LSV data in electrolyte solution 2 on plate anode

E / V	j / mAcm^{-2} at 0 hours	j / mAcm^{-2} at 141 hours	j / mAcm^{-2} at 432 hours	j / mAcm^{-2} at 548 hours	j / mAcm^{-2} at 616 hours	j / mAcm^{-2} at 645 hours
1.200	-0.870	-1.240	-1.500	-1.360	-1.510	-1.560
1.205	-0.750	-1.240	-1.450	-1.360	-1.500	-1.510
1.210	-0.600	-1.220	-1.420	-1.300	-1.430	-1.510
1.215	-0.350	-1.220	-1.420	-1.310	-1.420	-1.510
1.219	0.400	-1.210	-1.400	-1.300	-1.420	-1.510
1.224	0.890	-1.220	-1.370	-1.300	-1.400	-1.500
1.229	1.390	-1.190	-1.360	-1.280	-1.390	-1.460
1.234	1.910	-1.170	-1.340	-1.280	-1.390	-1.430
1.239	2.640	-1.160	-1.340	-1.280	-1.360	-1.400
1.240	3.390	-1.140	-1.330	-1.270	-1.360	-1.420
1.249	3.950	-1.110	-1.300	-1.240	-1.360	-1.420
1.254	5.070	-1.080	-1.270	-1.220	-1.340	-1.390
1.259	6.290	-1.040	-1.250	-1.190	-1.330	-1.360
1.263	7.630	-0.960	-1.220	-1.190	-1.340	-1.340
1.268	8.880	-0.850	-1.170	-1.170	-1.310	-1.310
1.273	10.590	-0.760	-1.130	-1.110	-1.270	-1.280
1.278	12.020	-0.700	-1.080	-1.110	-1.250	-1.250
1.283	13.930	-0.600	-0.980	-1.040	-1.220	-1.250
1.288	16.010	-0.460	-0.900	-1.010	-1.190	-1.220
1.293	18.260	-0.320	-0.780	-0.890	-1.170	-1.160
1.298	20.370	0.110	-0.660	-0.810	-1.130	-1.110
1.302	22.890	0.520	-0.530	-0.670	-1.080	-1.070
1.307	25.360	0.870	-0.350	-0.600	-1.020	-0.980
1.312	27.880	1.190	-0.170	-0.460	-0.980	-0.870
1.317	30.940	1.650	0.500	-0.320	-0.820	-0.790
1.322	34.210	1.980	0.840	-0.120	-0.750	-0.690
1.327	37.060	2.640	1.130	0.460	-0.610	-0.600
1.332	40.160	3.230	1.590	0.820	-0.470	-0.490
1.337	43.210	3.800	1.940	1.080	-0.340	-0.350
1.342	46.660	4.380	2.530	1.460	-0.110	-0.230
1.346	50.430	5.290	3.080	1.850	0.470	0.410

1.351	54.080	6.200	3.720	2.210	0.760	0.700
1.356	57.660	7.320	4.060	2.780	1.010	0.950
1.361	61.250	8.270	4.910	3.330	1.400	1.280
1.366	65.140	9.610	5.800	3.770	1.830	1.630
1.371	68.940	10.890	6.760	4.140	2.110	1.910
1.376	72.810	12.070	7.690	4.900	2.690	2.320
1.381	76.860	13.630	8.730	5.710	3.140	2.810
1.385	80.730	15.230	9.780	6.440	3.690	3.300
1.390	84.460	16.880	11.140	7.280	3.950	3.690
1.395	89.110	18.660	12.160	7.890	4.640	3.890
1.400	92.700	20.360	13.580	8.830	5.360	4.430
1.405	97.270	22.310	15.010	9.770	5.950	4.970
1.410	101.230	24.200	16.480	10.860	6.820	5.650
1.415	105.500	26.310	18.010	11.690	7.630	6.120
1.420	109.220	28.200	19.490	12.700	8.240	6.820
1.425	113.940	30.470	21.070	13.790	9.170	7.480
1.429	118.500	32.960	22.800	15.080	10.010	7.870
1.434	122.680	35.100	24.410	16.200	11.020	8.670
1.439	127.430	37.170	26.250	17.490	11.700	9.400
1.444	131.320	39.510	27.830	18.660	12.660	9.950
1.449	135.560	42.040	29.690	19.700	13.640	10.770
1.454	140.760	44.590	31.690	21.090	14.660	11.570
1.459	144.470	46.920	33.660	22.400	15.640	12.010
1.464	148.880	49.710	35.390	23.640	16.800	12.760
1.469	154.970	52.380	37.370	25.150	17.880	13.550
1.473	158.890	54.730	39.410	26.550	19.070	14.480
1.478	163.730	57.300	41.500	27.650	19.970	15.230
1.483	167.940	59.970	43.440	29.210	21.190	16.040
1.488	172.450	62.850	45.560	30.610	22.350	16.800
1.493	177.230	65.690	47.740	32.260	23.390	17.610
1.498	181.580	68.310	49.870	33.810	24.550	18.600
1.503	186.070	70.760	51.860	35.160	25.860	19.440

8. Current density dependence at 1.5 V data from LSV

Electrolysis time / h	j / mAcm^{-2} Electrolyte 2 on plate anode	Electrolysis time / h	j / mAcm^{-2} Electrolyte 1 on plate anode	Electrolysis time / h	j / mAcm^{-2} Electrolyte 1 on expanded titanium mesh
0	186.070	0	80.795	0	77.330
6	92.930	6	57.785	45	69.290
24	80.320	24	71.777	93	63.540
36	93.410	30	65.186	141	52.450
60		70	60.806	165	52.170
66	82.140	94	59.326	208	44.910
84	70.760	118	66.620	276	38.700
88	88.130	142	73.273	320	35.040
108	112.610	166	59.464	368	36.000
113	105.420	190	54.794	436	27.410
141	91.030	230	60.898	466	36.030
164	107.120	254	52.261	538	37.180
209	73.300	278	52.734	610	35.800
231	98.740	302	41.046	655	34.920
251	76.370	326	38.528	726	33.630
273	70.600	350	38.910	770	31.020
317	57.980	394	41.046	841.5	35.380
361	79.670	418	39.398	887.5	40.720
383		442	37.323	935	34.670
406		466	50.080	999	36.100
432	51.860	562	42.480	1059	13.420
475	41.380	610	41.430		
522		658	44.950		
548	35.160	749	42.920		
568		797	40.050		
616	25.860	843	28.180		
645	19.440	851	10.730		

9. Data for Tafel plot analysis

E / V	j / mAcm^{-2} at 0 hours	log |j|	j / mAcm^{-2} at 164 hours	log |j|	j / mAcm^{-2} at 317 hours	log |j|	j / mAcm^{-2} at 645 hours	log |j|
1.200	-0.870	-0.061	-1.240	0.092	-1.330	0.123	-1.560	0.192
1.205	-0.750	-0.126	-1.240	0.092	-1.300	0.113	-1.510	0.179
1.210	-0.600	-0.225	-1.220	0.087	-1.270	0.103	-1.510	0.179
1.215	-0.350	-0.455	-1.220	0.087	-1.280	0.108	-1.510	0.179
1.219	0.400	-0.402	-1.210	0.081	-1.280	0.108	-1.510	0.179
1.224	0.890	-0.053	-1.220	0.087	-1.270	0.103	-1.500	0.175
1.229	1.390	0.143	-1.190	0.076	-1.250	0.097	-1.460	0.166
1.234	1.910	0.280	-1.170	0.070	-1.220	0.087	-1.430	0.157
1.239	2.640	0.422	-1.160	0.064	-1.210	0.081	-1.400	0.147
1.240	3.390	0.530	-1.140	0.059	-1.170	0.070	-1.420	0.152

1.249	3.950	0.597	-1.110	0.047	-1.160	0.064	-1.420	0.152
1.254	5.070	0.705	-1.080	0.035	-1.140	0.059	-1.390	0.143
1.259	6.290	0.798	-1.040	0.016	-1.080	0.035	-1.360	0.133
1.263	7.630	0.882	-0.960	-0.017	-1.040	0.016	-1.340	0.128
1.268	8.880	0.948	-0.850	-0.068	-0.980	-0.010	-1.310	0.118
1.273	10.590	1.025	-0.760	-0.118	-0.870	-0.061	-1.280	0.108
1.278	12.020	1.080	-0.700	-0.154	-0.760	-0.118	-1.250	0.097
1.283	13.930	1.144	-0.600	-0.225	-0.700	-0.154	-1.250	0.097
1.288	16.010	1.204	-0.460	-0.339	-0.610	-0.214	-1.220	0.087
1.293	18.260	1.262	-0.320	-0.494	-0.410	-0.385	-1.160	0.064
1.298	20.370	1.309	0.110	-0.971	-0.290	-0.538	-1.110	0.047
1.302	22.890	1.360	0.520	-0.285	0.050	-1.339	-1.070	0.029
1.307	25.360	1.404	0.870	-0.061	0.530	-0.272	-0.980	-0.010
1.312	27.880	1.445	1.190	0.076	0.890	-0.053	-0.870	-0.061
1.317	30.940	1.491	1.650	0.217	1.160	0.064	-0.790	-0.100
1.322	34.210	1.534	1.980	0.297	1.600	0.205	-0.690	-0.163
1.327	37.060	1.569	2.640	0.422	1.950	0.291	-0.600	-0.225
1.332	40.160	1.604	3.230	0.510	2.490	0.396	-0.490	-0.311
1.337	43.210	1.636	3.800	0.580	3.040	0.482	-0.350	-0.455
1.342	46.660	1.669	4.380	0.641	3.690	0.567	-0.230	-0.640
1.346	50.430	1.703	5.290	0.724	4.040	0.607	0.410	-0.385
1.351	54.080	1.733	6.200	0.792	4.940	0.694	0.700	-0.154
1.356	57.660	1.761	7.320	0.865	5.810	0.764	0.950	-0.024
1.361	61.250	1.787	8.270	0.918	6.790	0.832	1.280	0.108
1.366	65.140	1.814	9.610	0.983	7.750	0.889	1.630	0.213
1.371	68.940	1.838	10.890	1.037	8.740	0.942	1.910	0.280
1.376	72.810	1.862	12.070	1.082	9.860	0.994	2.320	0.365
1.381	76.860	1.886	13.630	1.134	11.250	1.051	2.810	0.448
1.385	80.730	1.907	15.230	1.183	12.250	1.088	3.300	0.518
1.390	84.460	1.927	16.880	1.227	13.670	1.136	3.690	0.567
1.395	89.110	1.950	18.660	1.271	15.180	1.181	3.890	0.590
1.400	92.700	1.967	20.360	1.309	16.620	1.221	4.430	0.646
1.405	97.270	1.988	22.310	1.348	18.310	1.263	4.970	0.697
1.410	101.230	2.005	24.200	1.384	19.620	1.293	5.650	0.752
1.415	105.500	2.023	26.310	1.420	21.390	1.330	6.120	0.787
1.420	109.220	2.038	28.200	1.450	23.150	1.365	6.820	0.834
1.425	113.940	2.057	30.470	1.484	24.870	1.396	7.480	0.874
1.429	118.500	2.074	32.960	1.518	26.720	1.427	7.870	0.896
1.434	122.680	2.089	35.100	1.545	28.380	1.453	8.670	0.938
1.439	127.430	2.105	37.170	1.570	30.300	1.481	9.400	0.973
1.444	131.320	2.118	39.510	1.597	32.380	1.510	9.950	0.998
1.449	135.560	2.132	42.040	1.624	34.520	1.538	10.770	1.032
1.454	140.760	2.148	44.590	1.649	36.300	1.560	11.570	1.063
1.459	144.470	2.160	46.920	1.671	38.440	1.585	12.010	1.079
1.464	148.880	2.173	49.710	1.696	40.540	1.608	12.760	1.106
1.469	154.970	2.190	52.380	1.719	42.710	1.631	13.550	1.132
1.473	158.890	2.201	54.730	1.738	44.690	1.650	14.480	1.161
1.478	163.730	2.214	57.300	1.758	46.830	1.671	15.230	1.183
1.483	167.940	2.225	59.970	1.778	49.030	1.690	16.040	1.205
1.488	172.450	2.237	62.850	1.798	51.150	1.709	16.800	1.225

1.493	177.230	2.249	65.690	1.817	53.380	1.727	17.610	1.246
1.498	181.580	2.259	68.310	1.835	55.690	1.746	18.600	1.270
1.503	186.070	2.270	70.760	1.850	57.980	1.763	19.440	1.289

10. Determination of j_0

Estimation of the equilibrium potential $(\eta = 0; j = 0)$ of the working electrode for j_0 determination

The equilibrium potential, E_e may be measured directly or calculated from the Nerst Equation (1.6):

$$E_e = E_e^0 + \frac{2.3RT}{nF} \log \frac{c_O}{c_R}$$

Considering the anodic reaction: $H_2O \rightarrow \frac{1}{2}O_2^{\square} + 2H^+ + 2e^-$; R = 8.32 JK^{-1} mol^{-1}; F = 96485 Cmol^{-1}; T = 273+25 =328 K; n = 2 and $E_e^0 = 1.225$ vs. SHE

The Nernst Equation could be rewritten as:

$$E_e = E_e^0 + \frac{2.3RT}{2F} \log c_{H^+}$$

This is true if only $a_{H^+} = c_{H^+}$

Chromic acid CrO_3 is very soluble in water and Figure 1.2 shows the domains of relative predominance of its dissolved forms, H_2CrO_4, $HCrO_4^-$ and $Cr_2O_7^{2-}$.

Due to high concentration of the electrolyte mixture (3.02 M $H_2Cr_2O_7$ and 2.02 M $Na_2Cr_2O_7$), only the first dissociation can be assumed (under the condition that the first dissociation reaction goes to completion). Then, 1 mole litre^{-1}of $H_2Cr_2O_7$ releases 1 mole litre^{-1} of H^+. $c_{H^+} = 3.02$ moles litre^{-1}

$$CrO_3 + H_2O \rightarrow H_2CrO_4 \rightarrow H^+ + HCrO_4^-$$

or

$$2CrO_3 + H_2O \rightarrow H_2Cr_2O_7 \rightarrow H^+ + HCr_2O_7^-$$

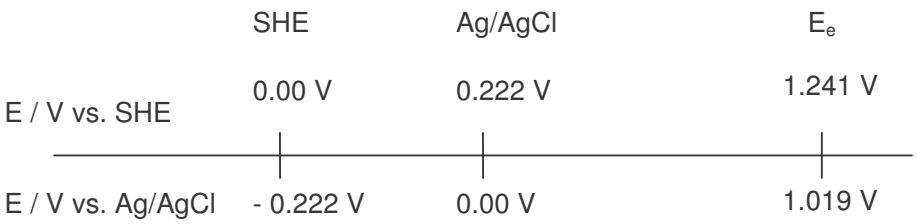
Now

$$E_e = 1.225 + \frac{2.3 \times 8.32 \times 328}{2 \times 96485} \log 3.02$$

$$E_e = 1.225 + 0.016$$

$$E_e = 1.241 \text{ V vs. SHE}$$

This equilibrium potential might be converted to the Ag/AgCl (1 M KNO_3) scale by subtracting 0.222 V.



i.e. $E_e = 1.019$ V vs. Ag/AgCl (1 M KNO_3).

The Tafel Equation related to the anodic process is (1.17):

$$\log j = \log j_0 + \frac{\alpha_A nF\eta}{RT}$$

The semilog plot of j vs. E data gives: $\log j = \log j_0 + \frac{\alpha_A nF(E - E_e)}{RT}$

The Tafel plot analysis gives: $y = 8.3674x - 9.5409$

The value of j_0 is obtained from the intercept of the straight line and the potential when $E = E_e$

$$y = 8.3674 \times 1.019 - 9.5409$$

$$y = -1.0145$$

$$\log j_0 = -1.0145$$

$$j_0 = 96.8\,\mu\text{Acm}^{-2}$$

The exchange current density value obtained in this work is in agreement with values reported in the literature. (Hamann et al., 1988)

11. CA data in electrolyte solution 2 on plate anode

t / s	j / mAcm^{-2} at 0 hours	j / mAcm^{-2} at 84 hours	j / mAcm^{-2} at 432 hours	j / mAcm^{-2} at 548 hours	j / mAcm^{-2} at 645 hours
0.010	289.307	225.372	174.454	99.136	66.513
0.020	226.151	168.533	147.369	76.950	53.650
0.030	211.060	132.843	126.953	63.187	44.968
0.040	207.245	110.962	110.443	53.772	38.498
0.050	205.521	98.969	97.275	47.440	33.615
0.060	204.407	92.590	86.777	43.289	29.831
0.070	203.476	89.264	78.735	40.482	27.298
0.080	202.759	87.387	72.662	38.635	25.589
0.090	202.133	86.166	68.146	37.277	24.307
0.100	201.599	85.449	65.018	36.407	23.499
0.110	201.111	84.854	62.393	35.767	22.995
0.120	200.714	84.412	60.577	35.263	22.552
0.130	200.287	84.091	59.311	35.080	22.232
0.140	199.905	83.923	58.441	34.958	21.973
0.150	199.539	83.756	57.739	34.714	21.713
0.160	199.219	83.633	57.190	34.561	21.576
0.170	199.005	83.481	56.702	34.363	21.469
0.180	198.700	83.374	56.397	34.225	21.439
0.190	198.395	83.206	56.046	34.134	21.362
0.200	198.105	83.069	55.801	34.103	21.317
0.210	197.815	82.886	55.573	33.981	21.194
0.220	197.556	82.687	55.374	33.905	21.164
0.230	197.342	82.474	55.191	33.798	21.042
0.240	197.128	82.214	55.023	33.707	21.042
0.250	196.915	82.031	54.871	33.630	20.950
0.260	196.686	81.924	54.749	33.585	20.950
0.270	196.472	81.772	54.642	33.493	20.859

0.280	196.274	81.635	54.581	33.493	20.859
0.290	196.060	81.497	54.489	33.356	20.782
0.300	195.862	81.406	54.398	33.371	20.767
0.310	195.694	81.299	54.291	33.279	20.676
0.320	195.480	81.284	54.230	33.264	20.691
0.330	195.328	81.268	54.138	33.234	20.599
0.340	195.221	81.299	54.047	33.234	20.615
0.350	195.114	81.299	53.955	33.173	20.569
0.360	194.962	81.329	53.894	33.173	20.569
0.370	194.840	81.299	53.803	33.142	20.523
0.380	194.687	81.314	53.757	33.142	20.538
0.390	194.565	81.253	53.711	33.127	20.493
0.400	194.412	81.207	53.665	33.112	20.508
0.410	194.290	81.116	53.619	33.096	20.462
0.420	194.168	81.039	53.558	33.081	20.462
0.430	194.061	80.933	53.482	33.051	20.416
0.440	193.970	80.811	53.436	33.035	20.447
0.450	193.863	80.643	53.360	32.990	20.401
0.460	193.787	80.475	53.329	32.990	20.401
0.470	193.680	80.307	53.253	32.959	20.355
0.480	193.588	80.185	53.223	32.928	20.386
0.490	193.512	80.109	53.162	32.883	20.279
0.500	193.436	80.109	53.131	32.867	20.309
0.510	193.420	80.078	53.085	32.837	20.248
0.520	193.375	80.109	53.070	32.806	20.279
0.530	193.359	80.154	53.009	32.776	20.203
0.540	193.329	80.231	52.979	32.745	20.248
0.550	193.314	80.322	52.918	32.745	20.187
0.560	193.283	80.429	52.887	32.730	20.203
0.570	193.283	80.475	52.856	32.700	20.142
0.580	193.268	80.566	52.826	32.684	20.157
0.590	193.222	80.566	52.795	32.669	20.096
0.600	193.161	80.551	52.780	32.669	20.126
0.610	193.131	80.490	52.750	32.639	20.065
0.620	193.115	80.460	52.734	32.623	20.096
0.630	193.115	80.353	52.719	32.608	20.050
0.640	193.085	80.277	52.704	32.578	20.081
0.650	193.069	80.185	52.673	32.608	20.035
0.660	193.100	80.124	52.658	32.562	20.065
0.670	193.085	80.093	52.628	32.532	20.020
0.680	193.069	80.078	52.612	32.486	20.050
0.690	193.100	80.063	52.582	32.501	20.004
0.700	193.069	80.063	52.582	32.501	20.020
0.710	193.069	80.063	52.536	32.455	19.974
0.720	193.024	80.093	52.506	32.410	20.004
0.730	193.069	80.109	52.490	32.410	19.958
0.740	193.008	80.154	52.460	32.379	19.989
0.750	193.039	80.170	52.444	32.410	19.943
0.760	193.039	80.261	52.414	32.364	19.974
0.770	193.039	80.261	52.383	32.379	19.913
0.780	193.008	80.292	52.383	32.333	19.943
0.790	192.993	80.292	52.353	32.379	19.882

0.800	192.947	80.292	52.338	32.318	19.913
0.810	192.902	80.261	52.307	32.318	19.852
0.820	192.871	80.231	52.307	32.288	19.882
0.830	192.871	80.154	52.277	32.333	19.836
0.840	192.810	80.109	52.292	32.272	19.852
0.850	192.795	80.063	52.246	32.288	19.791
0.860	192.764	80.032	52.246	32.257	19.836
0.870	192.703	79.987	52.216	32.272	19.791
0.880	192.642	79.956	52.231	32.242	19.806
0.890	192.596	79.941	52.200	32.242	19.775
0.900	192.505	79.926	52.200	32.227	19.806
0.910	192.474	79.941	52.185	32.242	19.745
0.920	192.474	79.971	52.170	32.211	19.775
0.930	192.459	80.002	52.170	32.227	19.730
0.940	192.474	80.032	52.139	32.211	19.775
0.950	192.459	80.048	52.124	32.211	19.714
0.960	192.413	80.078	52.109	32.196	19.745
0.970	192.413	80.078	52.094	32.196	19.699
0.980	192.383	80.093	52.094	32.181	19.745
0.990	192.383	80.078	52.063	32.196	19.684
1.000	192.337	80.063	52.063	32.196	19.730
1.010	192.337	80.032	52.032	32.181	19.669
1.020	192.307	80.002	52.032	32.150	19.714
1.030	192.307	79.926	52.017	32.181	19.669
1.040	192.352	79.865	52.017	32.150	19.699
1.050	192.383	79.788	51.987	32.166	19.653
1.060	192.322	79.727	51.987	32.150	19.699
1.070	192.337	79.681	51.971	32.150	19.653
1.080	192.291	79.636	51.971	32.135	19.699
1.090	192.276	79.605	51.941	32.120	19.638
1.100	192.261	79.605	51.941	32.104	19.669
1.110	192.276	79.590	51.910	32.120	19.623
1.120	192.246	79.636	51.910	32.089	19.669
1.130	192.200	79.636	51.895	32.120	19.608
1.140	192.169	79.681	51.910	32.120	19.653
1.150	192.139	79.681	51.880	32.120	19.608
1.160	192.093	79.727	51.880	32.074	19.653
1.170	192.078	79.697	51.865	32.089	19.608
1.180	192.032	79.727	51.880	32.074	19.638
1.190	192.001	79.681	51.849	32.059	19.608
1.200	191.940	79.666	51.834	32.028	19.623
1.210	191.940	79.636	51.834	32.043	19.592
1.220	191.910	79.605	51.834	32.013	19.638
1.230	191.895	79.559	51.819	32.043	19.608
1.240	191.879	79.544	51.834	32.043	19.623
1.250	191.818	79.498	51.804	32.074	19.592
1.260	191.788	79.483	51.819	31.998	19.623
1.270	191.818	79.483	51.804	32.028	19.577
1.280	191.788	79.468	51.804	31.967	19.623
1.290	191.742	79.468	51.773	32.013	19.592
1.300	191.696	79.483	51.773	32.013	19.623
1.310	191.650	79.483	51.758	31.998	19.577

1.320	191.589	79.529	51.758	31.937	19.608
1.330	191.544	79.529	51.743	31.967	19.592
1.340	191.528	79.559	51.758	31.921	19.608
1.350	191.513	79.529	51.743	31.952	19.577
1.360	191.467	79.544	51.743	31.906	19.608
1.370	191.467	79.514	51.727	31.952	19.577
1.380	191.437	79.498	51.727	31.906	19.592
1.390	191.437	79.453	51.727	31.921	19.577
1.400	191.406	79.422	51.727	31.906	19.592
1.410	191.406	79.361	51.712	31.921	19.562
1.420	191.391	79.315	51.712	31.891	19.592
1.430	191.437	79.285	51.712	31.906	19.562
1.440	191.391	79.285	51.682	31.845	19.592
1.450	191.391	79.239	51.666	31.891	19.562
1.460	191.376	79.224	51.682	31.891	19.592
1.470	191.360	79.208	51.636	31.937	19.562
1.480	191.345	79.224	51.651	31.906	19.577
1.490	191.345	79.224	51.605	31.921	19.547
1.500	191.360	79.269	51.605	31.906	19.577
1.510	191.391	79.285	51.590	31.876	19.547
1.520	191.376	79.315	51.621	31.830	19.577
1.530	191.376	79.315	51.575	31.845	19.562
1.540	191.360	79.361	51.605	31.830	19.577
1.550	191.360	79.376	51.559	31.891	19.547
1.560	191.360	79.407	51.575	31.815	19.562
1.570	191.360	79.361	51.544	31.830	19.547
1.580	191.345	79.346	51.575	31.784	19.562
1.590	191.345	79.285	51.514	31.815	19.547
1.600	191.330	79.269	51.559	31.815	19.562
1.610	191.360	79.193	51.514	31.830	19.547
1.620	191.345	79.163	51.544	31.830	19.562
1.630	191.345	79.132	51.498	31.830	19.531
1.640	191.330	79.132	51.514	31.769	19.547
1.650	191.330	79.102	51.483	31.769	19.531
1.660	191.330	79.086	51.498	31.738	19.547
1.670	191.330	79.086	51.453	31.754	19.531
1.680	191.330	79.102	51.483	31.723	19.547
1.690	191.330	79.102	51.437	31.738	19.516
1.700	191.315	79.117	51.483	31.723	19.547
1.710	191.315	79.132	51.422	31.738	19.516
1.720	191.315	79.147	51.453	31.708	19.531
1.730	191.299	79.147	51.407	31.723	19.516
1.740	191.299	79.178	51.437	31.708	19.531
1.750	191.330	79.178	51.392	31.723	19.516
1.760	191.315	79.178	51.422	31.693	19.531
1.770	191.315	79.163	51.376	31.708	19.516
1.780	191.315	79.147	51.422	31.693	19.531
1.790	191.315	79.117	51.376	31.693	19.501
1.800	191.299	79.102	51.407	31.677	19.516
1.810	191.299	79.086	51.376	31.677	19.501
1.820	191.284	79.056	51.407	31.662	19.516
1.830	191.269	79.041	51.361	31.662	19.501

1.840	191.238	79.025	51.376	31.662	19.516
1.850	191.269	78.980	51.346	31.662	19.501
1.860	191.238	78.995	51.361	31.647	19.516
1.870	191.208	79.010	51.331	31.693	19.501
1.880	191.162	79.025	51.361	31.662	19.516
1.890	191.162	79.025	51.315	31.647	19.501
1.900	191.193	79.056	51.346	31.631	19.501
1.910	191.162	79.056	51.315	31.631	19.485
1.920	191.116	79.086	51.331	31.616	19.501
1.930	191.101	79.086	51.300	31.631	19.485
1.940	191.086	79.117	51.331	31.586	19.516
1.950	191.101	79.086	51.285	31.616	19.485
1.960	191.086	79.086	51.300	31.586	19.501
1.970	191.040	79.086	51.270	31.601	19.485
1.980	191.071	79.041	51.315	31.570	19.501
1.990	191.071	78.995	51.254	31.586	19.485
2.000	191.010	78.980	51.285	31.570	19.501

12. CA data in electrolyte solution 1 plate anode

t / s	j / mAcm^{-2} at 0 hours	j / mAcm^{-2} at 278 hours	j / mAcm^{-2} at 562 hours	j / mAcm^{-2} at 843 hours	j / mAcm^{-2} at 851 hours
0.010	193.192	157.974	146.179	69.061	31.036
0.020	146.774	136.276	128.738	57.831	24.597
0.030	120.407	118.622	114.212	50.583	20.955
0.040	106.186	104.233	101.852	44.724	18.472
0.050	99.121	92.361	91.064	40.421	16.743
0.060	95.596	82.962	81.863	37.048	15.527
0.070	93.491	75.699	74.081	34.836	14.725
0.080	92.255	70.511	67.780	33.203	14.197
0.090	91.461	66.772	62.607	32.120	13.870
0.100	90.836	64.316	58.579	31.219	13.651
0.110	90.393	62.256	55.649	30.792	13.509
0.120	89.966	60.974	53.467	30.396	13.396
0.130	89.722	60.074	51.849	30.243	13.319
0.140	89.478	59.464	50.735	30.014	13.255
0.150	89.218	58.929	49.927	29.907	13.210
0.160	88.959	58.594	49.194	29.755	13.165
0.170	88.745	58.334	48.721	29.724	13.133
0.180	88.516	58.121	48.294	29.587	13.095
0.190	88.318	57.831	47.943	29.572	13.074
0.200	88.120	57.663	47.699	29.449	13.045
0.210	87.982	57.510	47.424	29.449	13.026
0.220	87.845	57.358	47.226	29.373	12.997
0.230	87.723	57.175	47.028	29.373	12.982
0.240	87.570	57.068	46.875	29.297	12.961
0.250	87.418	56.915	46.799	29.312	12.947
0.260	87.265	56.824	46.677	29.266	12.924
0.270	87.143	56.686	46.585	29.266	12.915
0.280	87.006	56.641	46.478	29.205	12.895
0.290	86.914	56.564	46.402	29.221	12.889

0.300	86.777	56.503	46.310	29.144	12.877
0.310	86.685	56.412	46.219	29.160	12.868
0.320	86.548	56.351	46.112	29.099	12.848
0.330	86.456	56.244	46.036	29.099	12.840
0.340	86.350	56.198	45.975	29.037	12.827
0.350	86.243	56.107	45.914	29.068	12.816
0.360	86.136	56.061	45.868	28.976	12.799
0.370	86.044	55.985	45.822	29.007	12.796
0.380	85.953	55.923	45.761	28.915	12.778
0.390	85.892	55.862	45.700	28.946	12.772
0.400	85.815	55.817	45.639	28.870	12.759
0.410	85.770	55.740	45.578	28.915	12.753
0.420	85.678	55.725	45.532	28.854	12.738
0.430	85.602	55.664	45.486	28.870	12.730
0.440	85.526	55.649	45.410	28.824	12.723
0.450	85.465	55.588	45.380	28.839	12.718
0.460	85.342	55.542	45.334	28.778	12.708
0.470	85.281	55.481	45.273	28.809	12.704
0.480	85.175	55.450	45.242	28.748	12.689
0.490	85.129	55.389	45.197	28.763	12.679
0.500	85.022	55.374	45.151	28.702	12.669
0.510	84.976	55.313	45.120	28.732	12.662
0.520	84.915	55.283	45.074	28.656	12.654
0.530	84.869	55.237	45.044	28.687	12.653
0.540	84.808	55.206	45.013	28.595	12.642
0.550	84.747	55.161	44.983	28.656	12.637
0.560	84.671	55.130	44.968	28.595	12.630
0.570	84.641	55.084	44.952	28.641	12.627
0.580	84.564	55.069	44.922	28.564	12.617
0.590	84.503	55.023	44.922	28.595	12.614
0.600	84.427	55.008	44.891	28.549	12.602
0.610	84.396	54.947	44.876	28.564	12.602
0.620	84.320	54.947	44.846	28.503	12.593
0.630	84.290	54.901	44.830	28.549	12.590
0.640	84.244	54.886	44.815	28.488	12.582
0.650	84.229	54.840	44.785	28.534	12.579
0.660	84.168	54.825	44.754	28.473	12.573
0.670	84.137	54.810	44.739	28.503	12.575
0.680	84.076	54.779	44.708	28.458	12.566
0.690	84.045	54.779	44.708	28.488	12.563
0.700	84.000	54.764	44.662	28.442	12.553
0.710	84.000	54.718	44.647	28.473	12.550
0.720	83.954	54.703	44.617	28.412	12.546
0.730	83.939	54.688	44.617	28.458	12.546
0.740	83.893	54.672	44.586	28.412	12.534
0.750	83.878	54.642	44.556	28.442	12.532
0.760	83.832	54.657	44.525	28.397	12.524
0.770	83.801	54.626	44.525	28.427	12.526
0.780	83.740	54.626	44.495	28.381	12.515
0.790	83.725	54.596	44.479	28.412	12.515
0.800	83.679	54.596	44.464	28.366	12.511
0.810	83.664	54.581	44.449	28.412	12.511
0.820	83.618	54.565	44.434	28.366	12.502
0.830	83.618	54.550	44.434	28.397	12.503

0.840	83.588	54.535	44.434	28.351	12.494
0.850	83.557	54.504	44.403	28.397	12.495
0.860	83.527	54.520	44.373	28.351	12.491
0.870	83.511	54.489	44.357	28.412	12.491
0.880	83.481	54.489	44.327	28.351	12.486
0.890	83.466	54.459	44.312	28.397	12.485
0.900	83.420	54.443	44.296	28.336	12.471
0.910	83.405	54.428	44.281	28.381	12.476
0.920	83.344	54.428	44.266	28.351	12.469
0.930	83.328	54.398	44.250	28.366	12.471
0.940	83.282	54.413	44.235	28.336	12.466
0.950	83.298	54.367	44.250	28.366	12.466
0.960	83.237	54.352	44.205	28.336	12.462
0.970	83.237	54.337	44.189	28.351	12.463
0.980	83.191	54.337	44.174	28.320	12.456
0.990	83.191	54.306	44.159	28.351	12.454
1.000	83.145	54.306	44.144	28.320	12.448
1.010	83.130	54.291	44.144	28.351	12.448
1.020	83.084	54.291	44.128	28.320	12.437
1.030	83.099	54.276	44.128	28.336	12.437
1.040	83.069	54.260	44.098	28.320	12.428
1.050	83.069	54.245	44.098	28.351	12.427
1.060	83.023	54.245	44.083	28.320	12.419
1.070	83.038	54.215	44.083	28.336	12.416
1.080	82.993	54.215	44.067	28.320	12.413
1.090	83.008	54.230	44.052	28.351	12.416
1.100	82.962	54.215	44.052	28.320	12.408
1.110	82.962	54.199	44.037	28.351	12.407
1.120	82.932	54.199	44.037	28.320	12.404
1.130	82.947	54.199	44.037	28.336	12.405
1.140	82.886	54.184	44.006	28.305	12.402
1.150	82.901	54.169	44.022	28.336	12.399
1.160	82.855	54.169	44.006	28.305	12.399
1.170	82.871	54.153	44.006	28.320	12.396
1.180	82.794	54.153	43.991	28.305	12.386
1.190	82.825	54.123	44.006	28.336	12.384
1.200	82.779	54.138	43.976	28.305	12.381
1.210	82.809	54.123	43.976	28.320	12.381
1.220	82.764	54.123	43.961	28.275	12.375
1.230	82.794	54.108	43.961	28.290	12.376
1.240	82.733	54.123	43.945	28.259	12.372
1.250	82.764	54.092	43.945	28.290	12.372
1.260	82.733	54.077	43.930	28.259	12.367
1.270	82.733	54.062	43.945	28.290	12.369
1.280	82.687	54.062	43.915	28.259	12.363
1.290	82.703	54.031	43.915	28.290	12.366
1.300	82.657	54.047	43.900	28.229	12.360
1.310	82.687	54.031	43.915	28.275	12.361
1.320	82.642	54.016	43.900	28.229	12.367
1.330	82.703	54.016	43.900	28.259	12.366
1.340	82.687	54.016	43.854	28.214	12.358
1.350	82.703	53.986	43.869	28.244	12.357
1.360	82.642	53.986	43.839	28.214	12.352
1.370	82.672	53.955	43.869	28.244	12.350

1.380	82.626	53.955	43.854	28.198	12.341
1.390	82.672	53.940	43.839	28.244	12.340
1.400	82.611	53.940	43.808	28.168	12.329
1.410	82.642	53.925	43.808	28.214	12.326
1.420	82.596	53.909	43.808	28.152	12.315
1.430	82.642	53.894	43.793	28.198	12.311
1.440	82.581	53.894	43.777	28.168	12.311
1.450	82.626	53.879	43.777	28.198	12.311
1.460	82.581	53.864	43.747	28.122	12.311
1.470	82.611	53.848	43.747	28.168	12.312
1.480	82.565	53.848	43.747	28.152	12.309
1.490	82.596	53.818	43.747	28.214	12.309
1.500	82.550	53.818	43.716	28.168	12.306
1.510	82.596	53.803	43.732	28.214	12.299
1.520	82.535	53.803	43.701	28.152	12.294
1.530	82.581	53.787	43.747	28.183	12.292
1.540	82.520	53.787	43.732	28.137	12.286
1.550	82.565	53.772	43.732	28.168	12.286
1.560	82.550	53.772	43.716	28.107	12.282
1.570	82.581	53.757	43.716	28.152	12.280
1.580	82.520	53.757	43.716	28.107	12.276
1.590	82.581	53.741	43.701	28.152	12.270
1.600	82.550	53.741	43.686	28.107	12.265
1.610	82.565	53.726	43.686	28.137	12.265
1.620	82.504	53.741	43.671	28.091	12.260
1.630	82.550	53.711	43.671	28.137	12.257
1.640	82.489	53.726	43.640	28.107	12.256
1.650	82.520	53.711	43.640	28.137	12.253
1.660	82.459	53.726	43.640	28.107	12.245
1.670	82.504	53.696	43.640	28.137	12.244
1.680	82.443	53.696	43.640	28.091	12.238
1.690	82.504	53.680	43.640	28.122	12.239
1.700	82.443	53.680	43.610	28.076	12.233
1.710	82.474	53.665	43.625	28.091	12.230
1.720	82.413	53.680	43.594	28.061	12.230
1.730	82.443	53.665	43.594	28.091	12.236
1.740	82.397	53.680	43.564	28.046	12.228
1.750	82.443	53.665	43.579	28.091	12.239
1.760	82.352	53.665	43.579	28.091	12.230
1.770	82.397	53.650	43.564	28.122	12.228
1.780	82.336	53.650	43.564	28.091	12.225
1.790	82.382	53.650	43.549	28.137	12.224
1.800	82.321	53.635	43.549	28.091	12.218
1.810	82.367	53.635	43.533	28.137	12.212
1.820	82.306	53.635	43.533	28.091	12.210
1.830	82.352	53.619	43.533	28.122	12.212
1.840	82.321	53.635	43.518	28.076	12.202
1.850	82.382	53.604	43.518	28.122	12.204
1.860	82.336	53.619	43.503	28.061	12.201
1.870	82.382	53.604	43.503	28.107	12.193
1.880	82.321	53.619	43.503	28.061	12.195
1.890	82.352	53.604	43.518	28.107	12.192
1.900	82.321	53.619	43.488	28.046	12.184
1.910	82.352	53.589	43.503	28.122	12.178

1.920	82.291	53.619	43.472	28.076	12.167
1.930	82.336	53.604	43.503	28.107	12.166
1.940	82.291	53.650	43.472	28.030	12.166
1.950	82.321	53.665	43.472	28.091	12.169
1.960	82.260	53.665	43.457	28.030	12.164
1.970	82.291	53.635	43.472	28.091	12.169
1.980	82.245	53.650	43.442	28.030	12.166
1.990	82.306	53.635	43.457	28.061	12.161
2.000	82.245	53.635	43.442	28.015	12.148

13. CA data in electrolyte solution 1 expanded titanium mesh

t / s	j / mAcm^{-2} at 0 hours	j / mAcm^{-2} at 208 hours	j / mAcm^{-2} at 538 hours	j / mAcm^{-2} at 842 hours	j / mAcm^{-2} at 999 hours	j / mAcm^{-2} at 999 hours
0.010	146.436	127.378	122.231	104.355	104.660	34.353
0.020	122.874	114.576	108.681	93.933	95.622	30.855
0.030	109.148	105.006	98.187	86.036	88.481	28.684
0.040	100.479	96.884	89.414	79.338	82.273	26.939
0.050	94.978	89.936	81.967	73.620	76.708	25.443
0.060	91.585	83.833	75.566	68.650	71.730	24.092
0.070	89.398	78.485	70.098	64.107	67.203	22.910
0.080	88.006	73.797	65.345	60.311	63.029	21.897
0.090	87.017	69.760	61.309	56.998	59.411	20.916
0.100	86.318	66.198	57.987	54.200	56.186	20.072
0.110	85.779	63.110	55.221	51.803	53.388	19.276
0.120	85.345	60.537	52.937	49.769	51.007	18.568
0.130	84.991	58.430	51.120	48.008	48.852	18.037
0.140	84.669	56.580	49.576	46.665	47.155	17.442
0.150	84.436	55.165	48.305	45.475	45.716	16.919
0.160	84.299	53.910	47.357	44.518	44.558	16.397
0.170	84.098	52.929	46.576	43.714	43.569	16.003
0.180	83.881	52.069	45.941	43.135	42.918	15.649
0.190	83.696	51.458	45.394	42.612	42.250	15.375
0.200	83.535	50.919	44.992	42.154	41.752	15.102
0.210	83.383	50.453	44.630	41.768	41.277	14.885
0.220	83.270	50.042	44.325	41.430	40.980	14.676
0.230	83.117	49.721	44.092	41.140	40.674	14.499
0.240	82.956	49.343	43.858	40.915	40.433	14.394
0.250	82.852	49.134	43.674	40.682	40.208	14.330
0.260	82.731	48.892	43.489	40.497	40.079	14.242
0.270	82.611	48.740	43.336	40.312	39.918	14.145
0.280	82.474	48.547	43.247	40.175	39.781	14.032
0.290	82.337	48.434	43.191	40.071	39.653	13.936
0.300	82.225	48.281	43.111	39.950	39.564	13.880
0.310	82.144	48.201	43.014	39.814	39.452	13.839
0.320	82.048	48.056	42.910	39.709	39.379	13.783
0.330	81.967	47.992	42.797	39.621	39.267	13.727
0.340	81.879	47.879	42.717	39.532	39.210	13.663
0.350	81.806	47.815	42.652	39.436	39.138	13.630

0.360	81.718	47.718	42.564	39.363	39.106	13.598
0.370	81.654	47.662	42.499	39.283	39.074	13.542
0.380	81.581	47.566	42.419	39.218	39.058	13.510
0.390	81.517	47.517	42.339	39.154	39.026	13.453
0.400	81.436	47.437	42.266	39.122	38.985	13.429
0.410	81.388	47.389	42.234	39.090	38.937	13.413
0.420	81.316	47.332	42.194	39.066	38.897	13.397
0.430	81.268	47.316	42.170	39.034	38.841	13.389
0.440	81.211	47.276	42.130	39.009	38.808	13.373
0.450	81.171	47.260	42.081	38.961	38.744	13.365
0.460	81.115	47.204	42.033	38.921	38.712	13.357
0.470	81.075	47.188	41.985	38.865	38.648	13.349
0.480	81.018	47.123	41.929	38.824	38.623	13.333
0.490	80.986	47.099	41.896	38.752	38.583	13.325
0.500	80.938	47.019	41.832	38.704	38.567	13.309
0.510	80.906	46.995	41.792	38.664	38.543	13.293
0.520	80.857	46.922	41.744	38.631	38.519	13.277
0.530	80.833	46.914	41.719	38.591	38.471	13.260
0.540	80.777	46.850	41.687	38.575	38.455	13.244
0.550	80.753	46.842	41.671	38.535	38.398	13.236
0.560	80.705	46.794	41.623	38.511	38.382	13.228
0.570	80.681	46.786	41.599	38.471	38.342	13.212
0.580	80.648	46.713	41.551	38.430	38.318	13.188
0.590	80.640	46.697	41.534	38.382	38.270	13.172
0.600	80.600	46.649	41.486	38.350	38.245	13.164
0.610	80.584	46.641	41.470	38.318	38.213	13.164
0.620	80.568	46.576	41.422	38.278	38.197	13.148
0.630	80.560	46.576	41.414	38.245	38.165	13.140
0.640	80.536	46.520	41.390	38.221	38.149	13.124
0.650	80.536	46.520	41.333	38.205	38.125	13.124
0.660	80.512	46.464	41.301	38.165	38.117	13.116
0.670	80.512	46.472	41.285	38.133	38.093	13.108
0.680	80.488	46.424	41.245	38.125	38.093	13.100
0.690	80.488	46.424	41.221	38.109	38.077	13.092
0.700	80.463	46.384	41.197	38.101	38.069	13.084
0.710	80.463	46.384	41.173	38.085	38.052	13.076
0.720	80.447	46.343	41.157	38.069	38.052	13.067
0.730	80.431	46.343	41.157	38.061	38.036	13.067
0.740	80.423	46.319	41.132	38.052	38.028	13.059
0.750	80.423	46.327	41.124	38.036	38.012	13.043
0.760	80.399	46.295	41.108	38.036	37.996	13.035
0.770	80.399	46.303	41.108	38.012	37.972	13.027
0.780	80.391	46.279	41.084	38.004	37.964	13.019
0.790	80.399	46.287	41.068	37.972	37.948	13.019
0.800	80.375	46.255	41.044	37.956	37.948	12.995
0.810	80.375	46.263	41.044	37.932	37.916	13.003
0.820	80.351	46.223	41.012	37.916	37.908	12.995
0.830	80.351	46.231	41.020	37.900	37.868	12.979
0.840	80.327	46.199	40.980	37.892	37.868	12.971
0.850	80.327	46.215	40.980	37.876	37.851	12.979
0.860	80.311	46.174	40.947	37.876	37.827	12.971
0.870	80.319	46.191	40.947	37.843	37.819	12.955
0.880	80.303	46.158	40.923	37.835	37.803	12.947
0.890	80.295	46.174	40.923	37.811	37.787	12.947

0.900	80.287	46.150	40.891	37.803	37.795	12.939
0.910	80.279	46.158	40.891	37.787	37.755	12.923
0.920	80.270	46.126	40.851	37.787	37.763	12.915
0.930	80.270	46.142	40.851	37.755	37.747	12.915
0.940	80.262	46.102	40.811	37.739	37.739	12.915
0.950	80.270	46.110	40.811	37.723	37.731	12.915
0.960	80.262	46.078	40.787	37.715	37.731	12.907
0.970	80.262	46.086	40.779	37.699	37.699	12.899
0.980	80.246	46.054	40.738	37.699	37.715	12.891
0.990	80.254	46.062	40.746	37.675	37.691	12.899
1.000	80.238	46.046	40.706	37.666	37.675	12.891
1.010	80.238	46.054	40.706	37.650	37.658	12.891
1.020	80.230	46.030	40.674	37.650	37.650	12.891
1.030	80.230	46.038	40.674	37.618	37.642	12.883
1.040	80.222	46.014	40.658	37.626	37.634	12.874
1.050	80.214	46.022	40.658	37.602	37.618	12.866
1.060	80.206	45.997	40.626	37.594	37.626	12.866
1.070	80.206	46.014	40.634	37.586	37.610	12.866
1.080	80.190	45.973	40.594	37.586	37.610	12.866
1.090	80.190	45.989	40.586	37.570	37.586	12.858
1.100	80.182	45.965	40.553	37.570	37.594	12.866
1.110	80.174	45.973	40.553	37.554	37.586	12.858
1.120	80.158	45.949	40.521	37.554	37.578	12.858
1.130	80.150	45.965	40.521	37.538	37.562	12.850
1.140	80.150	45.941	40.481	37.530	37.570	12.850
1.150	80.126	45.941	40.481	37.514	37.562	12.858
1.160	80.102	45.917	40.433	37.514	37.562	12.850
1.170	80.102	45.933	40.441	37.490	37.546	12.850
1.180	80.086	45.909	40.401	37.482	37.538	12.842
1.190	80.086	45.909	40.401	37.473	37.538	12.842
1.200	80.077	45.893	40.368	37.457	37.538	12.834
1.210	80.061	45.893	40.376	37.441	37.530	12.842
1.220	80.045	45.869	40.328	37.433	37.538	12.842
1.230	80.053	45.877	40.352	37.409	37.514	12.834
1.240	80.037	45.861	40.304	37.417	37.506	12.826
1.250	80.029	45.861	40.296	37.393	37.506	12.826
1.260	80.013	45.845	40.256	37.385	37.498	12.818
1.270	80.005	45.845	40.264	37.361	37.482	12.818
1.280	79.989	45.829	40.224	37.369	37.490	12.818
1.290	79.989	45.829	40.232	37.345	37.457	12.810
1.300	79.973	45.813	40.200	37.337	37.465	12.810
1.310	79.973	45.813	40.200	37.321	37.441	12.810
1.320	79.957	45.796	40.175	37.321	37.449	12.802
1.330	79.957	45.796	40.175	37.313	37.417	12.794
1.340	79.949	45.788	40.159	37.305	37.425	12.794
1.350	79.949	45.780	40.151	37.289	37.385	12.778
1.360	79.933	45.772	40.135	37.281	37.385	12.770
1.370	79.941	45.764	40.143	37.272	37.377	12.778
1.380	79.925	45.756	40.119	37.256	37.369	12.778
1.390	79.933	45.764	40.127	37.248	37.345	12.770
1.400	79.917	45.748	40.103	37.232	37.353	12.762
1.410	79.917	45.748	40.111	37.216	37.337	12.762
1.420	79.901	45.732	40.079	37.216	37.337	12.754
1.430	79.909	45.732	40.087	37.192	37.313	12.762

1.440	79.901	45.708	40.063	37.200	37.321	12.754
1.450	79.893	45.716	40.055	37.184	37.297	12.754
1.460	79.876	45.700	40.023	37.176	37.305	12.746
1.470	79.876	45.700	40.039	37.168	37.256	12.746
1.480	79.852	45.692	40.007	37.176	37.281	12.738
1.490	79.844	45.684	40.007	37.152	37.248	12.730
1.500	79.828	45.676	39.974	37.152	37.264	12.738
1.510	79.828	45.668	39.982	37.136	37.224	12.738
1.520	79.812	45.660	39.950	37.144	37.248	12.738
1.530	79.820	45.652	39.966	37.112	37.208	12.730
1.540	79.804	45.652	39.918	37.120	37.232	12.714
1.550	79.796	45.644	39.918	37.096	37.200	12.714
1.560	79.788	45.636	39.886	37.104	37.208	12.714
1.570	79.804	45.636	39.902	37.088	37.176	12.714
1.580	79.780	45.620	39.870	37.096	37.200	12.714
1.590	79.780	45.620	39.878	37.088	37.160	12.706
1.600	79.772	45.603	39.838	37.088	37.176	12.714
1.610	79.772	45.603	39.862	37.079	37.160	12.706
1.620	79.756	45.603	39.830	37.079	37.160	12.706
1.630	79.756	45.603	39.830	37.071	37.144	12.706
1.640	79.748	45.587	39.789	37.071	37.152	12.698
1.650	79.740	45.587	39.806	37.063	37.128	12.698
1.660	79.740	45.587	39.765	37.063	37.144	12.698
1.670	79.732	45.579	39.773	37.055	37.112	12.690
1.680	79.732	45.579	39.749	37.055	37.128	12.690
1.690	79.740	45.579	39.757	37.055	37.104	12.681
1.700	79.732	45.563	39.733	37.055	37.120	12.673
1.710	79.732	45.563	39.749	37.047	37.096	12.657
1.720	79.724	45.547	39.717	37.047	37.112	12.665
1.730	79.716	45.547	39.725	37.039	37.088	12.673
1.740	79.691	45.547	39.693	37.039	37.096	12.681
1.750	79.691	45.539	39.701	37.031	37.071	12.665
1.760	79.683	45.539	39.669	37.031	37.079	12.665
1.770	79.675	45.531	39.685	37.031	37.071	12.665
1.780	79.667	45.531	39.653	37.031	37.088	12.657
1.790	79.667	45.523	39.661	37.023	37.071	12.657
1.800	79.651	45.523	39.637	37.023	37.079	12.657
1.810	79.651	45.515	39.645	37.023	37.063	12.649
1.820	79.643	45.507	39.629	37.031	37.071	12.641
1.830	79.643	45.507	39.637	37.023	37.055	12.649
1.840	79.627	45.499	39.613	37.023	37.063	12.641
1.850	79.627	45.499	39.621	37.015	37.047	12.641
1.860	79.619	45.491	39.596	37.015	37.055	12.641
1.870	79.619	45.475	39.605	37.015	37.039	12.641
1.880	79.603	45.467	39.580	37.007	37.055	12.633
1.890	79.611	45.467	39.596	36.999	37.039	12.633
1.900	79.587	45.475	39.564	36.999	37.047	12.633
1.910	79.595	45.475	39.572	36.999	37.039	12.641
1.920	79.579	45.467	39.540	36.991	37.047	12.641
1.930	79.595	45.459	39.556	36.991	37.039	12.641
1.940	79.579	45.467	39.524	36.991	37.047	12.633
1.950	79.579	45.459	39.532	36.983	37.039	12.633
1.960	79.563	45.451	39.500	36.991	37.039	12.641
1.970	79.555	45.435	39.516	36.975	37.031	12.641

1.980	79.547	45.435	39.492	36.983	37.039	12.641
1.990	79.539	45.419	39.508	36.967	37.023	12.633
2.000	79.531	45.427	39.484	36.967	37.031	12.625

14. Data analysis of kinetic parameter (Φ_0)

Electrolysis time / h	j / mAcm^{-2} Electrolyte 2 on plate anode	Electrolysis time / h	j / mAcm^{-2} Electrolyte 1 on plate anode	Electrolysis time / h	j / mAcm^{-2} Electrolyte 2 on expanded titanium mesh
0	441.780	0	291.730	0	196.960
6	436.360	6	292.000	45	206.270
24	410.690	24	284.350	93	193.830
36	400.280	30	287.930	141	179.100
60	403.880	70	296.720	165	166.950
66	329.680	94	265.520	208	157.780
84	351.010	118	276.870	276	142.810
88	383.330	142	284.960	320	138.500
108	365.530	166	254.260	368	138.150
113	385.340	190	232.660	436	118.110
141	325.680	230	206.080	466	156.670
164	282.510	254	207.580	538	155.080
209	319.980	278	212.050	610	147.700
231	184.400	302	206.740	655	142.260
251	237.230	326	188.610	726	139.190
273	249.870	350	188.500	770	139.480
317	249.740	394	190.220	842	129.340
361	244.800	418	187.000	888	127.670
383	244.590	442	175.480	935	129.410
406	249.890	466	204.820	999	127.130
432	238.320	562	190.910	1059	41.587
475	186.480	610	185.110		
522	175.100	658	213.360		
548	143.300	749	181.740		
568	161.630	797	171.530		
616	94.089	843	92.920		
645	92.448	851	43.131		

15. Data variation in j from CA

Electrolysis time / h	j / mA cm^{-2} Electrolyte 2 on plate anode				Electrolysis time / h	j / mA cm^{-2} Electrolyte 1 on plate anode				Electrolysis time / h	j / mA cm^{-2} Electrolyte 2 on expanded titanium mesh			
	10 ms	20 ms	30 ms	200 ms		10 ms	20 ms	30 ms	200 ms			10 ms	20 ms	30 ms
0	289.306	226.151	211.060	198.105	0	193.192	146.774	120.407	88.120	0	0	289.306	226.151	211.060
6	262.756	175.201	133.865	98.358	6	184.753	135.574	105.698	64.117	45	6	262.756	175.201	133.865
24	270.386	201.309	155.014	97.733	24	199.356	146.561	114.395	74.799	93	24	270.386	201.309	155.014
36	273.743	217.621	177.414	87.433	30	193.512	148.743	118.073	67.902	141	36	273.743	217.621	177.414
60	265.808	201.782	156.326	87.585	70	201.431	158.417	127.548	65.384	165	60	265.808	201.782	156.326
66					94	184.799	148.804	122.696	66.040	208	66			
84	255.372	168.533	132.843	83.069	118	194.168	157.333	130.570	74.371	276	84	255.372	168.533	132.843
88					142	200.078	161.514	133.850	82.260	320	88			
108	241.242	185.639	149.780	106.278	166	182.053	151.657	128.265	65.750	368	108	241.242	185.639	149.780
113					190	169.000	144.000	123.000	65.000	436	113			
141	224.457	177.597	144.714	85.831	230	157.000	137.000	121.000	64.800	466	141	224.457	177.597	144.714
164	206.000	175.000	151.000	57.900	254	155.000	134.000	116.000	58.000	538	164	206.000	175.000	151.000
209	224.000	182.000	150.000	77.100	278	158.000	136.000	119.000	57.700	610	209	224.000	182.000	150.000
231	147.000	132.000	120.000	65.900	302	157.000	137.000	121.000	46.500	655	231	147.000	132.000	120.000
251	173.000	145.000	124.000	73.900	326	145.000	128.000	114.000	43.700	726	251	173.000	145.000	124.000
273	184.000	155.000	134.000	72.100	350	145.000	128.000	114.000	43.700	770	273	184.000	155.000	134.000
317	179.000	148.000	125.000	63.600	394	146.000	129.000	114.000	46.800	842	317	179.000	148.000	125.000
361	182.000	154.000	134.000	75.100	418	144.000	127.000	113.000	43.900	888	361	182.000	154.000	134.000
383	180.000	152.000	131.000	59.600	442	136.000	121.000	108.000	42.900	935	383	180.000	152.000	131.000
406	183.000	154.000	133.000	62.300	466	154.000	134.000	117.000	54.500	999	406	183.000	154.000	133.000
432	184.000	147.000	127.000	55.800	562	146.000	129.000	114.000	47.700	1059	432	184.000	147.000	127.000
475	141.000	122.000	108.000	46.400	610	143.000	127.000	113.000	45.500		475	141.000	122.000	108.000
522	119.000	92.500	77.300	53.500	658	161.000	141.000	124.000	50.800		522	119.000	92.500	77.300
548	99.100	77.000	63.200	34.100	749	141.000	126.000	113.000	47.300		548	99.100	77.000	63.200
568	111.000	85.400	69.700	36.500	797	133.000	118.000	106.000	44.900		568	111.000	85.400	69.700
616	66.500	53.600	45.000	21.300	843	69.100	57.800	50.600	29.400		616	66.500	53.600	45.000
645	65.400	52.900	44.400	20.200	851	31.000	24.600	21.000	13.000		645	65.400	52.900	44.400