Corrosion Behaviour of Zirconium Alloys in High Temperature Aqueous Environment By Electrochemical Impedance Spectroscopy

A thesis submitted to The University of Manchester for the degree of Doctor of Philosophy in the Faculty of Engineering and Physical Sciences

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SCHOOL OF MATERIALS Corrosion & Protection Centre

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UNIVERSITY OF MANCHESTER

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Doctor of Philosophy

Corrosion Behaviour of Zirconium Alloys in High Temperature Aqueous Environment By Electrochemical Impedance Spectroscopy

Abstract

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The corrosion behaviour of zirconium based alloys has been primarily investigated by electrochemical impedance spectroscopy (EIS). In-situ autoclave EIS experiments were performed in simulated primary coolant conditions in order to study the high temperature water corrosion of zirconium alloys in PWRs. In-situ impedance response of the corroding material was recorded throughout first kinetic transition.

A physical model of the zirconium oxide was proposed in accordance with the microstructural observation made by SEM analysis. Electrical properties of the oxide was evaluated with equivalent circuit model (ECM) which was constructed according to the physical oxide model. Evolution of various oxide parameters obtained from ECM was analysed in accordance with the microstructure observation made by SEM.

A two layer structure consists of a outer porous oxide and an inner barrier oxide, was found to be the most accurate description for the autoclave formed oxide. Supporting evidence from the SEM cross-section and surface analysis of the oxide had shown cracks and pores that were linked and connected with the environment. This observation is also confirmed by the in-situ EIS measurement which has shown porous electrode behaviour throughout the course of oxidation. The porous oxide behaviour was also confirmed by the ex-situ soaking experiment on samples with incremental exposure time.

Evolution of inner barrier layer oxide thickness was found to be correlated with kinetic transition which was determined from weight gain measurement. This indicated that barrier layer maybe the oxidation rate controlling layer and its thickness maybe reduced during transition. Thus, a thinner barrier layer would resulted in a rapid corrosion of zirconium alloys. Furthermore, maintaining the barrier layer thickness maybe the possible route to improve zirconium alloy corrosion resistance.

Declaration of Authorship

I, PENG WANG, declare that this thesis titled, 'CORROSION BEHAVIOUR OF ZIRCONIUM ALLOYS IN HIGH TEMPERATURE AQUEOUS ENVIRONMENT BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY' and the work presented in it are my own. I confirm that:

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Chapter 1

Introduction

1.1 Background

Worldwide, there is an urgent demand for reducing CO_2 emission and supplying of cleaner energy from renewable sustainable sources. This demand can only be fulfilled if the current nuclear generation capacity is maintained or increased. However, after the accident at Chernobyl in 1986, the level of research activity on all nuclear materials has been declining, also including zirconium alloy for fuel cladding. It is only recently, the issue of nuclear power is being debated once again due to its virtually negligible emission of CO_2 .

With the recent demands for higher fuel discharge burnup¹ towards better fuel utilisation and higher coolant temperatures for better thermal efficiency, there is a requirement for high performance corrosion resistive materials. As a result, zirconium alloys have been reconsidered even though a large amount of work has been carried out to understand its corrosion behaviour under nuclear operating conditions in the

¹ "Burnup" is defined as the total energy released per initial unit mass of fuel as a result of irradiation (IAEA 2010). Commonly used units are Megawatt-days-per-Metric-Ton (MWd/MT) of fuel or the same in GWd/MT (Adamson & Rudling 2002).

last 40 years. However, it seems there are still some aspects regarding the corrosion mechanisms which remain unclear for zirconium alloys.

Zirconium-based alloys are widely used in the nuclear industry as cladding and structural materials. These alloys were chosen due to their low thermal neutron cross-section area, superior corrosion resistance and excellent mechanical properties. The formation of the protective oxide, zirconium dioxide (ZrO_2), on the surface of the metal gives excellent corrosion resistance. However, the cyclic nature of the corrosion kinetics and accelerated breakaway corrosion are the limitations for zirconium cladding, that limits the burnup of the fuel.

1.1.1 Aim and Objectives

The work carried out in this study forms part of the Mechanistic Understanding of Zirconium Corrosion (MUZIC) program, which was undertaken by three institutions: Manchester, Oxford and Open Universities. The aim of this project is to develop a fully mechanistic understanding of the high temperature water corrosion of zirconium alloys, especially in a pressurised water reactor (PWR) environment. The outcome of the MUZIC project will support the development of a physicallybased lifetime prediction capability for corrosion of Zr alloys, that will be applicable to nuclear fuel cladding assemblies, and more generally, for Zr alloys used in highperformance heat exchanger systems in the chemical and food processing industries. In nuclear applications, corrosion of Zr-alloys (i.e., both oxidation and hydriding) is the limiting factor for increasing the efficiency of nuclear fuel usage. Thus, zirconium alloys with improved performance can boost the economy of current and future PWRs, extend refuelling cycles and reduce both operating costs and the production of nuclear waste. The MUZIC program has involved several researchers independently concentrating on the analysis of the same corroded materials in order to obtain complementary information. The characterisation has been performed using Synchrotron-XRD, TEM, High-Resolution TEM, Nano-Indentation, SEM, 3D-FIB and 3D Atom Probe, as well as some electrochemical techniques. This thesis describes the utilisation of electrochemical impedance spectroscopy (EIS) with high temperature autoclave facilities to characterise the electrical properties of zirconium oxide under primary coolant conditions, focusing in particular on a commercial Zr-Sn alloy (i.e., Zircaloy-4) and a Zr-Sn-Nb alloy (i.e., ZIRLOTM).

1.1.2 Hypothesis

The question was raised by the nuclear power industry on how to achieve the maximum duration of the nuclear fuel cladding material inside the reactor core. The logical solution would be fully understand the corrosion mechanisms of zirconium alloys in PWR primary coolant conditions, and improve the alloy's corrosion resistance by, varying its chemical composition, heat treatment, manufacturing processes, etc.

Much literature published on the topic of zirconium alloys has covered a wide variety of areas, including metallurgy, alloy composition and mechanical properties, etc, (Banerjee & Kamath 2005). However, very little information on corrosion had been mentioned. Therefore, understanding of the high temperature corrosion behaviour inside the nuclear reactor is essential for the higher burn-up situation. The only possible way to obtain such information is to apply in-situ measurement.

The MUZIC project hypothesis is to determine the consequence and cause of zirconium alloy corrosion behaviour, in which can be used to modify material manufacturer's production methods to improve material performance; it can also provide the reactor operator a guideline for the maximum in-core time of their nuclear fuel assemblies.

In particular, this PhD research will investigate the fundamental mechanism of zirconium alloy oxidation from an electrochemical point of view, and integrate the findings with other researchers. The hypothetical mechanism for cyclic corrosion of zirconium alloys was thought to be related with the formation of interfacial cracks at the metal/oxide interface during the kinetic transition. However, from an electrochemical point of view, such cracks would impede electron transfer through the oxide which is essential for corrosion reactions to proceed. Observations on the oxide structure during the kinetic transition period suggested that a bi-layer structure was formed after the transition, which consists of a porous outer layer and a dense inner layer. Further oxidation would increase the thickness of the porous outer layer but not the inner dense layer (Schefold et al. 2003). Due to the fact that zirconium oxide grows inward, porous oxide must be transformed from the dense oxide layer. As a result, the hypothesis for this research is that the inner dense oxide layer became porous and new inner dense layer subsequently formed during kinetic transition. If the inner oxide layer thickness can be detected by EIS measurement, a process of first thinning and then thickening of the inner layer would be expected during the transition period.

Electrochemical Impedance Spectroscopy (EIS) was employed to study the corrosion mechanism of zirconium alloys in an static autoclave which simulates the reactor coolant conditions. By making in-situ EIS measurements of the corroding zirconium sample continuously, an evolution of impedance spectra can be produced. Further analysis using an equivalent circuit model that is deduced from oxide microstructure examination, would give us insights into how the electrical properties of the oxide would change with oxidation time. Hence, by correlating the physical and electrical changes with oxidation time, a lifetime prediction of the zirconium cladding can be made.

1.1.3 Thesis Structure

Chapter 2 gives a brief introduction of the uses of zirconium in the nuclear industry and the corrosion problems associated with its application as fuel rod cladding. This chapter continues to describe the existing literature regarding the primary coolant loop corrosion of zirconium alloys, as well as the contributions of previous electrochemical studies. An overview of electrochemical impedance spectroscopy is described in Chapter 3, with further specification of the in-situ and ex-situ measurement used in the present study, data presentations, methods of analysis and interpretation of results. The materials that were analysed in this study and the instruments used for the in-situ autoclave EIS experiment, as well the processes involved with the preparation of samples for the SEM analysis are described in Chapter 4.

Chapter 5 details electrochemical impedance spectroscopy results and SEM analysis of the oxide layer. By analysing the impedance spectra collected with respect to oxidation time using equivalent circuit modelling, the impedance response can be described using electrical elements in various configurations, hence, with the aid of a physical model, the electrical elements can be assigned with specific physical properties to described the behaviour of the zirconium oxide. The main focus of the impedance spectroscopy study is the evolution of different zirconium oxide layers with oxidation time, especially during the kinetic transition. The changes of alloy chemistry are compared with respect to their impedance response. A discussion regarding the weight gain, microstructures and impedance data analysis is given at the end of this chapter. Finally, a summary of the findings, conclusions and further work are given in Chapter 6. Appendix A described the calculation that was used to determine the hydrogen concentration in the electrolyte.

Appendix B described the electroless nickel plating on zirconium oxide which helped edge retention during SEM sample preparation. The solution recipe and procedures are included.

Chapter 2

Literature Review

2.1 Introduction

Corrosion of zirconium alloys is an electrochemically driven process affected by the microstructure and chemistry of the alloy surface, the nature of the oxide layer, the temperature at the metal/oxide interface, the chemistry and thermohydraulics of the corrosive medium as well as the effects of oxidation time.

Since the first PWR reactor was built, some improved designs have been developed to reduce the construction cost and improve the efficiency of such reactors, and good progress had been made on nuclear materials development and fuel enrichment. One of the major challenges to the future of nuclear power lies in its economical competitiveness. To stay competitive, the nuclear industry needs to reduce maintenance and fuel cycle costs of their current reactors. One of the methods used to meet these objectives is extended burnup. By extending the in-core time of the fuel assemblies, a higher burnup level can be achieved with considerably shorter refuelling time.

However, the main limiting factor for achieving high burnups is cladding materials due to its limitation in corrosion resistance. From an economical point of view, the development of fuel assemblies that can operate under more severe fuel duty cycles, including higher coolant temperatures, higher discharge burnups and longer in-core residence times, can significantly improve the efficiency of current and future light water-cooled reactors.

To be able to sustain the degree of burnup, the corrosion properties of the cladding material must be fully understood, including its critical life-limiting factors, such as the thickness of the oxide layer, the onset of breakaway oxidation and the pick-up of hydrogen (e.g. hydride formation and its influence on the corrosion properties). The recent development of new Zr-based alloys has been based almost entirely on empirical research programmes, which have led to some degree of improvement in performance, but not added much to our systematic understanding of its corrosion behaviour. A greater improvement of burnup efficiency and commercial exploitation of these new alloys can only be achieved if a mechanistic understanding of cladding corrosion is developed.

This review will introduce the role of zirconium alloys in the nuclear industry and the life limiting problem of breakaway oxidation. A brief summary of the metal production methods (Section 2.3.2) and alloy development with information on the role of individual solute additions (Section 2.4.4) is given.

The oxidation processes in high temperature water environment and the oxides formed on zirconium and its alloys is described followed by a summary of proposed mechanisms of oxidation in the PWRs environment (Section 2.5).

The review covers a wide range of parameters that may affect the corrosion properties of zirconium alloys, however, irradiation field effects are not taken into account for the corrosion behaviour.

Parameter	Normal value
O_2 , ppb	<5
$H_2, mL/kgH_2O$	25 - 50
Cl, ppb	<50
F, ppb	$<\!50$
SO_4 , ppb	$<\!50$
suspended solids, ppb	<350
SiO_2 , ppb	<100

 TABLE 2.1: PWR primary system cooling water specification. Adapted from Kirk-Othmer (2007).

2.2 Pressurised Water Reactors (PWR) Environment

Pressurised water reactors (PWRs) utilise light water as the primary coolant to transfer the heat generated from the fission reaction. The heated primary coolant then flows to the secondary system where steam is generated to power the turbines which, in turn, drives the electric generator.

In PWRs, the primary loop coolant consists of boric acid and lithium hydroxide (i.e., H_3BO_3 and LiOH) with addition of hydrogen and is usually circulated continuously at 300°C and 15 MPa (150 bar) (Kirk-Othmer 2007). The primary loop coolant specifications for PWR are given in Table 2.1.

In PWRs, the primary coolant is kept alkaline to counteract the formation and transport of corrosion product. An excess amount of molecular hydrogen is dissolved in the coolant to maintain its reducing condition in order to prevent the accumulation of oxidants, such as oxygen and hydrogen peroxide, which are responsible for the corrosion of the primary loop. The molecular hydrogen participates in a number of reactions which recombine H, OH and H_2O_2 back to water (Pastina et al. 1999):

$$H + H_2 O_2 \to OH + H_2 O \tag{2.1}$$

$$H_2 + OH \to H + H_2O \tag{2.2}$$

$$H_2 + H_2 O_2 \to 2H_2 O \tag{2.3}$$

In PWRs, the typical dissolved hydrogen level is controlled within the range of 25-50 $cm^3(STP)/kg$ (i.e., 2.2~4.4 ppm). The early radiolysis studies conducted by Giraudeau et al. (2008) determined that excess hydrogen in the primary coolant promotes the back-reaction of the radiolysis of water by radiation in the core, hence, the potentially oxidising products such as oxygen or hydrogen peroxide are avoided. However, recent studies have determined that minimum level of dissolved hydrogen to prevent formation of oxidising conditions in the real reactor was within the range 10-15 $cm^3(STP)/kg$ (0.9-1.35 ppm) (Giraudeau et al. 2008).

Pastina et al. also stated that 2.58 $cm^3(STP)/kg$ (i.e., 0.23 ppm) of dissolved hydrogen was enough to avoid notable water decomposition and formation of oxidising radicals at 200°C. Oxygen concentration in solution has a negative temperature dependance, as solution temperature increases, the concentration of dissolved molecular oxygen and hydrogen decreases.

Apart from the dissolved gases listed in Table 2.1, other chemicals can be found in primary loop coolant. Boric acid is usually added as a neutron absorber in order to control the neutron activity in the reactor. A pure boric acid solution is only slightly more acidic than pure water (pH ~ 5.6 at 300°C), due to its relatively low ionisation at high temperatures (Kirk-Othmer 2007). However, this acidic condition created by introducing boric acid into the coolant would readily have an effect of the corrosion rate of the system materials. Hence, the pH value of the reactor coolant is controlled by the addition of lithium hydroxide. The presence of lithium hydroxide which has a much higher ionisation level, increases the pH value 1-2 unit above that



FIGURE 2.1: Lithium hydroxide-boric acid relationship for various pH at 300°C, adapted from Kirk-Othmer (2007).

of pure water at operating temperatures. A desirable pH value for the primary loop coolant is between 6.9 to 7.4 where it leads to a reduction in corrosion rates of system materials (a pH plot of the primary coolant as a function of boric acid and lithium hydroxide concentrations can be found in Figure 2.1) (Adamson et al. 2007).

The structural and pressure containing parts of the reactor and the primary steam generation systems are fabricated from stainless steel, nickel base alloys, and stainless steel-clad carbon steel. The use of zirconium as a fuel cladding material in light water reactors is well established (Krishnan & Asundi 1981), because of the combination of material properties. In addition to use as fuel cladding tubes which encase the uranium dioxide fuel pellets, zirconium is used for other reactor core internals such as fuel element supports, pressure tubes, core support members, instrumentation assemblies, etc. Despite the higher initial cost of zirconium compared with stainless steel and nickel base alloys, the superior qualities inherent in zirconium can offset the higher costs.

2.3 Zirconium Metal

The element, zirconium, was first discovered in 1789 by the German chemist Martin Heinrich Klaproth, and it was isolated in 1824 by Swedish chemist Jöns Jakob Berzelius, as an impure metal powder prepared by reduction of potassium fluorozirconate (ZrK_2F_6) with potassium metal (Schemel 1977). However, the purer and ductile zirconium metal did not become available until 1925, when Anton Eduard van Arkel, Jan Hendrik de Boer and the Phillips Gloei-lampenfabriken invented the iodide decomposition process, also known as the Iodide Crystal Bar process (see Section 2.3.2.1). The Iodide Crystal Bar production method for purer zirconium is still being used today as a method of purifying sponge zirconium and hafnium.

Several groups of scientists and engineers that were looking for metals and alloys for nuclear reactors in 1940s, had came across zirconium which seemed to meet all the requirements for fuel cladding application. Zirconium metal has good corrosion/oxidation resistance, resistance to irradiation damage, and transparency to thermal neutrons to sustain the nuclear reaction. However, the production of zirconium was very limited at the time; only a few hundred pounds of zirconium were produced in the US in 1945, and it was very expensive (Schemel 1977).

The commercial zirconium metal became largely available after the invention of the magnesium reduction method by Dr.William Justin Kroll, and The Kroll's Process was named after him (Kroll 1937). About the same time, Dr.Albert R.Kaufman of Massachusetts Institute of Technology and Dr. Sam Utermeyer discovered that the

early measurements of the thermal neutron cross section of zirconium were inaccurate because the metal tested had a large hafnium content which occurs naturally with zirconium in zircon. The approximately 2.5% naturally occurring hafnium in zirconium was proved later to be responsible for the high thermal neutron cross section at Oak Ridge (Weinberg 1994). A very low thermal neutron absorption cross section was reported once the impurity, hafnium, had been removed from the material (Table 2.2).

In the nuclear power industry, the first commercial nuclear power reactor used stainless steel to clad the uranium-dioxide fuel because it was easier and cheaper to fabricate. Zirconium was first used as a nuclear material in the U.S. Naval Nuclear Propulsion Program in the 1950s and subsequently became the prime choice for fuel cladding and structural materials for nuclear reactors. By 1965 the nuclear industry had made zirconium alloys the predominant cladding material for water-cooled reactors, and there was a worldwide recognition of these strong, corrosion-resistant zirconium alloys. At the same time, the chemical processing industry began to use zirconium in a variety of highly severe corrosive environments. Thanks to its remarkable corrosion resistance and biocompatibility, zirconium has found some medical applications, in surgical tools and instruments. Also, from a metallurgy point of view, zirconium is highly beneficial as an alloying element, such as magnesium-, aluminium-, and titanium-based alloys.

Zirconium and its alloys can be classified into two categories: nuclear and nonnuclear grade. The main difference between these two categories is the hafnium content. Nuclear grades are essentially free of hafnium (<100 ppm) (Schemel 1977). Non-nuclear grades may contain as much as 4.5 wt.% hafnium, which has a dramatic effect on the neutron cross section area (Table 2.2) but little effect on its mechanical and corrosion properties.

	Thermal Neutron Cross
Metals and Alloys	Section (Barns)
Mg	0.059
Zr	0.185
Zircaloy-4	0.22
Sn	0.65
Fe	2.4
Stainless Steel 300 Series	3.1
Ni	4.5
Ti	5.6
Hf	102
Cd	2400

TABLE 2.2: Thermal neutron absorption cross section of various materials. Adapted from Schemel (1977).

The majority of the nuclear grade materials are produced as tubing, which is used for nuclear fuel rod cladding, guide tubes, pressure tubes, and spacer grids. Sheets and plates are also produced and used for spacer grids, water channels, and channel boxes for nuclear fuel bundles. Non-nuclear grade zirconium is usually found in highly corrosion resistant equipment, including heat exchangers, condensers, reaction vessels, columns, piping systems, agitators, evaporators, tanks, pumps and valves.

In 1975, about 4000 tons of zirconium metal were produced in the United States, France, and the USSR (Schemel 1977). By 2008, 2600 tons of zirconium metal were produced in the US alone. It is used now in all water-cooled power reactors around the world and for a wide variety of other applications.

2.3.1 Physical and Chemical Properties

Zirconium is a lustrous, grayish white, ductile metal. A collection of properties of zirconium is given in Table 2.3. Properties and chemical compositions of the major zirconium alloys are described in Table 2.5.

Properties	Zirconium
Atomic number	40
Atomic weight	91.22
Atomic Radius	
(zero charge)	$1.60\text{-}1.62~\AA$
(+4 charge)	$0.80 ext{-}0.90\ \AA$
Density	
at $20^{\circ}C (g/cm^3)$	6.510
Melting point	$1845^{\circ}\mathrm{C}$
Boiling Point	$3577^{\circ}\mathrm{C}$
Lattice Parameters	
α -HCP (below 865°C)	$a=3.2312\text{\AA}(25^{\circ}\text{C})$
	$c=5.1477 \text{\AA} (25^{\circ}C)$
β -BCC (above 865°C)	$a=3.6090 \text{\AA}$ (862°C)
Coefficient of linear Thermal expansion	$5.89 \times 10^{-6} / ^{\circ}C$
per °C at 25° C	
Thermal conductivity	$100^{\circ}C, 0.049 \text{ cal/s/cm/}^{\circ}C$
Specific heat	0.067 cal/g/°C
Electrical resistivity	$40 \ \mu\Omega \cdot \mathrm{cm}$

TABLE 2.3: Physical Properties of Zirconium metal, adapted from Schemel (1977), Roberge (2000), Schweitzer (2003).

The microstructure of zirconium alloys depends on composition, phases present and lattice orientation. Zirconium metal has two stable crystallographic forms: α -Zr, with a hexagonal close packed (HCP) structure and β -Zr, with a body centred cubic (BCC) structure (Dupin et al. 1999). For pure zirconium, the α -Zr exists below 865°C, whereas the β -Zr forms above 865°C (Zhao et al. 2005). Lattice parameters of the α - and β -Zr are listed in Table 2.3. The α -Zr appears as a quilted structure, whereas the β -Zr consists of needle shaped structures (Danielson & Sutherlin 2004).

The melting temperature of pure zirconium is close to 1855° C, classifying it as a refractory metal (Lemaignan 2006). In the β phase, all the chemical additions to be discussed in the later section (Section 2.4.4) are fully soluble. Only limited solid solution of oxygen, tin and niobium are present in α zirconium phase.

Zirconium and its alloys that were used in nuclear applications also requires adequate mechanical properties at elevated temperatures and pressures, which is crucial for fuel assembly performance. Basic mechanical properties of the zirconium metal are shown in Table 2.4, and mechanical properties of its alloys would be considerably better.

TABLE 2.4: Mechanical Properties of Zirconium metal, adapted from Schemel (1977), Roberge (2000), Schweitzer (2003).

Mechanical Properties	Zirconium
Young's Modulus	68GPa
Shear Modulus	33 GPa
Vickers Hardness	903GPa
Poisson's Ratio	0.35
Yield Strength	$207 \mathrm{MPa}$
Tensile Strength	$379 \mathrm{MPa}$

Zirconium is highly reactive, as evidenced by its standard potential of -1.53V vs. the normal hydrogen electrode (NHE) at 25°C (Yau 2001, Meisterjahn et al. 1987). It also has a high affinity for oxygen. In an oxygen-containing atmosphere/medium, such as air, CO_2 , or H_2O , zirconium reacts with oxygen at ambient temperature and below to form an adherent, protective thin oxide film on its surface. This film is self-healing and protects the base metal from chemical and mechanical attacks.

Thermodynamically, zirconium behaves like most passive metals in both acidic and alkaline solutions, as shown in Figure 2.2. It is highly corrosion-resistant in most acids, salt solutions, alkaline solutions, and organic media. Zirconium metal is passive from pH=3.5 until the pH is at least pH=13, it exhibits excellent corrosion resistance over a wide range of pH. Furthermore, zirconium is passive over a large potential range (i.e., above -1.6V). However, the protective oxide films are difficult to form on zirconium's surface in a few media, such as hydrofluoric acid, concentrated

sulphuric acid, and certain dry organic halides (Schemel 1977). Any fluoride impurities in high concentration acids, e.g. sulphuric acid or phosphoric acid, can increase the corrosion rate of zirconium. Hydrofluoric acid and nitric acid are normally found as reagents in pickling process for autoclave sample preparations.



FIGURE 2.2: Potential-pH diagram (Pourbaix) diagram of zirconium in water at 25°C. Adapted from Yau (2001).

At PWR conditions (i.e., $pH = 6.9 \sim 7.4$, 360°C), the passivation region on the Pourbaix diagram of $Zr - H_2O$ system will have a very narrow pH range due to the promoted corrosion processes at high temperatures as shown in Figure 2.3d. This



could be the reason of which zirconium is impossible to passivate in high temperature water.

FIGURE 2.3: Potential-pH diagram (Pourbaix) diagram of zirconium in water at elevated temperature a) at 298K b) at 333K c) at 373K d) at 423K. Adapted from Chen et al. (2004).

pH Value

pH Value

2.3.2 Metal Production Methods

Zirconium is the 11^{th} most abundant element in the earths crust. It is more abundant than copper, lead, nickel, or zinc (Benedict & Pigford 1981). The most common zirconium ore is zircon (ZrSiO₄), a by-product of the mining and processing of beach sands for the titanium and tin minerals. Major steps of zirconium production are shown in the Figure 2.4.

2.3.2.1 Zirconium Sponge Production

In order to produce zirconium metal, the beach sand zircon need to be converted into ZrCl_4 , through a carbon-chlorination process at 1200°C, this technique is also know as the Kroll process. The chemical reaction involved is shown below.

$$ZrO_2(SiO_2 + HfO_2) + 2C + 2Cl \rightarrow ZrCl_4(SiCl_4 + HfCl_4) + 2CO$$
(2.4)

The sand containing zircon $(ZrSiO_4)$ is usually heated with carbon in an electric furnace to form a cyanonitride, which is subsequently treated with chlorine gas to form the volatile tetrachloride (i.e., $ZrCl_4$, $HfCl_4$). Silicon tetrachloride (SiCl_4) as a by-product can be removed after chlorination process (Schemel 1977).

Hafnium is subsequently removed from the tetrachloride mixture (i.e., ZrCl_4 , HfCl_4) by a solvent extraction method, which is based on the difference of solubility of metal thiocyanates in an organic solvent, methyl isobutyl ketone (MIBK) (Schemel 1977). After reaction with ammonium thiocyanate, $\operatorname{SCN}\cdot\operatorname{NH}_4$, a solution of hafnyl-zirconylthiocyanate, $(\operatorname{Zr/Hf})O(\operatorname{SCH})_2$ is obtained. A liquid-liquid extraction is performed with MIBK and finally a hafnium-free ZrCl_4 is obtained. A calcination process then converts the chloride to ZrO_2 and a second carbo-chlorination produces ZrCl_4 . After the above processes, gaseous ZrCl_4 is passed through a simple sublimation process in an inert atmosphere and then chemically reduced into zirconium metal sponge using molten magnesium as the reductant at 850°C.

The zirconium sponge can be further purified by the "Van Arkel - de Boer" process, also known as the "Iodide Crystal Bar" process. It involves reacting the sponge metal with iodine to form volatile iodide (i.e., ZrI_4) that is thermally unstable. By using a hot wire, ZrI_4 can be decomposed into zirconium metal and iodine vapour, resulting in pure crystalline zirconium (Schemel 1977).



FIGURE 2.4: Flow diagram for production of zirconium and hafnium due to their co-existent nature. Adapted diagram from Schemel (1977).
2.3.2.2 Ingot Manufacturing

Sponge metal, recycled materials (e.g. scraps from earlier production) and alloying elements are assembled and electron beam welded into a large consumable electrode in a controlled atmosphere to prevent oxidation.

The subsequent melting stage is usually done in vacuum to prevent oxygen and nitrogen pickup from the atmosphere. The consumable electrode is then melted into a water cooled copper mould by a partial melting process, only a small fraction of the whole electrode is molten at any time during the melting process. The homogeneity of the final product is ensured by repeating the melting process three or four times before it was moved onto the next production stage (Adamson & Rudling 2004).

2.3.2.3 Final Product Fabrication

An overview of the tube, plate and sheet manufacturing process is shown in Figure 2.5.

The first step is accomplished by hot forging in the β -phase, $(\alpha+\beta)$ -phase or the upper α -phase, where the temperature is high enough to promote dynamic recrystallisation. The forging is usually carried out at about 1100°C in a number of steps bring down the size of the ingot to workable size billets or logs (Adamson & Rudling 2004). The workpiece is reheated several times during the forging process to increase its plasticity.

During the later part of the manufacturing process, plastic deformation is done by cold rolling (e.g., for plate and sheet), or extrusion and a series of cold pilgering steps (e.g., for tubes) at temperature below 100°C, where recrystallisation will not occur during deformation (Adamson & Rudling 2004).



FIGURE 2.5: Final product manufacturing process, adapted from Lemaignan & Motta (1994).



FIGURE 2.6: Schematic illustration of cold pilger process, adapted from Salzgitter Stainless Tubes, Germany

The final heat treatment, after the last pilgering pass of the cladding tubes may be performed within two temperature ranges, corresponding to two types of microstructures:

• The *stress – relieved* state (SR) is mostly carried out at a temperature of 475°C for 2 hours under protective atmosphere (Lemaignan 2006). The aim for this heat treatment is to reduce the dislocation density within the material,

but without significant recrystallisation. The resulting grain shape remains elongated and highly deformed.

• The recrystallised state (RX) is usually carried out at higher temperature of 550 to 600°C. The resulting grains are more equiaxed, with an average grain size in the range of 5 to 7 μ m (Lemaignan 2006). The heat treated material has a much lower dislocation density, the yield strength is reduced, balanced by a higher resistance to creep deformation. For the Zr-Nb alloys, the RX heat treatment is generally used.

Production methods involving deformation processing (i.e. cold rolling of plates and pilgering of tubes) lead to the development of a strong crystallographic texture of the final products. Although the texture affects the physical and mechanical properties significantly (e.g. anisotropy in thermal expansion), it does not have a large impact on the corrosion behaviour (Adamson & Rudling 2002). However, it affects the by-product of the corrosion process, which is the hydrogen absorption process. Hydrogen-pickup during corrosion leads to the precipitation of brittle hydride phases upon cooling at regions below the metal/oxide interface, the orientation of these platelet hydrides is closely controlled by the metal texture (Adamson et al. 2007).

2.4 Zirconium Alloys

Broadly, two series of zirconium alloys have been the major constituents of the nuclear industry, Zr-Sn and Zr-Nb alloys, which were developed for fuel claddings in particular. Important commercial alloys in both series are shown in Table 2.5.

Alloying elements in zirconium alloys are usually transition metals (e.g. Fe, Cr, and Ni). These elements are almost insoluble in the α -Zr phase and precipitate

TABLE 2.5: List of zirconium alloy claddi	ngs used for thermal reactor applications
and their chemical $compositions(wt\%)$.	Data courtesy of Banerjee & Kamath
(2005), Lemaignan (200	06), Schweitzer (2003).

Zirconium Alloys	Sn	Fe	Cr	Ni	Ο	Nb
Zr-Sn Alloys						
Zircaloy-2	1.20 - 1.70	0.07 - 0.20	0.05 - 0.15	0.03 - 0.08		
Zircaloy-4	1.20 - 1.70	0.18 - 0.24	0.07 - 0.13	—		
Zr-Sn-Nb Alloys						
ZIRLO TM	1.00	0.10				1.00
Alloy 635	1.20	0.40				1.00
Zr-Nb Alloys						
Zr-1Nb						1.00
Alloy M-5	—	—	—	—	0.10	1.00

out as intermetallics, whose size distribution has significant impact on the corrosion behaviour of the alloys.

2.4.1 Zirconium-Tin Based Alloys

Tin, as a substitutional element, is primarily used as a solid solution hardener to increase the strength and creep resistance of zirconium alloys (Hong et al. 2002). The first Zr-Sn based alloy, Zircaloy-1, contained 2.5 wt% tin and had very little impact on enhancing corrosion resistance during high temperature long-term autoclave tests (Nikulina et al. 2006).

2.4.1.1 Zircaloy-2

After the failure of Zircaloy-1, other elements such as Ni and Fe were added to improved its corrosion properties, which resulted in development of Zircaloy-2. In Zircaloy-2, Sn was set to a lower content at 1.5 wt%, Fe at 0.15 wt%, Ni at 0.05 wt% and Cr at 0.10% (Mondal et al. 2007). The Cr content in the alloy was picked up from the stainless steel reaction vessel as an impurity. However, this accidentally added element proven to be beneficial for corrosion resistance. Zircaloy-2 was found to have tensile properties equivalent to that of Zircaloy-1 with far better high temperature corrosion resistance. However, later studies had found that Ni increased hydrogen absorption dramatically; subsequent development of removing Ni from Zircaloy-2; resulted in Zircaloy-3 (which was immediately abandoned due to its unacceptably low strength) (Adamson & Rudling 2004).

2.4.1.2 Zircaloy-4

Based on the failure of Zircaloy-3, an increased level of Fe was added, to compensate for the removal of Ni, which resulted in the early version of alloy Zircaloy-4, containing 1.5 wt% Sn, 0.22 wt% Fe and 0.10 wt% Cr. It has a high temperature corrosion resistance comparably good as Zircaloy-2, but with only has half of the hydrogen pick-up of Zircaloy-2 (Mondal et al. 2007). Later, Zircaloy-4 became the work-horse for cladding tubes in PWRs.

Further modification on corrosion resistance of Zircaloy-4 was done by having amall amount of Ni addition, which resulted in better resistance to nodular corrosion (non-uniform oxide thickness) without sacrificing the desirable uniform corrosion resistance and low hydrogen pickup rate (Weidinger et al. 1987).

2.4.2 Zirconium-Niobium Based Alloys

The addition of elements, such as Nb, increases the strength and ductility of zirconium alloys as well its corrosion resistance (Park et al. 2004). Such improvement is due to a reduction in the Nb supersaturation of the matrix during the formation of β -Nb phase precipitates (Jeong et al. 2002, Jeong 2003). The equilibrium concentration of Nb in the matrix can thus be maintained and may be one of the reasons for the good corrosion protection. The creep properties are also improved for Zr-Nb alloys, with the niobium atoms forming solute spheres around dislocations, which prevent dislocation glide under suitable conditions (Charit & Murty 2008).

2.4.3 Zirconium-Tin-Niobium Based Alloys

The aim of developing high performance alloys for nuclear fuel cladding materials, would be to achieve the desired properties of high corrosion resistance to withstand the longer in-core time for extended burn-up and reduced hydrogen pick-up. It would be beneficial to have the strength and creep resistance from the Zr-Sn alloys (i.e., Zircaloy-2 and Zircaloy-4) and the corrosion resistance and ductility from the Zr-Nb alloys (i.e., M5 and Zr-1Nb). The new alloys namely the Zr-Sn-Nb series was developed for the above purposes. Important alloys in this series are ZIRLOTM (Zr-1Sn-1Nb-0.1Fe) and Alloy 635 (Zr-1.2Sn-1Nb-0.4Fe) (Adamson & Rudling 2004).

2.4.4 Alloying Elements and Impurities

The location and behaviour of both the alloying elements and the impurities in the metal are important factors in many understanding of the mechanical properties as well as the corrosion mechanism. However, this review only covers the major alloying elements (e.g. O, Fe, Cr, Ni, Sn and Nb) and impurities (e.g. C, Si, N).

Even in the most pure zirconium, there are atomic impurities and vacancies occupying various positions in the zirconium lattice which can influence the its lattice structure. For an impurity atom that occupies the site of a zirconium atom, the element is called a substitutional impurity (see Figure 2.7 for point defects in crystallise materials). The substitutional impurities in zirconium alloys are alloying



FIGURE 2.7: Crystallographic defects in a crystal lattice.

TABLE 2.6: Approximate atomic radius and atomic weight of elements, adapted from (Pierson 1996)

Element	Atomic Number	Atomic Radius (nm)	Atomic Weight
C	6	0.078	12
Ν	7	0.074	14
Ο	8	0.066	16
Cr	24	0.126	52
Fe	26	0.126	56
Ni	28	0.124	59
\mathbf{Zr}	40	0.159	91
Nb	41	0.145	93
Sn	50	0.141	119

elements with smaller atomic radius compare to zirconium, such as Sn and Nb (see Table 2.6). As a result, the lattice parameter would decrease under the influence of these alloying elements.

2.4.4.1 Tin

Tin is soluble in zirconium at about 1 wt% at 400°C and 9 wt% at 980°C, shown in Figure 2.8 (Lustman & Kerze 1955). The Zr_4Sn phase has a slow precipitate

rate in zirconium, even with long annealing time at higher temperature, tin is still considered as solid solution in Zr alloys (Adamson et al. 2007).



FIGURE 2.8: Binary phase diagram of Zr-Sn system, adapted from Lustman (1979).

2.4.4.2 Niobium

As shown in Figure 2.9, Nb is soluble in zirconium at up to 0.6 wt%. At higher concentrations, Nb can stabilise the β -Zr phase (at ~20 wt% Nb) above ~615°C or precipitate as β -Nb (at 80% Nb). The SPPs present in the Nb containing alloys are different from other alloys, the stable species present in these alloys are: Zr(Nb,Fe)₂ and (Zr, Nb)₄Fe₂ (Adamson et al. 2007).

Tin improves the mechanical properties, mainly the creep resistance, since it is occupying the substitutional sites which can hinder slip planes movement. Niobium is very effective for increase alloys corrosion resistance (Crepin et al. 1995).



FIGURE 2.9: Binary phase diagram of Zr-Nb system, adapted from Lustman (1979).

However, if the element is situated in the gaps between zirconium atoms in a lattice, the element is classified as an interstitial impurity. Since the interstitial site is generally much smaller than the radius of any alloying element, occurrence of these defects would cause a slight increase of the lattice parameters. The common alloying elements and impurities that occupy interstitial sites in the hexagonal cell in zirconium are O, Fe, Cr and Ni.

2.4.4.3 Oxygen

Oxygen was initially considered as impurity but later was regarded as alloying element due to its solution strengthening effect. It has been added intentionally in the form of ZrO_2 powder between the range of 800 ~ 1600 ppm (wt.%) during alloy manufacturing (Adamson & Rudling 2004). Since oxygen atom occupies the interstitial sites in the zirconium lattice that can hinder lattice plane movement as well. A Zr-O phase diagram is shown in Figure 2.10



FIGURE 2.10: Zr-O phase diagram, adapted from Abriata et al. (1986).

Together with alloying element tin, both oxygen and tin can improve the plastic deformation resistance of zirconium alloys due to the beneficial changes in the lattice structure and hindering effect on lattice plane movement (Callister 2006).

2.4.4.4 Iron, Chromium and Nickel

Low solubilities of Fe, Cr and Ni have been observed in zirconium in the range of $100 \sim 200$ ppm (Adamson et al. 2007). In a relatively pure zirconium, a Zr₃Fe phase is commonly precipitated as SPPs. However, in the Zircaloys, which contain two or three alloying elements from the transition metals, the resulting SPPs are more complicated in composition. Many precipitates maybe present in the alloy, such

as $Zr(Cr/Fe)_2$ or $Zr_2(Fe/Ni)$ (Adamson et al. 2007). Zr-Cr, Zr-Fe and Zr-Ni phase diagrams are shown in Figure 2.12 to 2.13, respectively.



FIGURE 2.11: Binary phase diagram of Zr-Fe system, adapted from Lustman (1979).

2.4.4.5 Other Impurities

Other impurities (i.e., carbon and silicon) with low solubilities in zirconium (~100ppm) are normally present as small precipitates (i.e., ZrC or Zr_4Si). Controlled nitrogen content (i.e., ~10 ppm) can be present in zirconium, however, its content is very low compared with its solubility in zirconium. As a result, all the nitrogen should be in solid solution (Adamson & Rudling 2004).



FIGURE 2.12: Binary phase diagram of Zr-Cr system, adapted from Lustman (1979).



FIGURE 2.13: Binary phase diagram of Zr-Ni system, adapted from Lustman (1979).



FIGURE 2.14: Partial diagram of the Zr-N system, adapted from Lustman (1979).

2.5 Corrosion of Zirconium Alloys

Corrosion is defined as the spontaneous degradation of a reactive material by an aggressive environment, it occurs by the simultaneous occurrence of at least one anodic (e.g., metal oxidation) and one cathodic (e.g., reduction of dissolved oxygen) reaction.

Zirconium and its alloys are highly reactive metals and in oxygen containing atmospheres, there is always a thin oxide film on their surface (Cox 1976). Hence, "air-formed" oxide is the most appropriate description for this type of oxide.

In order to assess the performance of zirconium alloys under high temperature primary coolant conditions, a knowledge of the corrosive environment (Section 2.2), corrosion system and the properties of the oxide film are essential. The corrosion of zirconium was thought to be a diffusion process in which oxygen ions are transferred to the metal/oxide interface through the developing oxide. Marker experiments had confirmed the diffusion of oxygen ions and more importantly the oxide growth direction which is inward growth (Revie & Uhlig 2008).

The in-core corrosion process is reviewed with the aim of determine the properties and characteristics of the oxide film formed on zirconium cladding. A brief summary is given here based on the more detailed literatures and reviews having been published elsewhere (Adamson et al. 2007, Cox 1976).

Electrochemical studies have showed that oxide growth is driven by the large electric field present across the developing oxide layer. As the oxide thickens, the electronic resistivity of the film has a limiting effect on oxide growth, due to its resistance to the electron transport process which was required to support water reduction at the oxide/environment interface (Cox & Pemsler 1968). Subsequent film growth is also governed by the coupled currents of anions/anion vacancies (i.e., O^{2-} and V_O^{\cdot}).

TEM study suggested the microstructure of zirconium oxide consisted of layers of columnar grains with periodically occurrence of equiaxed grains (Yilmazbayhan et al. 2006). However, no barrier layer was found that has distinct differences from the stoichiometric oxides.

For zirconium alloys, the oxidation process is further complicated by the possible formation of various intermediate non-stoichiometric oxides and the possible dissolution of oxygen into the metal substrate (Rudling & Wikmark 1999). Mass spectrometry investigations carried out by Hutchinson et al. (2007) had shown, that an oxygen gradient was observed in the immediate metal region below oxide/metal interface, indicating oxygen diffused into the metal to form a suboxide layer. Within this layer, the oxygen concentration reaches the solubility limit of ~29% of oxygen in α -Zr, which might resulted in precipitation of small ZrO₂ crystallites. A mechanism based upon the similarity between the oxidation of zirconium in oxygen and water has been proposed by Chirigos and Thomass (1952) cited by Lustman (1979). From an electrochemical point of view, the oxidation process was considered as an electrochemical cell reaction, that the anodic and cathodic reactions associated with the corrosion process are shown in Equation 2.5 and 2.6, respectively. Water molecules were reduced into hydrogen and oxygen ions at the oxide/solution interface. The rate of this reaction would be controlled by the electron transport rate through the oxide.

The anodic reaction at the oxide/metal interface produces oxygen vacancies and electrons which are both essential for the cathodic reaction (i.e., water reduction) at the oxide/solution interface. The oxygen vacancies formed at metal/oxide interface will diffuse towards the oxide/solution interface to facilitate the water reduction reaction, which have been shown to diffuse preferentially via the oxide-crystallite boundaries (Cox & Pemsler 1968, Adamson et al. 2007).

The anodic half-cell reaction at the oxide/metal interface is:

$$Zr + 2O'' \to ZrO_2 + 2V_O'' + 4e' \tag{2.5}$$

The cathodic half-cell reaction at the oxide/environment interface is:

$$V_O^{-} + H_2 O + 2e' \to O^{2-} + 2H^{-}$$
 (2.6)

The charge transfer will take place via a few possible paths (e.g., electron transfer through metallic SPPs or single-electron tunnelling through the oxide). The hydrogen atoms released at the oxide/solution interface can recombine to form hydrogen molecules (which will dissolve in water) or they can diffuse inwards to the oxide/metal interface if there was an available path through the oxide film (Ramasubramanian 1996).

2.5.1 Oxidation Kinetics

The oxidation kinetics can be divided into two events. Ghosal et al. (2001) and his research team have shown that there are two types of oxidation kinetics involved with zirconium and its alloys - one associated with the cyclic oxidation and the other with accelerated/breakaway behaviour (Figure 2.15). It has been reported that cyclic oxidation followed a cubic/parabolic rate law, while a linear rate has been observed for the accelerated/breakaway period (Cox 1976).



Exposure Time [d]

FIGURE 2.15: Schematic illustration of transition of oxidation kinetics.

Furthermore, the cyclic oxidation period can then be subdivided into three stages: initial growth stage and linear growth stage followed by a transition stage. Lyapin et al. (2005) found that the initial stage is governed by a rapid growth of nonstoichiometric oxide with large number of defects (i.e., oxygen vacancies) at the metal/oxide interface. The zirconium oxide formed during the initial stage is dense, composed mainly of monoclinic and tetragonal ZrO_x crystallites (Simic 2000). It has also been demonstrated many times by the measurement of the electrical potential that develops across the oxide film during oxidation. Bradhurst et al. (1965) have shown that the oxide/metal interface develops a negative potential immediately after oxidation starts. This large accelerating potential promotes rapid electron transport, which results in fast corrosion rate. As the oxide thickens, the potential drop across the developing oxide is reduced by the increasing oxide thickness. Thus, the electron transport became less sufficient.

Continued growth of the oxide film during the second linear growth stage can be approximately described by the stoichiometric ZrO_2 on top of the non-stoichiometric oxide (see Figure 2.15). Early study of oxygen transport rate within the zirconium oxide indicated that oxygen transport rate is correlated with oxidation kinetics, and the results suggested that oxygen/oxygen vacancy transport occurs primarily along crystallite boundaries (Cox & Pemsler 1968).

Despite the fact that the diffusion process is slow and rate limited by the electron transport through a very electrically resistive oxide, it still continues until a certain oxide thickness is attained, at which time, a different corrosion mechanism was observed, and this event is referred as "transition" by many researchers (Schefold et al. 2003, Adamson et al. 2007, Cox & Pemsler 1968). The transition oxidation mechanism is not well established, however, many hypotheses have been proposed (Schefold et al. 2003, Adamson et al. 2007), and cracks/porosities formation under the influence of stress built up within the oxide was proposed as the general cause of the kinetic transition.

Some researchers (Adamson et al. 2007, Barberis & Frichet 1999, Cox et al. 1996) also refer to the region before and after the kinetic transition as the pre-transition region (equivalent to initial growth stage) and the post-transition region (equivalent to linear growth stage), respectively. After the transition, the post-transition oxidation kinetics would repeat the initial and linear growth stage kinetics as described previously. This cyclic growth behaviour was thought to be the result from the cracks/porosities formation during the kinetics transition. Such cracks would give access to the oxidising species which would shorten the path for oxygen vacancy and electron transport and thereby increase the corrosion rate. The resulting oxide would have an outer porous part composed of m-ZrO₂ crystallites, and an inner dense and insulating oxide as indicated by Oskarsson et al. (2001) and Pecheur et al. (1994).

After a number of kinetic transitions, the kinetics would enter into a linear region, with almost linear oxidation rate. This linear corrosion kinetics has also been referred as breakaway kinetics which would lead a catastrophic failure of the oxide.

Oxidation kinetics are determined by measuring the weight-gain of the samples as a function of exposure time, and each point of the kinetic curve represents the average weight-gain of all the samples as illustrated in Figure 2.15. Segall et al. (1988) indicated that zirconium oxide has a very low dissolution rate in high temperature water environment. Since all the oxygen ions produced from the cathodic reaction would go into the oxide, there is a direct link between oxide thickness and the measurable weight gain of the specimen. Hence, the oxide thickness can be evaluated in terms of weight gain data according to the relationship stated by Ghosal et al. (2001), in Equation 2.7.

$$14.7mg \cdot dm^{-2} \approx 1\mu m \tag{2.7}$$

2.5.2 Oxide Microstructure Evolution

A fully detailed mechanistic understanding of the corrosion process and oxide formation process is needed in order to understand the kinetic transition behaviour of zirconium alloys, and it can be explored from several angles. Microstructural development of a growing oxide is a very good starting point.



FIGURE 2.16: Proposed schematic description of the advancement of the oxide layer during oxidation. Modified from Motta et al. (2004).

A schematic for the oxide growth during oxidation is shown in Figure 2.16 proposed by Motta et al. (2004). The growth of the oxide layer and evolution of microstructures can be described in the following steps:

- (a) The initial "air-formed" oxide present on all Zr alloy surfaces consists of layers of roughly equiaxed nano-crystals of ZrO_2 , with many different orientations relative to the orientation of the metal grain on which they form. These crystallites are ~ 2nm in diameter and are either cubic or tetragonal zirconia (Ploc 1980).
- (b) At elevated temperatures some of these crystal orientations grow preferentially to develop into arrays of columnar crystallites. Rapid growth appears on those grains that are perpendicular to the plane of the interface. The preferential crystallite orientations are those that will minimise stress due to the volume change on going from Zr metal to ZrO_2 (the Pilling-Bedworth ratio of ~ 1.56).
- (c) However, the growth of these columnar grains does not continue indefinitely. Some of the columnar grains would cease growth due to the large amount of defects generated at the oxidation front during initial rapid growth (Lyapin et al. 2005). Intergranular cracks (bold black lines) could be formed where crystallite defects concentration is high. Under the influence of large growth stresses accumulated in the oxide, a network of cracks is created allowing a free path to be close to the metal/oxide interface. Alloys with the best corrosion resistance (e.g. Zr-2.5% Nb) show the greatest continuity in the growth of columnar grains in water environments, whereas poorer alloys show imperfect development of columnar grains, or repeated growth and breakdown of the columnar grain structure (e.g. Zircaloy-4).
- (d) The breakdown of the columnar crystallite type oxide may be generating pores or cracks in the oxide both in the normal and lateral directions, leading to an

increase in the oxidation rate in high temperature water. Some alloys appear to make repeated attempts to re-grow a columnar crystallite type oxide, and this can result in a cyclic development of the oxidation kinetics (Bryner 1979).

(e) As the stress accumulates in the oxide, the intergranular cracks may form again in the newly grown columnar oxide layer, causing further rapid growth of the equiaxed grains then subsequence columnar grains. A network of cracks/porosities from the oxide/water interface into the body of the oxide is required to shorten the diffusion path for oxidising species to be delivered at the oxide/metal interface.

As a result, the ability of an alloy to maintain the growth of completely columnar grain structure is important for better corrosion performance. Unfortunately, in PWR environment, the presence of Li ions has a detrimental effect on the continuous growth of the columnar grains. In fact, as Cox et al. (1996) had described, all oxides grown in high concentration LiOH solutions are completely equiaxed microcrystaline oxides. The failure to produce columnar oxide crystallites seems to derive from two factors. Firstly, the oxide grain boundaries could be attacked by LiOH, and causes the oxide to break down, which allows a large increase in post-transition corrosion rates. Secondly, the accumulation of alloying elements (e.g., Nb in Zr-2.5%Nb alloy) and impurities at the ends of columnar oxide crystallites disrupts the growth of columnar grains, instead of forming ZrO_2 , NbO₂ is formed. When further oxidised, the volume expansion from NbO₂ to Nb₂O₅ is much larger than that involved in the tetragonal to monoclinic transformation of ZrO_2 . The volume expansion of NbO₂ to Nb₂O₅ can introduce a tensile stress field to the surrounding ZrO_2 matrix which could lead to cracking of the oxide (Adamson et al. 2007).

	Cubic	Tetragonal	Monoclinic
Temperature range, °C	2370-2680	1170-2370	up to 1170
Density, g/cm^3	5.640	5.860	5.830
Cell Parameters, nm	a=b=c=0.5113	a=b=0.5082	a = 0.5147
		c = 0.5185	b = 0.5206
			c = 0.5313
	$\alpha = \beta = \gamma = 90^{\circ}$	$\alpha = \beta = \gamma = 90^{\circ}$	$\alpha = \gamma = 90^{\circ}$
			$\beta = 99.23^{\circ}$

TABLE 2.7: Phase and lattice parameters of zirconium dioxide, adapted from Wang et al. (1999), and Buschow et al. (2001).

2.6 Properties of zirconium oxide

Zirconium dioxide, also known as zirconia, is an extremely refractory material. It is the only oxide of zirconium that is stable chemically at temperatures below 2000K (Benedict & Pigford 1981). During corrosion, the metal/oxide interface would be in compression since the oxide and metal has a high P-B ratio (~ 1.56).

2.6.1 Various Oxide Phases

Zirconium oxide exhibits three temperature-dependent polymorphs, namely monoclinic, tetragonal and cubic. The transition temperature is shown in Table 2.7 (Benedict & Pigford 1981, French et al. 1994, Koski et al. 1999). Although the operating temperature of PWRs is significantly lower than the transition temperature for tetragonal-ZrO₂ to occur. However, the tetragonal phase can be stabilised by the large compressive stress built up due to the large P-B ratio (Benedict & Pigford 1981). During cooling, the transition of the tetragonal phase to the monoclinic structure exhibits a volume expansion (i.e., a +4% volume strain) which leads to a further increase of compression stress in the surrounding matrix (Reidy & Simkovich 1993, French et al. 1994). As oxidation progresses, the inward diffusion of oxygen would create an oxygen concentration gradient in the metal substrate. When moving from the metal towards the metal/oxide interface, the phases changes from metallic Zr to Zr-O solid solution, to a mixture of Zr-O and monoclinic m-ZrO₂ and finally to the pure m-ZrO₂ phase (Benedict & Pigford 1981).

As the oxide thickens, the compressive stresses built up within the oxide cannot increase without limits. For an oxide layer with the thickness in the range of 2 \sim 3 μ m, a relaxation process may occur. Once the stress level has dropped below the required stress for stabilising tetragonal phase at reactor temperature, tetragonal to monoclinic transformation would occur. In an ionic bonding material, such as zirconia, this process could induce internal cracking due to the volume expansion of phase transformation.

After this transition, the oxide consists of an internal layer, rich in the tetragonal phase and considered to be dense and protective, which was covered by an outer porous layer that consists mostly of monoclinic zirconium oxide (Benedict & Pigford 1981).

2.6.2 Ionic and Electronic Conductivity

In pure zirconia, the common defects are oxygen interstitial defects and oxygen vacancies, produced by the 2.8 (Reidy & Simkovich 1993):

$$ZrO_2 = Zr_{Zr}^{\times} + 2V_O^{``} + 2O_i^{''} \tag{2.8}$$

$$ZrO_2 + \frac{1}{2}Cr_2O_3 = Zr_{Zr}^{\times} + Cr_{Zr}' + \frac{1}{2}V_O^{\cdots} + \frac{7}{2}O_O^{\times}$$
(2.9)

In zirconium alloys, reacting alloying elements that have a lower valence (i.e., Fe^{2+} , Fe^{3+} , Cr^{3+}) would induce the formation of oxygen vacancies (see Equation 2.9).

The ionic conduction through the oxide layer would take place through two types of point defect (i.e., interstitials and oxygen vacancies), since the alloying element doping effect would promote vacancy formation, the ionic conduction through doped zirconium oxide via oxygen vacancy would be the dominating mechanism.

Considering zirconium oxide is doped by lower valence element, a Zr^{4+} site would be occupied by a lower valence cation which would produce a net negative charge. At low oxygen activities ($P_{O_2} < 10^{-23}$ atm), n-type electric conductivity has been observed due to the excess electrons produced by Equation 2.10 (Reidy & Simkovich 1993).

$$O_O^{\times} = \frac{1}{2}O_2(g) + V_O^{\cdot} + 2e^-$$
(2.10)

At high oxygen activities, oxygen is incorporated into the vacant oxygen sites and creates electron holes.

$$\frac{1}{2}O_2(g) + V_O^{``} = O_O^{\times} + 2h^{`} \tag{2.11}$$

However, the higher oxygen activity is generally not observed in the PWRs. Thus, the major charge carriers within the oxide is oxygen vacancies and electrons.

2.7 High Temperature EIS Studies

The study of the corrosion behaviour of zirconium cladding tubes under PWR conditions is normally analysing the oxide layer after autoclave corrosion test. However, the results obtained from these ex-situ examinations cannot fully describe the corrosion behaviour of the system during the oxidation process. Due to the limitation on available techniques in studying in-reactor corrosion processes, many literature have been characterising out-of-pile oxide since the 1990s (Pecheur et al. 1994).

Many scientists have demonstrated the effectiveness of impedance spectroscopy technique in the field of coatings, passive films and corrosion processes on pre-oxidised specimens at relatively low temperatures (Oskarsson et al. 2001, Ai et al. 2007, Ai et al. 2007, Ai et al. 2008). High temperature corrosion tests are often considered as a very costly and difficult experiment. However, these obstacles can be overcome by utilising a static autoclave in order to mimic the PWR primary coolant conditions. The combination of EIS with an autoclave is ideal setup for studying the corrosion behaviour of zirconium alloys in aqueous environment.

Satoh et al. had used in-situ EIS technique to study the oxide film formed on stainless steel in BWR water environment using a Ag/AlCl reference electrode. A double layer model was proposed for the oxide film formed in such conditions.

Oskarsson et al. had also conducted an experiment on Zircaloy-2 and Zircaloy-4 samples using an autoclave in water and in lithiated water (70 ppm) in order to evaluate the influence of both the alloy compositions and the effect of lithium on the oxidation kinetics at two different temperatures, 288°C and 360°C. The impedance measurements at room temperature show that the oxides formed in above conditions in the pre-transition regime have a layered structure and for samples oxidised in LiOH solution the inner protective layer is thin compare with the sample that was oxidised in pure water.

J. C. Ai (Ai et al. 2007, Ai et al. 2007, Ai et al. 2008) and D. D. Macdonald had conducted a study on the passive zirconium oxide film using Point Defect Model (PDM) and EIS at 250°C (under BWRs water conditions), a two time-constants equivalent circuit was used to describe the different oxide layers (Ai et al. 2007). Although a two-layer structure was proposed, the interpretation of the model was contrary to Oskarsson et al. (2001)'s on the origin where diffusional impedance response was observed. Ai et al. has used the Warburg element to model the transport of defect within the inner oxide layer, whereas Oskarsson et al. has stated that the diffusional impedance response was from the outer porous layer. Despite the fact that numerous experiments had been performed at room temperature and relatively high temperatures (e.g. 250 - 280°C), there is very little information about aqueous corrosion behaviour of zirconium alloys in PWR conditions.

Chapter 3

Electrochemical Impedance Spectroscopy (EIS)

3.1 History of impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a powerful and well established technique for investigating electrochemical reactions, measuring the properties of porous electrodes, oxides and coatings. This section briefly reviews the history of EIS and some related aspects of the technique.

The fundamental work of EIS was carried out by Heaviside around the 19^{th} century. His application of Laplace transformation to the transient response of electrical circuits created the foundation for impedance spectroscopy, which enables the conversion of the current flow in a RCL circuit into simple algebraic equations using Laplace-transforms (Macdonald 2006).

Later, impedance spectroscopy was introduced to physical systems by W. Nernst in 1894 in measuring the dielectric properties of aqueous electrolytes. E. Warburg also developed expressions for the impedance response of the diffusion processes and introduced the electrical circuit analogue for electrolytic systems in which the capacitance and resistance were found to be dependent with frequency (Orazem & Tribollet 2008).

In the 1940s, Grahame (1947) and Frumkin (1940) made an contribution to the understanding of the double-layer structure on themercury electrode, while Dolin & Ershler (1940) and Randles (1947) developed and applied equivalent circuits in EIS measurement. Further development of equivalent electrical circuit by Macdonald & Schoonman (1977) and Boukamp (1986) laid down the foundation for nonlinear complex regression techniques which were later widely applied in practise to analyse impedance data. The equivalent electrical circuit approach became the predominant method for analysing impedance data.

In the early 1950s, R. de Levie developed transmission line models for the impedance response of porous electrodes (de Levie 1967). His work became the theoretical bases for porous electrode investigation and modelling.

Validation of the impedance data was ensured by the application of Kramers-Kronig transformation which employed to determine the validity of the measured data in order to identify the non-stationary behaviour of the system under investigation (Macdonald & Urquidi-Macdonald 1985). By the 1980s, researches on electrodeposition and corrosion began to show increasing interest in EIS and it has been used in corrosion studies ever since.

3.2 Background

EIS technique can be applied to many research areas (e.g., paint/coating industry, corrosion protection, etc). Although the applications may be different, the technique remains fundamentally unchanged. In corrosion studies, when an a.c. potential signal (i.e., a small voltage signal $5\sim10$ mV) is applied to an electrode (usually the

metal or a metal substrate with coating), and the response current signal is recorded. The measuring equipment measures the voltage-current relationship corresponding to each frequency, in order to obtain the impedance spectrum.

In d.c. systems, resistance can be defined by Ohms law R = V/I, where R is resistance in ohms (Ω) , V is voltage applied across the resistor, in volts (unit: V), and I is the resulting current flow through the resistor in amperes (unit: A). However, in a.c., many systems exhibit a more complex behaviour and a specific term was given, impedance, Z. By definition, Z is a measure of a circuits tendency to resist (or impede) the flow of an alternating electrical current. The equivalent mathematical form is expressed as:

$$Z = \frac{V_{ac}}{I_{ac}} \tag{3.1}$$

where V_{ac} is a.c. potential applied across the system under investigation, I_{ac} is the response a.c. current output, and Z is the system impedance.

Since V_{ac} and I_{ac} are both frequency dependent variables, Z can also be written as a function of the frequencies. Equation 3.1 also assumed that the system under investigation is linear (i.e., the relationship between current and voltage are signal amplitude independent). Unfortunately, electrochemical systems are often non-linear, however, it is often assumed that they can be treated as linear system, providing the amplitude of any fluctuation is small (i.e., perturbation signals with very small amplitude should give reasonable linear behaviour) (Cottis & Turgoose 1999).

3.2.1 Electrical Circuit Elements

Electrochemists utilises electrical circuit elements (i.e., passive circuit elements) to describe the response of an electrochemical system. Passive circuit elements are components that do not generate current or potential in an electrical circuit.



FIGURE 3.1: Passive elements inductor, resistor and capacitor that serves as components in an electrical circuit.

Electrical circuit models can then be constructed from the passive elements shown in Figure 3.1. The fundamental relationship between current I and potential V for the these elements can be summarised as the following.

For a resistor R,

$$V(t) = RI(t) \tag{3.2}$$

When a sine wave is applied across a resistor, the instantaneous current response to the changing voltage across it indicates that the resulting current signal is exactly in phase with the voltage signal.

For an inductor L,

$$V(t) = L \frac{dI(t)}{dt}$$
(3.3)

The inductor L behaves like a conducting wire, and it is equivalent to a short circuit under steady-state condition (i.e., dI(t)/dt = 0).

For a capacitor C

$$I(t) = C \frac{dV(t)}{dt}$$
(3.4)

Under steady-state condition the capacitor C behaves like an open circuit, allowing no current passing through. However, under the alternating potential, the capacitor is constantly switching between a charging and discharging process, and the current reaches a maximum when the voltage is changing the quickest, as it crosses through zero. When a sine wave potential signal is applied across the capacitor, the resulting current response would be in the form of a cosine, which is 90° out-of-phase. In EIS, a sinusoidal perturbation potential signal is normally applied to the system under investigation, which has the general form shown in Equation 3.5 (Orazem & Tribollet 2008).

$$V(t) = |\Delta V| \cos(\omega t) \tag{3.5}$$

The current response is given by:

$$I(t) = |\Delta I| \cos(\omega t + \varphi) \tag{3.6}$$

where ω is the angular frequency¹ and φ is the phase angle shift of the current signal with respect to the potential signal. According to the relationship of phasor transformation: $\cos(\omega t + \varphi) = \operatorname{Re} \{ exp[j(\omega t + \varphi)] \} = \operatorname{Re} \{ exp(j\varphi) \cdot exp(j\omega\varphi) \},$ where Re is the real part of the exponential function. Equation 3.6 can then be rewritten as

$$I(t) = Re\{|\Delta I|exp(j\varphi) \cdot exp(j\omega\varphi)\}$$
(3.7)

where $\Delta I = |\Delta I| exp(j\varphi)$, Equation 3.7 can be written as:

$$I(t) = Re\{\Delta I \cdot exp(j\omega t)\}$$
(3.8)

and due to the fact that

$$\frac{d}{dt}Re\{f(t)\} = Re\left\{\frac{df(t)}{dt}\right\}$$
(3.9)

If we substitute f(t) with Equation 3.8, the derivative of I(t) with respect of time (t) can be expressed as:

$$\frac{dI(t)}{dt} = Re\left\{\frac{\Delta I \cdot exp(j\omega t)}{dt}\right\}$$
(3.10)

$$\frac{dI(t)}{dt} = Re\left\{j\omega\Delta I \cdot exp(j\omega t)\right\}$$
(3.11)

¹Angular frequency, where $\omega = 2\pi f$, unit is s^{-1}

In the same way, the derivative of V(t) with respect of time (t) can be found as:

$$\frac{dV(t)}{dt} = Re\left\{j\omega\Delta V \cdot exp(j\omega t)\right\}$$
(3.12)

Since the derivatives of the sinusoidal signals are already established, the response of individual passive circuit element shown in Figure 3.1 can be derived.

The expression for a resistor, according to Equation 3.2 can be expressed as:

$$\Delta V = R \cdot \Delta I \tag{3.13}$$

Notice that the potential and current are in-phase with each other.

For the capacitor response given in Equation 3.4, the equation can be rewritten using Equation 3.12 and 3.8,

$$Re\{\Delta I \cdot exp(j\omega t)\} = C \cdot Re\{j\omega\Delta V \cdot exp(j\omega t)\}$$
(3.14)

As $j = exp(j\pi/2)$, Equation 3.14 can then be expressed as:

$$Re\{\Delta I \cdot exp(j\omega t)\} = C \cdot Re\{\omega \Delta V \cdot exp[j(\omega t + \pi/2)]\}$$
(3.15)

The current response is $\pi/2$ out of phase with the potential difference, and the frequency domain current response to a sinusoidal potential signal for a capacitor can be expressed as:

$$\Delta I = jC\omega\Delta V \tag{3.16}$$

As for the inductor response in Equation 3.3, the response can be rewritten as:

$$Re\{\Delta V \cdot exp(j\omega t)\} = L \cdot Re\{j\omega\Delta I \cdot exp(j\omega t)\}$$
(3.17)

or

$$Re\{\Delta V \cdot exp(j\omega t)\} = L \cdot Re\{\omega \Delta I \cdot exp[j(\omega t + \pi/2)]\}$$
(3.18)

Equation 3.18 confirms that the potential difference is $\pi/2$ out of phase with the current response. The response of an inductor to a sinusoidal signal can be expressed as:

$$\Delta V = j\omega L\Delta I \tag{3.19}$$

The $\Delta V - \Delta I$ relationship with respect to each circuit element can be used to develop their impedance response. The impedance response of circuit element can be defined as:

$$Z = \frac{\Delta V}{\Delta I} \tag{3.20}$$

According to Equation 3.13, 3.16 and 3.19, passive circuit elements can be expressed as:

for a resistor R,

$$Z_{resistor} = R \tag{3.21}$$

for a capacitor C,

$$Z_{capacitor} = \frac{1}{j\omega C} \tag{3.22}$$

and for an inductor L,

$$Z_{inductor} = j\omega L \tag{3.23}$$

The mathematical expressions developed above for impedance response of resistors, inductors and capacitors can be used to construct equivalent circuit which describes the impedance response of a system under investigation.



FIGURE 3.2: Electrical circuit consisting of (a) a solution resistance R_e in series with a double layer capacitor C_{dl} and (b) a charge transfer resistance R_{ct} in parallel with a double layer capacitor C_{dl} . Modified from Orazem & Tribollet (2008).

3.2.2 Series and Parallel Circuit Configurations

There are many ways circuit elements can be connected in an electrical circuit. The two simplest configuration are series and parallel, which can be considered as the fundamental configurations of all circuitry. These two configurations can also be applied to the impedance response of the electrochemical system. For series configuration, impedance contributions from each element are additive, whereas for the parallel configuration, the inverse values of the impedance, or the admittances² (Y = 1/Z), are additive. As shown in Figure 3.2(a) for a blocking electrode, two passive elements are in series configuration, the same current flows through R_e and into C_{dl} , and the overall potential difference is the sum of the potential difference for each individual element. Thus, the impedance for circuit element connected in series configuration shown in Figure 3.2(a) can be expressed as,

$$Z = Z_{R_e} + Z_{C_{dl}} = R_e + \frac{1}{j\omega C_{dl}}$$
(3.24)

where R_e is the electrolyte resistance and C_{dl} is the double-layer capacitance.

²In electrical engineering, the admittance (Y) measures how easily a circuit or device will allow a current to flow (Ushida et al. 2003)

For an electrochemical interface, the representative circuit is illustrated in Figure 3.2(b) and the impedance for the parallel configuration can be written as,

$$Z = \left[\frac{1}{Z_{R_{ct}}} + \frac{1}{Z_{C_{dl}}}\right]^{-1} = \left[\frac{1}{R_{ct}} + \frac{1}{\frac{1}{j\omega C_{dl}}}\right]^{-1} = \frac{R_{ct}}{1 + j\omega R_{ct} C_{dl}}$$
(3.25)

where R_{ct} is the charge transfer resistance.

Figure 3.2(b) can be further complicated by adding a resistive term (R_e) that represents the electrolyte resistance in series. The resulting circuit can then be used to model the simplest electrochemical system, as knows as the reactive circuit (Figure 3.3).



FIGURE 3.3: Electrical circuit consisting of a solution resistance R_e in series with a charge transfer resistance R_{ct} in parallel with a double layer capacitor C_{dl} .

The impedance of the circuit shown in Figure 3.3 can be expressed as,

$$Z = Z_{R_e} + \left[\frac{1}{Z_{R_{ct}}} + \frac{1}{Z_{C_{dl}}}\right]^{-1} = R_e + \left[\frac{1}{R_{ct}} + \frac{1}{\frac{1}{j\omega C_{dl}}}\right]^{-1} = R_e + \frac{R_{ct}}{1 + j\omega R_{ct} C_{dl}} \quad (3.26)$$

The circuitry can be more complicated for real electrochemical systems, hence, the mathematical equation for such system became even more complex. However, the impedance can still be calculated using the basic rules for series and parallel configurations shown in Equation 3.24 and 3.25.

3.2.3 Fundamental Relationship

The impedance response are often found in the form of complex numbers,

$$Z = Z_r + jZ_j \tag{3.27}$$

where Z_r represents the real part of impedance, and Z_j represents the imaginary part of impedance and j is the imaginary unit $(j = \sqrt{-1})$.



FIGURE 3.4: Phasor diagram showing the magnitude of impedance |Z|, real part of impedance Z_r , imaginary part of impedance Z_j and phase angle ϕ .

A much clearer demonstration of complex impedance can be done using the phasor diagram (Figure 3.4) (Barsoukov & MacDonald 2005), where the magnitude and phase angle is more pronounced. The impedance can be expressed as,

$$Z = |Z| \exp(j\phi) \tag{3.28}$$

where |Z| represents the magnitude of the impedance vector and ϕ represents the phase angle.
|Z| can be expressed as components on real and imaginary axis,

$$|Z(\omega)| = \sqrt{Z_r(\omega)^2 + Z_j(\omega)^2}$$
(3.29)

The phase angle ϕ can be defined as

$$\phi(\omega) = \tan^{-1} \left(\frac{Z_j(\omega)}{Z_r(\omega)} \right)$$
(3.30)

According to Equation 3.29 and 3.30, the Z_r and Z_j values with respect to frequency can also be expressed as,

$$Z_r(\omega) = |Z(\omega)|\cos(\phi(\omega)) \tag{3.31}$$

and

$$Z_j(\omega) = |Z(\omega)|\sin(\phi(\omega)) \tag{3.32}$$

where ω is the angular frequency of the perturbation signal.

Since the basic forms of impedance spectroscopy data are established, the actual data can be represented as function of log frequency (i.e., Bode plots, log|Z| vs. logf or ϕ vs. logf), or real and imaginary components (i.e., Nyquist plots, Z_r vs. $-Z_j$).

The passive elements shown in Figure 3.1 can then be expressed in terms of magnitude and phase angle shown in Table 3.1.

3.2.4 Electrochemical Cell

Unlike the linear response of a pure resistor, the impedance behaviour of the electrochemical cell is considerably different. For a simple electrochemical cell consists of two inert electrodes (e.g., platinum) and an electrolyte (e.g., Na_2SO_4 dissolved

Impedance	Magnitude $ Z $	Phase Angle ϕ
Z = R + 0j	R	$\tan^{-1}(0) = 0$
$Z = 0 - j \frac{1}{\omega C}$	$\frac{1}{\omega C}$	$\tan^{-1}(-\infty) = -\pi/2$
$Z = 0 + j\omega L$	ωL	$\tan^{-1}(\infty) = \pi/2$
	Impedance $Z = R + 0j$ $Z = 0 - j\frac{1}{\omega C}$ $Z = 0 + j\omega L$	ImpedanceMagnitude $ Z $ $Z = R + 0j$ R $Z = 0 - j\frac{1}{\omega C}$ $\frac{1}{\omega C}$ $Z = 0 + j\omega L$ ωL

 TABLE 3.1: Impedance of circuit elements for equivalent circuit modelling.

 Adapted from (Orazem & Tribollet 2008)

in distilled water). The ohmic resistance of the electrolyte R_e , has an influence on the current flow through the cell, but the reactions at the surface of the electrode (i.e., Equation 3.33 and 3.34) requires charge transfer and hence a charge transfer resistance R_{ct} is in series with R_e . The only electrochemical reactions that can take place at the two inert electrodes are decomposition of the water into hydrogen and oxygen. The two reactions can be described as cathodic and anodic reactions. For the cathodic half-cell reaction, hydrogen evolution is occurred,

$$H_2O + e^- \to \frac{1}{2}H_2 + OH^-$$
 (3.33)

which is accompanied by the anodic half-cell reaction, the oxygen evolution reaction.

$$H_2 O \to \frac{1}{2} O_2 + 2H^+ + 2e^-$$
 (3.34)

A critical cell potential is required for these two reactions to take place, and the cell potential must exceeded the critical cell potential before any current can flow in the cell under standard conditions (i.e., at 25° C, ion concentration of 1M and 1 atom of pressure). This critical potential is often associated with electrode materials at standard conditions. For example, the critical cell potential of the water decomposition reactions shown in Equation 3.33 and 3.33 is well established as +1.229V (Oxtoby et al. 2007). Hence, no reactions can occur between the potential range

from -1.229V to +1.229V.

3.2.5 Potential and Capacitance Contribution of the Cell

The cell potential can be expressed as sum of the potential required to drive each individual reaction at the electrodes, and the Ohmic potential drop across the electrolyte. For example, the potential contributions of a simple electrochemical cell consists of one anode and one cathode can be expressed as

$$E_{cell}^0 = E_{anodic}^0 + E_{electrolyte}^0 + E_{cathodic}^0 \tag{3.35}$$

where E^0_{anodic} represents the potential contribution from the anodic reactions and $E^0_{cathodic}$ represents the potential contribution from the cathodic reaction. The term $E^0_{electrolyte}$ represents the potential drop across the electrolyte.

As mentioned earlier, for an electrochemical interface, charge redistribution or dielectric phenomena can lead to arise of capacitance at the interface where charge redistribution takes place at an electrolytic double layer.

For an electrochemical cell at open circuit, since there is no current flow through the cell. Although the cell potential exists, the electrodes can be considered as ideally polarised. Uniform potential within the electrolyte is also assumed if no current passage occurred through the cell. Thus, potential only changes at the electrode-electrolyte interface. In this region, the field strength is very large, due to the thickness of this region (i.e., $2\sim3$ monolayer thick). A redistribution of charge is possible because the electrons that accumulate near the metal surface have made the metal negatively charged. Some ionic species within the electrolyte may have a tendency to accumulate at the electrode-electrolyte interface forming a Stern layer which consists of positively charged ions that are specifically absorbed on the electrode surface

(assume metal electrode is negatively charged). Finally, the electrode-electrolyte interface must comserve electrical neutrality, hence, a diffusion region of charge may be present between the bulk of the electrolyte and the Stern layer (a typical diffuse region thickness is on the order of 10\AA) (Orazem & Tribollet 2008).

The combined structure of Stern layer and diffuse layer is called the double layer, which behaves like a parallel-plate capacitor. Experiment on measuring double-layer capacitance has been conducted by many researchers, however, the most well known was conducted by Grahame (1947), on a mercury electrode in NaCl solution at room temperature, and the double-layer capacitance (C_{dl}) was determined to have values in the range of 14 ~ 50 μ F cm⁻¹ which is strongly influenced by the potential and ionic concentration of the electrolyte.

Furthermore, the capacitance contribution of the electrode can be complicated by the addition of dielectric coating (e.g., paint or oxide). For example, if the metal electrode is covered with an impermeable oxide, capacitance behaviour can arise due to the oxide dielectric properties which can be expressed as,

$$C = \frac{\varepsilon \varepsilon_0 A}{d} \tag{3.36}$$

where d is the oxide thickness, ε is the relative permittivity of the oxide material, and ε_0 is the permittivity of vacuum $\varepsilon_0 = 8.8542 \times 10^{-12}$ F/m. The capacitance of such oxide layers is typically very small, so according to the expression for capacitors connected in series (Equation 3.37), the capacitance of an interface is dominated by the part with the smaller capacitance ($C_{cell} \approx C_{oxide}$).

$$C_{cell} = \left[\frac{1}{C_{oxide}} + \frac{1}{C_{dl}}\right]^{-1}$$
(3.37)

3.3 Electrochemical Instrumentation

The most important aspect of electrochemical instrumentation is the development and utilisation of potentiostats and galvanostats for impedance measurement, and the essential building block of these instruments is the operational amplifier (opamp).

3.3.1 Operational Amplifier



FIGURE 3.5: The circuit symbol of ideal operational amplifier, showing the five principle terminals. V_+ is the non-inverting input, V_- is the inverting input, V_{out} is the output, V_{S+} is the positive power supply and V_{S-} is the negative power supply. Adapted from OmegatronGraphic (2007).

The operational amplifier is a device that can sense the voltage difference between the two input terminals, and the output-voltage difference is the result of boosting the input-voltage difference by a factor of A_{OL} (open-loop gain of the amplifier), and the output-voltage can be expressed as

$$V_{out} = A_{OL}(V_+ - V_-) \tag{3.38}$$

However, the output-voltage V_{out} is limited to the value of the power supply $V_{S\pm}$.

For an ideal amplifier, A_{OL} is infinite. According to Equation 3.38, the ideal op-amps would have an infinitely small input-voltage difference.

$$\frac{V_{out}}{A_{OL}} = V_{+} - V_{-} \approx 0 \tag{3.39}$$

However, for a real op-amps, the open-loop gain A_{OL} is on the order of 10⁴ to 10⁶. The large gain of the op-amp means a very small input-voltage could drive the output-voltage to the supply level (i.e., often $V_{S\pm}$ is between 10 to 15V). Note that if the input-voltage drives the output-voltage to the supply level, the amplifier will become saturated, which will lead to error in determining the input-voltage. The input-voltage range can be on the order of mV to μ V, which is ideal for electrochemical impedance studies where small perturbation is used (Orazem & Tribollet 2008, Doelling 2005).

3.3.2 Potentiostat

By introducing the negative feedback-loops to the op-amps, an operation under "close-loop" condition is created. This close-loop operation gives the operational characteristics which are important for electrochemical instrumentation. The most interesting example is potentiostats, which are essential to electrochemical impedance studies.

For an op-amp, if a voltage is feed into the non-inverting input (V_+) , the output will be an amplified voltage (or current) of same sign; if a voltage is feed into the inverting input (V_-) , the output will be a voltage (or current) with the same magnitude, but of opposite sign. When a negative close-loop condition is applied between the output and input, the voltage difference between the two inputs of the op-amp will diminish. Rising the voltage on the inverting input forces a complementary current on the output, which counteracts the input voltage difference.



FIGURE 3.6: A schematic diagram of a simple potentiostat that is constructed from an operational amplifier. Adapted from Doelling (2005).

By using such properties of an op-amp, one can build a simple potentiostat to control the cell potential. As illustrated in Figure 3.6, the working electrode is connected to the non-inverting input (V_+) , the reference electrode is connected to the inverting input (V_{-}) , and the counter electrode is connected to the output. When the input and output loop are closed (i.e., by immersing the electrodes into an electrolyte), the passing of current between counter electrode and working electrode via electrolyte will polarise working electrode to the extent that the difference between working electrode and reference electrode is zero. Hence, the potential of the working electrode can be kept exactly on the potential of the reference electrode. If a specific potential of working electrode is desired, the potential of the working electrode can be shifted by inserting a voltage in series between reference electrode input and the reference electrode (which can be monitored by a voltmeter). A potential adder is often designed to produce potential signals with required waveform, an illustration of the potential adder design is shown in Figure 3.7. Furthermore, to measure the current flow through the counter electrode, a resistor must be included in the counter electrode wiring, across which a voltage can be measured, proportional to the current flow.



FIGURE 3.7: A schematic diagram of a simple potentiostat that is constructed from an operational amplifier. Adapted from Autolab (2008).

3.3.2.1 Passive I/E Converters

The passive I/E converter (Figure 3.8(a)) is well suited to potentiostats with large output currents (e.g. mA ~ A). The current path for passive I/E converter only traverses passive components such as wires and resistors. The current measurement resistor (R_m) is connected between the working electrode and the potentiostat's power supply ground. As a result, the working electrode voltage depends on the current flow through it and its potential will be at (iR_m) volts.

3.3.2.2 Active I/E Converters

The active I/E converter design (Figure 3.8(b)) has a shunt resistor (R_m) that is free of load, so the voltage drop across it is compensated. As a consequence, very high ohmic resistors can be used in order to measure very small current very precisely. The working electrode is at the same potential as the potentiostat's electric ground (e.g. earth ground). The active I/E converter not only convert the current into voltage, but it is also responsible for maintaining the working electrode at virtual ground.



FIGURE 3.8: A schematic diagram of a potentiostat that is constructed from three op-amps. (a) passive I/E converter (b) active I/E converter. Adapted from R. S. & R. (2011).

3.4 Experimental Methods

In the early days before the use of digital computers, all electrochemical studies were made in either the time domain or the frequency domain by processing and analysis of analog signals. For time domain measurement, input and output signals maybe recorded as a function of time initially, and the impedance as a function of frequency can then be calculated by time-to-frequency conversion (i.e., Laplace or Fourier transformation). For frequency domain measurement, input and output signals maybe directed measured as a function of frequency.

Fourier analysis and phase-sensitive-detection (PSD) are well established methods to transform time domain signals into the frequency domain. They have replaced the Lissajous analysis for direct measurement using an oscilloscope, however, for understanding the fundamentals of impedance measurement, oscilloscopic method is very good for demonstrating how current-potential relationship is measured for a particular frequency.

3.4.1 Oscilloscopic Methods



FIGURE 3.9: Direct measurement of interfacial impedance under a.c. and d.c. potentiostatic control. Adapted from Barsoukov & MacDonald (2005)

For a particular cell setup shown in Figure 3.9, the potential (e) between the WE and RE is recorded, and the current (i) across a series resistance R_m is calculated from the measurement of potential drop across R_m . A recorded waveform is presented in Figure 3.10, where the magnitude of the impedance (|Z|) can be calculated from the ratio of two peak-to-peak voltage signals using the expression,

$$|Z| = \frac{e}{i} = \frac{|e|}{\frac{|e_{R_m}|}{R_m}} = \frac{R_m|e|}{|e_{R_m}|}$$
(3.40)

The phase shift between the input and output signals (ϕ) can be directly observed from the peak shift (i.e., distance b is equivalent to 2π radians, a is relevant phase shift between input and output signals, and it is measured in radians). Since the phase shift ϕ is determined, the real and imaginary components of the impedance can be expressed in terms of ϕ ,

$$Z_r = |Z|\cos(\phi) \tag{3.41}$$

$$Z_j = |Z|\sin(\phi) \tag{3.42}$$

In modern instruments (e.g. Gamry), the graphic illustration of single-beam oscilloscope ('X-Y' recorder) in Figure 3.11, are also used to demonstrate the progress of measuring impedance parameters.



FIGURE 3.10: The direct measurement plot obtained using a twin-beam oscilloscope for the setup shown in Figure 3.9. Adapted from Barsoukov & MacDonald (2005).

The voltage e and current i has the form of as expressed as,

$$e = |e|\sin(\omega t) \tag{3.43}$$

$$i = |i|\sin(\omega t + \phi) \tag{3.44}$$

The data are plotted in a X - Y fashion, X-axis being the potential, and Y-axis being the current. The magnitude of the impedance |Z| can be expressed as the dimensions of the ellipse using Equation 3.45 and 3.46,

$$|Z| = \Delta e / \Delta i \tag{3.45}$$

and the phase shift can be expressed as,

$$\sin(\phi) = \Delta i' / \Delta i = \alpha \beta / (\Delta i \Delta e) \tag{3.46}$$



Potential, e

FIGURE 3.11: Lissajous plot for the potential-current relationship at a particular frequency. Adapted from Barsoukov & MacDonald (2005).

Lissajous analysis is an useful way to learn impedance spectroscopy, and it can give real-time assessment of the quality of impedance measurements.

3.4.2 Phase-Sensitive Detection (Lock-in Amplifier)

The main functionality of a lock-in amplifier is the ability to recover real signals from the actual system response among other signals that were originated from noise. The heart of the lock-in amplifier is the phase-sensitive detector (PSD), or demodulator, when in conjunction with a potentiostat, it can measure the complex impedance. The PSD functions as a multiplexer or a mixer that multiplies the input signal by a reference signal. There are two modes can be selected for operation of PSD, namely the sine-wave responding mode (Walsh mode) and square-wave responding mode (flat mode) (PerkinElmer Instruments 2000).

In the case of square-wave responding (flat) mode, the resulting output signal is a d.c. output proportional to the components of the input signal and phase-locked reference signal and its odd-harmonics, with the gain being inversely proportional to the harmonic number n. However, in most experimental situations, the odd-harmonics can be undesirable and cause errors when at or near the odd-harmonics of the reference frequency.

For a sine-wave responding (Walsh) mode demodulator (e.g., Solartron 1170 and 1250 series), a sine-wave reference signal is used, and the output signal is a d.c. signal response and there are no response to reference harmonics except for the first harmonic. Modern PSD instruments employ more than one reference signal and can avoid the undesired correlation (i.e., odd harmonics).

The instrument used for impedance measurement in this study (i.e., Newtons4th Ltd., PSM1735) is a phase-sensitive device which was set to Walsh mode (Newtons4th 2005). When a sine-wave perturbation signal $P(t) = P^0 sin(\omega t)$ is applied to the system, where P^0 is the amplitude and ω is the frequency. The response signal of the system under investigation with a transfer function of $|Z(\omega)|e^{j\phi(\omega)}$ may be expressed as,

$$S(t) = P^0 |Z(\omega)| \cdot \sin[\omega t + \phi(\omega)] + \sum_m X_m \sin(m\omega t - \phi_m) + N(t)$$
(3.47)

where the second term in Equation 3.47 is the response of harmonics, and N(t) is the response of noise that picked up from the environment (PerkinElmer Instruments 2000). System response S(t) is then multiplied with the reference signals. By applying the discrete Fourier transform analysis, Equation 3.47 yields two components, a in-phase component a and a quadrature component b (Newtons4th 2005). The fundamental expression for a and b are given by,

$$a = \frac{1}{2\pi} \int_0^{2\pi} S(t) \sin(\omega t) \cdot dt \qquad (3.48)$$

$$b = \frac{1}{2\pi} \int_0^{2\pi} S(t) \cos(\omega t) \cdot dt$$
 (3.49)

For a particularly sampled signal, Equation 3.48 and 3.49 can be expressed as,

$$a = P[Z(\omega)|\cos[\phi(\omega)]$$
(3.50)

$$b = P[Z(\omega)|\sin[\phi(\omega)]$$
(3.51)

Since the in-phase and quadrature component of the output signal is determined, the magnitude |Z| and phase shift ϕ can be expressed as,

$$|Z| = \sqrt{a^2 + b^2} \tag{3.52}$$

$$\phi = \tan^{-1}(b/a) \tag{3.53}$$

3.5 Data Representation

Impedance data are presented in different formats to emphasise specific behaviour of the system. The most commonly used representations are Bode and Nyquist plots. These graphic representations have great impact on visualising and interpreting impedance data.

3.5.1 Bode Plot

For Bode plot, magnitude $\log |Z|$ and phase angle ϕ are plotted against log frequency f shown in Figure 3.12. The advantage of using a logarithmic scale for frequency is to reveal the important detail seen at low frequencies. For illustration purposes, the |Z| of the reactive system shown in Figure 3.3 can be expressed as

$$|Z| = \sqrt{\left[R_e + \frac{R_{ct}}{1 + (\omega R_{ct} C_{dl})^2}\right]^2 + \left(\frac{\omega C_{dl} R_{ct}^2}{1 + (\omega R_{ct} C_{dl})^2}\right)^2}$$
(3.54)

At high frequencies, |Z| approaches electrolyte resistance R_e as frequency approaches ∞ . At low frequencies, |Z| approaches $R_e + R_{ct}$ as frequency approaches zero. A transition region with a slope of -1 is shown between the low frequency and high frequency plateau on the log|Z| vs. logf plot.



FIGURE 3.12: Bode representation of the impedance response for a electrical circuit shown in Figure 3.3, $R_e = 100\Omega$, $R_{ct} = 1000\Omega$, $C_{dl} = 10^{-6}$ F.



FIGURE 3.13: Real and imaginary parts of the impedance response for the reactive electrical circuit in Figure 3.3, $R_e = 100\Omega$, $R_{ct} = 1000\Omega$, $C_{dl} = 10^{-6}$ F.

The phase angle ϕ for the reactive system in Figure 3.3 can be expressed as

$$\phi = \tan^{-1} \left(\frac{\omega R_{ct}^2 C_{dl}}{R_{ct} + R_e (1 + (\omega R_{ct} C_{dl})^2)} \right)$$
(3.55)

As it shown in Equation 3.55, the phase shift ϕ at high and low frequencies approach 0° when current and potential are in phase, and it approaches a peak value when the |Z| has steepent slope.

The two impedance parameters represented in the Bode plot have their own unique advantages in analysing impedance data. The phase shift ϕ plots are a very good way to compare equivalent circuit models to experiment data, since ϕ is sensitive to system parameters. The magnitude |Z| plots are not sensitive to system parameters, however, they are good indicators for d.c. resistance $R_e + R_{ct}$ and electrolyte resistance R_e at low and high frequencies, respectively. The real Z_r and imaginary Z_j impedance component can also be represented in a Bode plot (as shown in Figure 3.13). The minimum of imaginary value have a characteristic frequency of $\omega_c = 1/\tau_c$ (where ω is the angular frequency, $\omega = 2\pi f$, τ_c is characteristic time constant related to $R_{ct}C_{dl}$) (Orazem & Tribollet 2008). The dashed line corresponds to the characteristic frequency f_{RC} of the $R_{ct}C_{dl}$ pair, and it can be expressed as,

$$f_{R_{ct}C_{dl}} = 1/(2\pi R_{ct}C_{dl}) \tag{3.56}$$

In the Z_r/Z_j vs. log f plot, estimation of capacitance value C_{dl} can be straightforward, since $C_{dl} = 1/(2\pi f_{R_{ct}C_{dl}}R_{ct})$ according to Equation 3.56. Estimation of R_{ct} can be made from the log|Z| vs. log f plot, and $f_{R_{ct}C_{dl}}$ can directly observed as the frequency where Z_j peak located.

3.5.2 Nyquist Plot



FIGURE 3.14: Complex impedance plane or Nyquist representation of the electrical circuit in Figure 3.3, $R_e = 100\Omega$, $R_{ct} = 1000\Omega$, $C_{dl} = 10^{-6}$ F.

The complex impedance plane or Nyquist representation of the impedance for the electrical circuit shown in Figure 3.3 is presented in Figure 3.14. The data are plotted on x - y coordinates with real impedance values Z_r on the x - axis and imaginary impedance values $-Z_j$ on the y - axis. The Nyquist plot is often presented as a locus of points, where individual data point corresponds to a unique measurement frequency. Note that the Nyquist plots are often plotted on isotropic axes.

Since the frequency information for data points on Nyquist plot are missing, the frequency dependence is sometimes difficult to compare. This disadvantage can be solved by labelling some data points with the characteristic frequencies. The distinctive semicircle shape of the plot give many advantages when analysing the data. R_e and $R_e + R_{ct}$ can be determined from the high frequency intercepts between semicircle and the real-axis. Thus, determination of the resistance values for the circuit is straightforward with a Nyquist plot. The characteristic frequency for the system is shown at the apex where the imaginary impedance Z_j reaches a minimum value. It should be noted that the apex of the Nyquist plot has a real impedance value of $R_{ct}/2 + R_e$.

Nyquist plots are very useful because the shape of the locus of points gives indication of possible mechanisms or governing phenomena. This will be illustrated in the later section of data analysis. If the locus of points trances a perfect semicircle, a single activation energy controlled system would be expected. On the contrary, a complex system (i.e., multiple control mechanisms or governing reactions), it would have multiple time constants, resulting in the Nyquist plot consisting of multiple semicircles, overlapping semicircles or a depressed semicircle.

3.6 Data Validation

It is commonly accepted that EIS data have to be validated as conforming to Kramers-Kronig (KK) relations before being analysed quantitatively. KK transformation is given by the formula in Equation 3.57 and 3.58, which can be used to transform the real impedance Z_r into the imaginary impedance Z_j and vice versa.

$$Z_j(\omega) = \frac{2\omega}{\pi} \int_0^\infty \frac{Z_r(x) - Z_r(\omega)}{x^2 - \omega^2} dx$$
(3.57)

$$Z_r(\omega) = Z_r(\infty) + \frac{2}{\pi} \int_0^\infty \frac{xZ_j(x) - \omega Z_j(\omega)}{x^2 - \omega^2} dx$$
(3.58)

where $\omega = 2\pi f$, f is frequency in hertz (Hz), Z_r and Z_j are real and imaginary components of the impedance expressed as functions of angular frequency ω , and x is the angular frequency variable used for integration in the whole range of frequencies (i.e., 0 to ∞) (Sadkowski et al. 2009).

KK is a useful test for EIS data verification, only the experimental data that passes the KK transforms should be used to describe the response of the system in terms of its linearity, stability and causality constraints. However, KK transformations are purely mathematical calculation results and do not give concerns about the physical properties of the system.

Small discrepancies between the KK transformation results and EIS data are usually observed at low frequencies, this problem is due to the differences between the impedance measurement bandwidth (finite) and K-K transform definition bandwidth (infinite) in frequency. In theory, KK transformation is applied to the whole range of frequencies, however, the experimental data are usually measured within several decades of frequencies due to the limitation of the instrument.

3.7 Data Analysis Methods

Nyquist plots that consist of a single semicircular arc can be directly analysed by the graphical method which was demonstrated in Figure 3.14. R values can be estimated from the two intercepts where semicircular arc meet the real axis and the C value can be calculated from the associated ω value at the apex of the semicircle, $\omega = (RC)^{-1}$. Other methods have also been described for slightly more complex situations (i.e., two or more overlapping arcs, pseudoinductance) by Franceschetti et al. (1979) and Orazem & Tribollet (2008). However, the direct methods are only applicable to restricted situations where single/possibly two semicircular arcs/overlapping arcs are present. Sometimes, it may be useful for estimating the initial values for use in the complex nonlinear least-squares fitting.

3.7.1 Complex Nonlinear Lease-Square (CNLS) Regression

The complex nonlinear least-squares (CNLS) regression technique was developed in the late 1960s (Orazem & Tribollet 2008), unlike other techniques, it utilises all the data simultaneously to fit the parameters in a given equivalent circuit model at all frequencies. However, it should be noted that the CNLS regression relies on good initial estimates for the parameter values. The regression process becomes insensitive if the initial parameter value is far from the correct value. Good estimated values will facilitate regression and improve accuracy, while poor estimated values may lead to instability of the regression function which does not reflect the physical properties of the system. A physical model of the system may be required as a guideline for constructing an equivalent circuit model and proper estimation of the parameters. Hence, an adequate understanding of the system and the physical and chemical properties of the materials are required.

Chapter 4

Experimental Work

Autoclave testing is time consuming and only two specimens can be measured during the experiment due to the limited number of electrical feedthroughs built into the autoclave. Surface preparation plays an important role in corrosion kinetics, so adequate surface finish is required for specimen preparation before corrosion test. Furthermore, microscopic examination requires highly polished areas of metal/oxide interface, which involves a lot of skills and practice. Hence, it is vital that the technique is fully utilised and understood.

4.1 Materials Used

Two materials were used during the course of this study: Zircaloy-4 and ZIRLOTM. Chemical analysis of the batches of material used is shown in Table 4.1.

TABLE 4.1: Chemical composition of materials used (Composition are wt%, all samples are recrystallised annealed). Data courtesy of Westinghouse Electrical Company Ltd and EDF Energy.

Alloy	Supply	Cr	Fe	Nb	Ni	Sn
Zircaloy-4 (sheet)	Rolls-Royce	0.09	0.19	< 0.01	< 0.01	1.37
$ZIRLO^{TM}$ (tube)	Westinghouse	0.01	0.09	$0.87 {\sim} 0.91$	< 0.01	$0.89 \sim 0.92$



FIGURE 4.1: Optical cross-section micrograph of the electrochemically etched recrystallised ZIRLOTM tube sample. Courtesy of Jianfei Wei, University of Manchester.

4.2 Microscopic Characterisation

4.2.1 ZIRLOTM

 $ZIRLO^{TM}$ tubes were supplied by the Westinghouse Electric Company. Tube samples had undergone extensive processing steps and heat treated to fully recrystallised condition at 595°C. The final recrystallisation process created an equiaxed microstructure, which is illustrated in Figure 4.1

4.2.2 Zircaloy-4

Zircaloy-4 sheet material was supplied by Rolls-Royce, which had undergone a similar thermal processing route and heat treated at 620°C for 2 hours. Microstructure of Zircaloy-4 material is shown in Figure 4.2.



FIGURE 4.2: Optical micrograph of electrochemically etched Rolls-Royce Zircaloy-4 plate materials.

4.2.3 SEM Sample Preparation

The large samples were cut to small pieces using a manual cutting wheel with a SiC disc, while the small samples were cut using an automated precision cutting machine. Sufficient cooling fluid was applied to the piece while cutting, because zirconium fines can give sparks or even catch fire if cooling is insufficient.

The sample was then mounted in Bakelite, a hot mounting resin with glass filler as reinforcing material. Subsequent grinding and polishing steps was carried out as described in Table 4.2. Between each stage, the samples were rinsed in water then with methanol and then dried in hot air.

A rough grinding step with P800 silicon carbide coated paper with oil-based lubrication for 5 minutes should remove most of the surface roughness, resulting in a flat surface with scratches on the order of ~ 20μ m. A subsequence grinding step, using a finer P1200 paper with oil-based lubrication for 3 minutes would smooth the previous scratches, and result in a reflective finish. It is important to use oil-based lubricant, because water readily reacts with zirconium metal and leaves a thin scale (i.e., ZrO_2) on the metal surface which gives a dull appearance.

Polishing was carried out on a micro-fibre pad disc with various grades of polishing diamond paste; the same oil-based lubricant was applied to prevent zirconium reacting with water. Thorough cleaning of the polished surface was carried out on finishing each step, in order to prevent contamination of the following polishing pad. Prolonged polishing on diamond paste wheel should be avoided, as longer polishing time may create a tilted surface at the metal/oxide interface due to dissimilar hardness between zirconium metal and its oxide. A final step which involves polishing by colloidal silica (OPS) for 30 minutes, gives a scratch free mirror finish, which is ideal for SEM investigation. Alternatively, an OPS polishing can be performed after the last grinding step, in which case similar results were obtained, however, longer polishing time were required.

Grinding					
Materials	Grit	Lubricant	Time (min)		
Silicon Carbide	P800	oil-based	5		
Silicon Carbide	P1200	oil-based	3		
Polishing					
Materials	Grit	Lubricant	Time (min)		
Diamond paste	$6\mu m$	oil-based	1		
Diamond paste	$1 \mu { m m}$	oil-based	1		
Diamond paste	$0.25 \mu \mathrm{m}$	oil-based	1		
Colloidal Silica (OPS)	$0.05 \mu m$	water-based	30		

TABLE 4.2: Grinding and Polishing Procedures.

4.3 Specimens Preparation Using EDF Autoclave

The oxide layer under investigation were pre-formed on the zirconium alloys at EDF Energy facilities with an electrolyte that has a chemistry similar to PWR primary coolant (i.e., 1000 ppm B as H_3BO_3 and 2 ppm of Li as LiOH in DI water). The zirconium alloys used in this study are Zircaloy-4 and ZIRLOTM, a Zr-Sn alloy and a Zr-Sn-Nb alloy respectively. The Zircaloy-4 samples were plates of size 30x20x5mm, and the ZIRLOTM were tubes of outer diameter 10mm and 30mm in length, with 0.7mm wall thickness.

The preliminary treatment of the samples consists of mechanical polishing, which removed all the roughness caused by cutting, and subsequence chemical etching in a mixture of acids HF (40%), HNO₃ (65%) and DI water in a 1:3:4 ratio (vol.) at a temperature of 60°C for 1 minute. Thereafter, the oxide was formed at the surface of the samples, a thermal oxide, which was produced by the oxidation of zirconium in high temperature high pressure water at 360°C for 80-160 days. Autoclave oxidation was interrupted every 20 days of exposure, for introducing new samples into the autoclave. At the end of each 20-day test, the samples in the autoclave would have different exposure times with a increment of 20 days. During each interruption, the weights of the samples were recorded in order to record a weight gain profile for each sample. From the weight gain data, the kinetics transition can be determined by the sudden change of rate. As a result, at the end of autoclave oxidation, a set of samples with exposure time covering the whole transition period were obtained. Subsequent in-situ EIS measurements on all the samples were carried out. The morphology of the sample surface and cross-section of the oxide were analysed with the application of SEM. A description of the condition of each sample is given in Table 4.3

Form	Sample ID	Conditions	Pre-oxidation Time (days)	EIS Duration
	Z4RXRR1		160	160 - 275
	Z4RXRR5		140	140 - 160
Sheet	Z4RXRR9	RXA	120	120 - 130
	Z4RXRR13		100	100 - 110
	Z4RXRR17		80	80 - 95
	Z4RXRR0		0	0 - 35
	ZLR1		160	160 -275
	ZLR5		140	140 -160
Tube	ZLR9	RXA	120	120 - 130
	ZLR13		100	100 - 110
	ZLR17		80	80 - 95
	ZLR0		0	0 - 35

TABLE 4.3: List of samples used in this study.

4.4 In-situ EIS

4.4.1 Static Autoclave

The high-temperature (360°C), high-pressure (18-19 MPa) environment was generated using a static autoclave (Manufactured by Cormet, Finland). The autoclave was machined from two solid pieces of type 316 stainless steel. The top part has three electrical feed-throughs and a pressure release valve, and the bottom part serves as a container to hold the electrolyte, working and reference electrode. Two additional openings were machined in the bottom part, one for the thermocouple and one for the drain, which connected with a high-pressure regulator that was set at 200 bars for operation safety, in case the autoclave pressure exceeds such high pressure. Three electrical feed-through on the top part of the autoclave were designed to introduce the electrical connection into the autoclave body, and to permit wide frequency band-width impedance measurements to be carried out on the growing oxide film as a function of time. The in-situ measurements were performed using a three-electrode cell, in a solution similar to the EDF autoclave corrosion test. For the counter electrode, a Pt plate was used, which has a total area of 4 cm^2 . The reference electrode was a Pd/H₂ high temperature electrode, mounted in the bottom of the autoclave, which has a relative potential of +10mV compare to normal hydrogen electrode (NHE). The working electrode (i.e., zirconium sample) was connected to a zirconia tubing shielded pure zirconium wire feed through the upper part of the autoclave body.

The water tightness of the electrical feed-throughs is ensured by a PTFE seal element. During normal operation, the electrical feed-through tube which is connected to the autoclave body, can reach the temperature that cause the PTFE seals to degrade. Due to the fact that the PTFE creeps above 200°C, and undergoes serious degradation about 250°C, a special cooling systems had been installed under these electrical feed-throughs, which cools the feed-through tube sufficiently preventing degradation of the sealing materials.

4.4.2 Electrolyte Resistance

Solution resistance is often a significant factor in the impedance spectroscopy measurement. A very dilute solution consists of DI water (i.e., conductivity is about $0.067 \ \mu$ S·cm at 25°C), with 1000ppm *B* as H_3BO_3 and 2 ppm *Li* as *LiOH* for pH stabilisation (pH ≈ 6.4 -6.7 at room temperature), which served as an electrolyte in a static autoclave at high temperature and pressure (i.e. 360°C and 18.5 MPa). Note that very little ionisation of boric acid occurs, however, lithium hydroxide will fully ionise and controls the pH of the solution. At 360°C, the conductivity of such electrolyte is about 200 μ S·cm which was determined from in-situ EIS measurement. The electrical resistance of the electrolyte (ionic solution) normally depends on the ionic concentration of the dissolved ionic species, temperature and the geometry of the area in which a current pass through. For a defined volume of electrolyte with area *A* and length *l* that carries a uniform current, the electrolyte resistance R_e can be described as:

$$R_e = \rho \frac{l}{A} \tag{4.1}$$

where ρ is the solution resistivity. In electrochemistry, the reciprocal of resistivity, conductivity σ is often used. Unfortunately, most electrochemical cells do not have uniform distribution of current through a defined electrolyte area. The main concern here is the uncertainty of current flow path and geometry of the electrolyte that carries the current.

In the frequency range that in-situ EIS measurement was carried out, the electrolyte response is mainly ohmic. This results from its volume relaxation frequency determined by its conductivity σ_e and relative dielectric constant $\varepsilon_{r,e}$

$$f_{vol,e} = (2\pi RC)^{-1} = (2\pi)^{-1} (\sigma/\varepsilon_0 \varepsilon_r)$$

$$(4.2)$$

where impedance is mainly ohmic for frequency lower than $f_{vol,e}$.

The electrical resistance of this solution is high, due to small amount of solute. Electrolyte conductivity at 360°C is about $\sigma_e \approx 200 \ \mu\text{S}\cdot\text{cm}$ (Andresen et al. 2005, Schefold et al. 2003) and dielectric constant of water, $\varepsilon_{r,e} \approx 15$ at 360°C (Venkateswarlu 1996). According to Equation 4.2, the calculated relaxation frequency for the electrolyte is $f_{vol,e} \approx 24$ MHz, a value that is beyond the scope of the frequency range used in the impedance measurement.

In the static autoclave test, before heating up to experimental temperature, the water is in contact with a gas mixture of nitrogen 95 vol.% and hydrogen 5 vol.%. According to Henry's law, the solubility of a gas in a liquid depends on temperature, the partial pressure of the gas over the liquid, the nature of the solvent and the nature of the gas. The partial pressure controls the number of gas molecule collisions with the surface of the solution. If the particle pressure is doubled the number of collisions produce

more dissolved gas. Gas solubility is always limited by the equilibrium between the gas and a saturated solution of the gas.

By controlling the gas pressure in the autoclave for purging the solution, the concentration of dissolved molecular hydrogen can be controlled to a value that is sufficient to suppress the water decomposition process in Equation 4.3

$$2H_2O \rightleftharpoons 2H_2 + O_2 \tag{4.3}$$

For the purpose of deaeration and hydrogenation of the testing solution, ensuring to largely suppress the formation of molecular oxygen and hydrogen peroxide, a concentration of the dissolved hydrogen 2.98 cm³(STP)/kg (0.265 ppm) was used (calculation of the hydrogen concentration is shown in Appendix A).

4.4.3 Electrodes

The static autoclave has four outlets, three were used as electrical feed throughs which were occupied by two working electrodes and a counter electrode, the high temperature reference occupied the bottom outlet.

4.4.3.1 Working electrode

Working electrode consists of zirconium sample resistive spot welded onto the pure zirconium contact wire that is 1mm in diameter (Goodfellow UK). Contact wires made of other metals were test welded to the zirconium sample, only zirconium wire shown good strength of the joint and reproducibility of the welding process. Zirconia insulation tubes were also used to cover the contact wires. Two samples can be monitored at the same time.



FIGURE 4.3: A schematic illustration of the autoclave and electrical feed-throughs.

4.4.3.2 Counter electrode

The counter electrode consists of a solid plate platinum laser welded to a platinum wire. A specially made zirconia tube covers the portion of electrical feed-through wire (i.e., platinum wire) that is exposed to the high temperature water inside the autoclave. The zirconia tube works as an electrical insulation preventing current flow between the autoclave body and wire, thus majority of the current would flow through the platinum plate.

4.4.3.3 Reference electrode

A cathodically polarised palladium reference electrode has been used in the autoclave test, due to its temperature stability. The mechanism of hydrogen evolution reaction has been extensively studied and well understood. In addition, the species (H_2 , H^+) are stable over the temperatures of interest and they do not contaminate the environment where the measurements are carried out, since the autoclave test is conducted in the primary coolant which is hydrogenated.

It contains two metal electrodes, a Pd wire surrounded by a Pt coil. The Pd wire is cathodically polarised with respect to the Pt coil. Usually a constant 10 μ A polarisation current was used to prevent too much H₂ gas building up.

Palladium was chosen because the effect of dissolved oxygen on the palladium potential is limited. The palladium-hydrogen electrode is acting as reversible hydrogen electrode (RHE). Platinum anode produces H⁺ through the reaction shown in Equation 4.4,

$$2H_2O \to 4H^+ + O_{2(q)} + 4e^-$$
 (4.4)

and absorbed at the palladium electrode surface as shown in Equation 4.5 (Munasiri et al. 1992).

$$H_{ad}^+ + e^- \to H_{(ab)} \tag{4.5}$$

4.4.4 Impedance Measuring Device

The in-situ autoclave EIS measurements were performed using a Phase Sensitive Multimeter PSM1735 from Newton4th Ltd. It employes phase sensitive detection (PSD) technique as described in Section 3.4.2, coupled with an active shunt (Section 3.3.2.2) designed specifically for electrochemical impedance measurement. The analysis of impedance spectra was performed with the aid of software ZView[®] by

means of the complex nonlinear least squares (CNLS) method for both the real and the imaginary components of impedance. The quality of the fitting of impedance data in accordance with the equivalent circuits proposed was assessed by KK transformation.

4.4.5 Experimental Considerations

The experimental design parameters described in this section are influenced by the system under investigation, the objective of the investigation, and the capabilities of the instrumentation. The objective is to maximise the information content of the measurement while minimising bias and errors.

4.4.5.1 Frequency Range

The objective of impedance measurements is typically to capture the frequency response of the system under study. The measured frequency range should be sufficient to cover all the featuring responses. However, instrumental limitations often are the limiting factors in measuring impedance response. The range of measured frequencies extended from 100 mHz to 100 kHz with a logarithmic scale of seven points per decade.

4.4.5.2 Open Circuit Potential (OCP)

Open circuit potential is measured and used as d.c. offset for the perturbation signal during impedance measurement. During the in-situ EIS measurement, the OCP value of a pre-exposed sample decreases slightly (e.g., -250 mV to -298 mV vs. SHE) in the first couple of days of exposure and then reached almost a constant potential throughout the course of the experiment (e.g., -298 mV vs SHE). Noticeably, the OCP drop observed on a fresh sample (i.e., just etched with HF containing solution)

is similar compared to the pre-exposed samples, which suggests that the OCP drop is related to the exposure of metal directly to the electrolyte. Once the zirconium metal is covered by a layer of oxide with decent thickness, the OCP would remain at a constant value. As a result, a d.c. offset with a fixed value of -300 mV (vs. SHE) was used for impedance measurement at OCP.

4.4.5.3 Linearity

Linearity in electrochemical systems is controlled by potential perturbation. The use of a small-amplitude perturbation allows the assumption of a linear model for potential-current behaviour of the system under investigation. However, there are some compromises between the linear response (i.e., requires small amplitude perturbation) and the signal-to-noise ratio in the impedance response (i.e., larger the amplitude, the better the signal-to-noise ratio).

The amplitude applied also depends on the individual system under investigation. For systems exhibiting a linear current-voltage curve, a large amplitude can be used, or vice versa.

4.4.5.4 Current Measuring Range

The current signal is converted into a potential signal through a special circuitry (i.e., usually a known value resistor R, and the voltage drop is measured across R) in the potentiostat. Potentiostats may employ a version of a current follower, for example, as described in Section 3.3.1. A mismatch between the current sensing resistor R and cell impedance can result in error of the measurement. Estimating the correct current range may be required for some instruments.

Zirconium oxide has high electrical resistivity, range from $10^8 \sim 10^{11} \Omega \cdot \text{cm}$ at 25°C (Zircoa 2011), and $\sim 10^5 \Omega \cdot \text{cm}$ at 400°C (Lazer et al. 2005). At 360°C, the estimated

electrical resistivity for ZrO_2 would be in the order of $10^6 \sim 10^7 \ \Omega \cdot \text{cm}$, which could lead to the resulting current signal in the order of pA. To avoid errors by mismatching the cell impedance with current sensing resistor, appropriate current sensing range was selected.

4.4.5.5 Integration Time/Cycle

Stochastic errors can be significantly reduced by increasing the time allowed for integration and number of cycles for each frequency. The number of cycles required to achieve a set error level at each frequency depends on the frequency of the measurement. Compromise between integration time/cycle and time required for each measurement needs to be considered, since the time required to complete each cycle at low frequency is significantly longer than for high frequency cycles. A integration cycle of 10 was used for all the impedance measurement carried out on PSM1735.

4.4.5.6 Amplitude of Modulated Signal

As described in Section 4.4.5.3, the polarisation curve for a given system dictates the modulation amplitude that may be used while retaining a linear system response. Many high-impedance systems (e.g., zirconium oxide) are characterised by a relatively large linear range of potential. In the case of zirconium metal covered with ZrO_2 , a modulation amplitude of 30 mV was used.

4.4.5.7 Electric Field Interferences

External devices such as electric motors, pumps, and fluorescent lighting emanate electric fields that can contribute significantly to the apparent noise in a system. This influence, observed mostly in high-impedance systems, can be minimised by use of a Faraday cage. Autoclave in-situ measurement has the advantage of shielding these electric field since the autoclave body is grounded for safety reasons. However, precautions had been taken for the exposed electrical feed-throughs, shielding of the feed-through wires was applied.

4.5 Ex-situ EIS

The specimens were prepared by further oxidising the pre-oxidised specimens for an extended period of time in simulated PWR water at 360°C (individual in-situ EIS experiments were carried out on these specimens).

A good electrical contact was ensured by drilling a 2mm diameter hole into the top of the specimen to a depth of approximately 1 mm, exposing the zirconium metal, followed by spot welding of a zirconium wire to the bare metal. An area of the specimen was then masked off using 45-stopping off lacquer (Canning) and then further covered with beeswax, the area exposed was $\approx 1 \text{ cm}^2$.

Ex-situ EIS measurements were taken using the same instrument as for the in-situ measurement, PSM1735 with LCR active head interface. The software used for data acquisition was the commercial software PSMComm which was supplied with the instrument. Impedance analysis was carried out using ZView supplied by Scribner Associates, Inc.

An a.c. potential signal with amplitude of 5 mV (signal-to-noise ratio is much higher at room temperature, due to the stable system) was swept between 100 kHz ~ 100 mHz at open circuit potential. A standard three-electrode electrochemical cell was constructed using a platinum counter electrode, a saturated calomel reference electrode (+0.24V vs. SHE at 25°C) and the oxidised substrate as the working electrode. A Faraday cage was also used to minimise the effect of other electrical interferences, such as the lightings and computer cooling fans. Fundamentals of impedance measuring technique can be found in Chapter 3. The electrolyte solutions of Na_2SO_4 were made using DI water, a concentration of 0.5M was used. Deaeration of the electrolyte was carried out prior to immerse the specimen using nitrogen. Specimens were immersed in the solution and an initial EIS measurement was taken. This was repeated at hourly intervals until the sample had been immersed for 24 hours in total.
Chapter 5

Results and Discussion

5.1 Weight Gain

The weight gain (WG) data recorded on each of the materials under investigation were carried out at EDF's research facilities in France by a fellow student on the MUZIC program, Jianfei Wei. Static autoclave testing was the primary method to prepare specimens and study their weight gain. It has the same experimental condition as the in-situ autoclave EIS experiment.

The surface area of each specimen was determined with 3D laser scanner to measure the dimensions of the sample at EDF's facility. Initial and final weight was recorded on a analytical balance that has a readability of 0.01mg. Weight gain values were determined by the equation:

$$WG = \frac{m_1 - m_0}{A} \tag{5.1}$$

where m_1 and m_0 are the final and initial weight of the specimen, respectively. A is the area of the specimen.

From the weight gain plot in Figure 5.2, the oxidation kinetic of $ZIRLO^{TM}$, it is not clear whether the data fits a cubic or parabolic kinetic law. Figure 5.2(b) and



FIGURE 5.1: Corrosion weight gain as a function of autoclave exposure time for the ZIRLOTM tube and Zircaloy-4 sheet specimens supplied by Westinghouse. Data courtesy of Jianfei Wei.



FIGURE 5.2: ZIRLOTM tube corrosion weight gain as a function of (a) $t^{1/2}$ parabolic law kinetic and (b) $t^{1/3}$ cubic law kinetic.



FIGURE 5.3: Zircaloy-4 sheet corrosion weight gain as a function of (a) $t^{1/2}$ parabolic law kinetic and (b) $t^{1/3}$ cubic law kinetic.

5.3(b) indicated that pre-transition kinetics has a slope of $\sim 6 \text{ mg} \cdot \text{dm}^{-2} \cdot \text{d}^{-1/3}$ and the trendlines for both plots seem to go through the origin. However, as mentioned in the previous section, zirconium metal is always covered with a thin layer of oxide.

The initial air-formed oxide should be included in m_0 , and its small value can be negligible. Hence, the trendline for pre-transition data points should have an intercept with the Y-axis at the origin. The observation on Figure 5.2(a) and 5.3(a), where the trendlines intercept with the axis indicated that the metal already had oxide layer on the surface (as the weight gain) at zero exposure time. But the oxide layer thickness determined from the weight gain plot at zero exposure ($\sim 8 \text{ mg/dm}^2 \approx 500$ nm) is much thicker than those found in the literature (i.e., $\sim 10 \text{ nm}$). Although the pre-transition weight gain data fits cubic kinetic law better than parabolic law, it is difficult to fit the post-transition data.

5.2 Visual Examination

One of the main concerns of this section is to perceive the differences in appearance of oxide formed in different stage of oxidation. The idea is to relate these differences to the corrosion kinetics and to the stability of the oxide. To that purpose, a systematic characterisation of the oxide appearance was performed by examining the colour of the oxide. These observations are summarised and illustrated by the relevant images. As shown in Figure 5.4, the clearest difference between the general



(a) 140 days

(b) 160 days

FIGURE 5.4: ZIRLOTM tube specimens that were autoclave oxidised at 360°C for (a) 140 days, still in the pre-transition regime and (b) 160 days in the post-transition regime. Image courtesy of Jianfei Wei.

aspect of oxide formed during pre- and post-transition behaviour is their colour. Generally, in Figure 5.4(a), the pre-transition oxide tends to be black, adherent and shiny, while post-transition oxide (Figure 5.4(b)) tends to be grey, matt and patchy. At the earlier stage of transition, the oxide appears to be patchy, which islands of whitish oxide surrounded by black oxide. As the oxidation progresses, these whitish island of oxide spread out over the whole surface of the specimen, eventually the whole sample surface was covered with post-transition oxide. Zircaloy-4 specimens had shown the same patchy surface on the post-transition regime sample as observed on the ZIRLOTM tubes.

It should noted that the sample marking produced by laser engraving appeared to be fully oxidised (fully oxidised zirconia has a white colour due to its stoichiometry). The laser etched area had a much rougher surface compared with the chemically



(a) 140 days

(b) 160 days

FIGURE 5.5: Zircaloy-4 sheet specimens that were autoclave oxidised at 360°C for (a) 140 days, kinetic still in the pre-transition regime and (b) 160 days in the post-transition regime. Image courtesy of Jianfei Wei.

etched sample surface, this indicated that laser etched areas were more susceptible to faster corrosion. The faster oxidation had also been observed on scratched/rough areas, such as shown in Figure 5.5(a), where the top corner near the markings appeared to be white, indicating that local oxidation rate is much higher.

5.3 Microscopic Characterisation

To illustrate the nature of the oxide films formed on zirconium in the pre-transition, transition and post-transition regime, corrosion samples from each of these regimes were examined. The corrosion samples that were examined were removed from 360°C autoclave test and small portions were cut from the sample and coated with Ni alloy to prevent surface oxide spallation during grinding and polishing, it also enhanced edge retention when polishing. The recipe for nickel plating is described in Appendix B. The specimens were then mounted in hard bakelite resin with glass filler using a hot press.

Scanning electron microscopy (SEM) examinations of both the surface of the oxide layer and its cross-section were performed. Prior to SEM examination the oxide surface was sputtered with a layer of gold to enhance the conductivity of the sample surface.

Although large number of images were obtained by SEM on various specimens, only representative ones are shown in this section.

5.3.1 ZIRLOTM

5.3.1.1 Pre-transition oxide

The oxide layer formed during initial oxide growth is shown in Figure 5.6(a). At 25 days, the oxide layer has an uniform thickness $\sim 1.5 \ \mu$ m, with very small undulation at the metal/oxide interface. However, interfacial cracks were found at a few areas where local oxidation had stopped at regions beneath the crack. This indicated that interfacial cracks occur at a very early stage and throughout the entire exposure time, not, as suggested in the literature, only close to the kinetic transition. Surface

	and the second		03		
	Mounting				
	Ni Coating	the second s			
	Zirconium Ox	ide			
	Zirconium Me	etal			
		*			
2 µm		EHT = 15.00 kV WD = 10.0 mm	Signal A = BSD Mag = 8.00 K X	Date :21 Dec 20 Sample ID =	10 ZEISS

(a) Cross section image





FIGURE 5.6: SEM images of ZIRLOTM tube sample oxidised for 25 days at 360°C in primary water condition. (a) cross section image taken in BSE mode (b) oxide surface image taken in SE mode. The average oxide thickness is 1.10 μ m.



FIGURE 5.7: SEM cross sectional view of ZIRLOTM tube sample oxidised for 130 days at 360°C in primary water condition (Electroless nickel plating layer is next to the black resin, where as the oxide is next to the light colour metal). Average oxide thickness is 2.22 μ m. Image taken in BSE mode.

analysis of the 25 days ZIRLOTM tube specimen showed a smooth surface virtually free of surface cracks and no grain boundaries were observed in Figure 5.6(b).

A ZIRLOTM specimen that had exhibited a final weight gain of 30.4 mg/dm^2 after 130 days at 360°C, was under investigation. The specimen was expected to exhibit cubic pre-transition corrosion kinetics since at 360°C the specimen is still in the pre-transition regime as predicted from Figure 5.2(b).

The cross-sectional image as seen with the SEM is shown in Figure 5.7. The bulk of the oxide has an average thickness of approximately 2.22 μ m from SEM analysis. There are instances where, in cross section, large undulations of metal/oxide interface were observed. Interfacial cracks were also seen where, at metal/oxide interface, the oxide film thickness at the cracked region seems to be thinner compared with the



FIGURE 5.8: SEM cross sectional view of ZIRLOTM tube sample oxidised for 140 days at 360°C in primary water condition. The average oxide thickness is 2.60 μ m. Image taken in BSE mode.

dense regions where the oxide appeared to be crack free. These interfacial cracks are not randomly distributed within the oxide layer, these features seem to appear in a band that is 1-2 μ m away from the oxide outer surface (however, the distance between the cracks and the metal/oxide interface varies with exposure time). It should be noted, a very thin layer of oxide was observed at regions beneath the interfacial cracks, this indicated that oxidation process has resumed at those regions.

According to weight gain plot in Figure 5.2 an oxide weight gain of 31.15 mg/dm² (i.e., 2.12 μ m thick oxide) is expected for 140 days exposed sample. However, SEM examination determined that the average oxide thickness is approximately 2.60 μ m, this is probably caused by the uncertainty in estimating average oxide thickness (e.g. interfacial cracks have certain thickness, oxide layer are usually undulated, etc.).

In Figure 5.7, majority of the cracks were located ~ 300nm away from the metal/oxide interface, a newly formed oxide layer was observed. Interestingly, a similar layer was also found on the 140 days specimen (Figure 5.8), with an average thickness of ~ 1 μ m. This newly formed oxide layer had indicated that oxidation was resumed underneath the interfacial cracks, which implies there had to be a transport mechanism for the reactants to be delivered to the cracks.

Another observation is where regions with a large number of cracks seem to be thinner compared with regions with fewer cracks. From an corrosion rate point of view, interfacial crack formation may have influences on the corrosion kinetics, especially in the later pre-transition regime (i.e., from ~ 50 to 100 days, where weight gain is almost linear).

5.3.1.2 Post-transition oxide

In Figure 5.9(a), a cross section SEM image of a specimen with 180 days exposure at 360°C is shown. It had attained an average final oxide thickness of 5.70 μ m measured by SEM.

As shown in Figure 5.9(a), a cross-sectional SEM examination of this specimen found that for the most part of the specimen, it is covered by a thick adherent corrosion film. In contrast to the pre-transition regime film, the oxide has a more uniform thickness, the undulation at the metal/oxide interface is less pronounced. Interfacial cracks observed in the pre-transition regime specimens are further away from the metal/oxide interface. Density of the cracks had increased after the transition, and also there are a lot very fine cracks appeared after the kinetic transition. New cracks were also observed at the metal/oxide interface.

Oxide surface cracks were also observed in the cross-sectional image in Figure 5.9(b), small cracks that were normal to the surface, penetrating 500~800 μ m into the oxide.



(a) 2000x



(b) 4000x

FIGURE 5.9: SEM cross sectional view of ZIRLOTM tube sample oxidised for 180 days at 360°C in primary water condition. The average thickness is 5.70 μ m. Images taken in BSE mode.

Noticeably, the oxide beneath these surface cracks is generally thicker compared with nearby regions that are free of surface cracks.

The oxide surface on ZIRLOTM tube was examined in both SE and BSE mode (in Figure 5.10). Grain boundary topography was observed as well as the surface cracks indicated in Figure 5.10(b). The roughness of oxide surface on the post-transition specimen (Figure 5.10(a)) was very much pronounced than the pre-transition oxide. Surface cracks were observed which confirmed the cross section observation of surface cracks in Figure 5.9(b).

5.3.2 Zircaloy-4

5.3.2.1 Pre-transition oxide

SEM examination of the 25 days Zircaloy-4 specimen has shown interfacial crack formation as early as 25 days, with oxide thickness about $1\sim1.5\mu$ m. Local corrosion has paused at cracked regions, indicated by the relatively thin oxide. Other regions that are free of cracks have uniform oxide thickness and very small undulations. The oxide surface is relatively smooth and flat, no grain boundary topography was observed in Figure 5.11(b). Surface cracks on Zircaloy-4 specimens were observed as early as 93 days exposure (see Figure 5.12), crack length varies from couple of μ m to over 20 μ m with a width about 100 nm. The majority of these surface cracks are associated with surface features developed during the oxidation, such as surface topography of the original metal grain boundary, which was not observed on the early stage oxide. Surface examination on the 130 days Zircaloy-4 specimen (Figure 5.13) indicate that local swelling of the oxide surface is observed. Surface crack is usually associated with this type of surface swelling. Combining with the cross sectional observations of the oxide layer, usually a thicker oxide layer would be expected under these surface cracks, also the outer surface of the oxide would have



(a) SE mode



(b) BSE mode

FIGURE 5.10: SEM surface examination of ZIRLOTM tube sample oxidised for 180 days at 360°C in primary water condition. (a) SE mode (b) BSE mode with surface crack indicated in the dashed square.



(a) Cross section image



(b) Surface image

FIGURE 5.11: SEM examination of Zircaloy-4 sheet sample oxidised for 25 days at 360°C in primary water condition. (a) BSE mode cross sectional image (b) SE mode surface image. The average thickness is 1.21 μ m.



⁽a) SE mode



(b) BSE mode

FIGURE 5.12: SEM images of surface oxide on Zircaloy-4 sheet specimen oxidised for 93 days at 360°C in primary water condition. (a) SE mode image (b) BSE mode image. The average thickness is 1.85 μ m.



⁽a) SE mode



(b) BSE mode

FIGURE 5.13: SEM examination of Zircaloy-4 sheet sample oxidised for 130 days at 360°C in primary water condition. (a) SE mode image (b) BSE mode image. The average thickness is 2.11 μ m.

convex profile, probably due to the high local oxidation rate caused by forming an easy path way through the surface cracks.

The oxide layer on Zircaloy-4 specimens in the pre-transition regime shared some similarities with the ZIRLOTM specimens, interfacial cracks were observed on all the pre-transition specimens, and their density of occurrence increases with increasing exposure time.

5.3.2.2 Post-transition oxide

The post-transition oxide of Zircaloy-4 is thinner than that of the ZIRLOTM specimen at the same oxidation time, an average oxide thickness of 3.44 μ m was determined by SEM. Cross sectional image of the 180 days oxide layer is shown in Figure 5.14(a). Large number of pre-existing interfacial cracks were accumulated at a band region which is about 2 μ m away from the outer surface, some finer cracks were also observed in this band region interconnecting the larger cracks. Hence, a large network of cracks would be expected.

Oxide surface roughness is more pronounced in the post-transition regime specimen, shown in Figure 5.14. As exposure time increases, the oxide outer surface become rougher, surface topographies arise from the metal substrate grain boundaries were observed in Figure 5.14. Some areas of surface oxide appeared to have "terracing" features covering the whole areas of parent metal grains. Cracks are often associated with these features.



(a) Cross section image



(b) Surface image

FIGURE 5.14: SEM micrograph of the oxide formed on 180 days Zircaloy-4 sheet specimen that was oxidised in 360°C primary water condition. (a) BSE mode cross section image (b) SE mode surface image. The average thickness is 3.44 μ m.

5.4 In-Situ EIS

In general, ZrO_2 consisted of the porous oxide outer layer and the dense barrier oxide layer. The penetration of the electrolyte through the open pores or cracks of the oxide layer reduce the electrical resistance of the oxide layer and accumulation of these cracks causes the accelerated corrosion. EIS is suitable method to evaluate these electrical properties without destruction of the oxide.

Validity of the measured impedance data was checked both experimentally and theoretically. The data were checked experimentally by stepping the frequencies from high-to-low and then immediately back from low-to-high, with the impedance being measured twice at each frequency step, to ensure that the same values were obtained at equivalent frequencies in the two directions. Autoclave oxidation of zirconium alloy can be considered as steady state process if the measurement was carried out in a relatively short period of time (less than an hour), which means that the thickness of the oxide and the current passing through the cell can be assumed to be independent of time, the impedance data should match in two frequency step directions. Figure 5.15 shows that the impedance data measured in the two step directions coincide with each other, except for the very low frequency end, where the impedance data seems very noisy and signal distortion appears. The signal distortion is probably caused by the current measuring limit at lower frequencies and insufficient time allowed for the system to settle. The high frequency discrepancy is probably due to the stray capacitance from the circuitry. This coincident of the measurement was checked frequently during the experiment, and particularly good test stability was observed with the in-situ experiment setup. The quality of the impedance data was also checked using the Kramers-Kronig transformation algorithm shown in Section 3.6. An illustration of EIS data and KK transformation results are shown in Figure 5.16. A good agreement is obtained, except for the small discrepancies at low



FIGURE 5.15: Bode plot of impedance spectrum measured from high-to-low frequency and low-to-high frequency. Impedance spectrum measurement was made on the Zircaloy-4 sheet specimen, that has been oxidised in the autoclave for 180 days at 360°C primary water.

frequencies, due to the KK transform definition bandwidth (infinite) in frequency (also see Section 3.6).

Autoclave EIS measurement were taken at the open-circuit-potential (i.e. OCP) E_{ocp} at frequencies f about 10^{-1} to 10^{6} Hz, using Newton4th PSM1735 phase sensitive multimeter and LCR active head attachment. Data acquisition was done with commercial software (i.e. PSMComm), supplied by Newton4th. The parameters (i.e. integration time, current-range switching) for data acquisition was fixed during the course of the in-situ experiment.



FIGURE 5.16: Data validation using KK transformation on EIS data collected from in-situ measurement.

5.4.1 Results - ZIRLOTM

5.4.1.1 Initial Exposure and Pre-transition Regime

A freshly prepared ZIRLOTM tube specimen was oxidised in static autoclave at 360°C under primary water condition. Initial oxide growth causes a rapid increase in cell impedance, magnitude of cell impedance increased rapidly in the first 20 days. A typical set of impedance spectra are shown in Figure 5.17. Further corrosion has a very little effect on cell impedance, the cell impedance increased only slightly from 30 to 130 days. From the weight gain measurement, it has been determined that the zirconium oxide growth kinetics were governed by a cubic law relationship. Higher oxide growth would be expected at the initial oxidation stage which then slows down until the transition regime.



(b) phase shift ϕ

FIGURE 5.17: Illustration of rapid initial cell impedance increase of ZIRLOTM tube specimen in electrolyte-resistance-subtracted Bode plot representation (|Z| and phase angle ϕ).



FIGURE 5.18: Nyquist plot of cell impedance developed during initial oxide growth for ZIRLO^{TM} tube specimen.

The high frequency capacitance response (i.e., 1 kHz ~ 100 kHz) has a slope of -1 (shown in Figure 5.17(a)), however, the intermediate frequency response (i.e., between 10 Hz ~ 1 kHz) has a lower slope, indicating a second time constant must exist. At low frequency, a phase angle minimum and an increase of the modulus with a slope of -0.2 was observed. The second time constant at intermediate frequencies (10 Hz ~ 1 kHz) was greatly masked by the high frequency capacitance response on the phase angle plot, but it can be distinguished by the change of the slope from the impedance modulus plot in Figure 5.17(a). Impedance spectra shown in Figure 5.18 indicated initial zirconium oxide (i.e., 1 day) has two distinctive time constants, two semicircles were observed initially in the spectra. As oxidation progresses, a dispersive semicircle became the dominating response. However, high frequency semicircle behaves consistently. Low frequency impedance spectra has some diffusional characteristics (i.e. low frequency phase angle is not zero, almost constant value of -10°), a diffusional tail was observed.

5.4.1.2 Transition regime

During the kinetic transition regime, cell impedance response can be characterised by two stages. The first stage can be described as falling cell impedance accompanied by decreasing of the phase relaxation peak at intermediate frequencies (i.e., $100 \sim 1000$ Hz), which has been referred to as the "degrading" stage. The second event is the regaining of cell impedance and increase of the intermediate phase relaxation peak, also known as the "repassivation" stage.

During the degradation stage, the modulus of cell impedance gradually decreases at all frequencies with increasing exposure time. The impedance response of the cell had dropped to a value that is equivalent to 30 days oxidation (as it shown in Figure 5.17), for both the magnitude and phase angle. The phase angle response shown in Figure 5.19 indicates that the high frequency behaviour is capacitive and less dispersive. The phase angle at intermediate frequencies (100 ~ 1 kHz), had shifted largely from -40° to -20°, indicating the intermediate frequency response was reduced during this stage.

A large depressed semicircle with a diffusional tail was observed for the Nyquist plots shown in Figure 5.20. Noticed that the diffusional tails have similar angle with respect to the real-Z axis. This means that the diffusional characteristic of the impedance spectra remained the same during the degradation stage and only the intermediate frequency response affected the shape of the Nyquist plots. As oxidation progresses, these semicircles become more and more depressed to the real-Z axis.

The repassivation stage of the transition regime is shown as the gradual increase of cell impedance at all frequencies and increase of phase angle at intermediate frequencies (in Figure 5.21). The impedance spectra obtained during the course of this second stage are very similar to the initial growth stage spectra.



FIGURE 5.19: Impedance spectra evolution on $ZIRLO^{TM}$ tube specimen (ZLR5) during 143 to 150 days of exposure. Electrolyte-resistance-subtracted Bode plot.



FIGURE 5.20: Nyquist plot of impedance spectra evolution on ZIRLOTM tube specimen (ZLR5) during 143-150 days of exposure.



FIGURE 5.21: Impedance spectra evolution on $ZIRLO^{TM}$ tube specimen (ZLR5) during 152 to 163 days of exposure. Electrolyte-resistance-subtracted Bode plot.



FIGURE 5.22: Nyquist plot of impedance spectra evolution on ZIRLOTM tube specimen (ZLR5) during 152-163 days of exposure. Electrolyte-resistance-subtracted Bode plot.

Figure 5.22, shows the Nyquist plot, an increase of the imaginary impedance was observed. Although the plots share a similar shape, the magnitude of the depressed semicircle are very different.

During the kinetic transition, two distinct stages was observed, the degrading stage and repassivation stage. Only one phase relaxation peak was observed at high frequencies (i.e., 10 kHz) which remains consistent during transition. However, significant phase angle shift was observed at intermediate frequencies (i.e., $10 \sim 1$ kHz). Thus, evolution of phase angle at intermediate frequencies could be contributed from the changes of the oxide layer during transition. Notably, the high frequency term only changed slightly during transition, which means, at high frequency, the total oxide responses are affected very little by the transition process, disregarding the physical changes happened to the oxide during this period. However, the intermediate frequency phase angle behaviour seem to trace the kinetic transition very well (Figure 5.19 and 5.21). The evolution of the phase angle (e.g. at $10 \sim 1$ kHz) at transition period reflects on a two-layer response of the oxide during transition, where one layer remained the same; one layer changes during transition.

5.4.1.3 Post-transition regime

Post-transition regime impedance response of the ZIRLOTM specimen are shown in Figure 5.23. The post-transition behaviour has some characteristics of the impedance response similar to the initial growth. Rapid impedance modulus increase was observed at the beginning of the post-transition regime, and gradually slow down as oxidation progresses. High frequency phase angle increased from -85° to -90°, with a slight shift of the relaxation peak position from higher frequency to lower frequency. This suggests oxide response at high frequencies was influenced by the growth of new oxide layer as observed on Figure 5.9. Evolution of phase angle at intermediate frequencies was small, compared with the large variation observed during the kinetic



transition. Low frequency impedance spectra reached minimum (-10°) at about 1 Hz indicating that a diffusional process is probably present.

FIGURE 5.23: Bode plot of impedance spectra for ZIRLOTM tube specimen (ZLR1) from 165 to 225 days of exposure. Electrolyte-resistance-subtracted Bode plot.

5.4.2 Results - Zircaloy-4

5.4.2.1 Initial Exposure and Pre-transition Regime

Impedance spectra collected on Zircaloy-4 sheet specimens (Figure 5.24) shown similar behaviour to ZIRLOTM tube. Generally, a high frequency capacitive relaxation peak was always present in the spectra, and the linear response of modulus (with a slope of -1) at high frequency (1 kHz ~ 100 kHz) indicating that zirconium oxide



FIGURE 5.24: Evolution of impedance spectra on Zircaloy-4 sheet specimen (Z4RXRR0) from 1 to 30 days of exposure. Electrolyte-resistance-subtracted Bode plot.

behaves like a dielectric material in this frequency range. Notice that the high frequency phase angle is about -90° for frequencies above 10 kHz, this is not observed in other measurements. A stray capacitance effect may be responsible for this behaviour, such capacitance term could arose from the cabling or the instrument. The increasing phase angle response at intermediate frequencies was observed which had the same characteristic as the ZIRLOTM specimens at initial stage. A diffusional behaviour was observed for all the spectra collected at low frequency, indicating a diffusional process is always present through out the experiment. Initial oxide growth caused a rapid increase in cell impedance, impedance at low frequency has increased one order of magnitude over the initial 30 days of exposure. The high frequency phase relaxation peak (at 10 kHz) evolved gradually with time, indicating an increase in oxide thickness. The change of slope of the modulus and phase angle shift from -10° to -40° at intermediate frequencies indicated that a second time constant began to appear as the oxidation progresses. Another relaxation peak was observed at about 1 Hz, with a low phase angle ($-20\sim-30^{\circ}$). Notably, impedance data become noisy below 1 Hz, due to the rapid increase of cell resistance, the current passing through the cell became lower. A larger perturbation signal can be used to boost the low frequency current detection, however, to maintain the linearity of the system, such practice was abandoned and lower frequency end of the spectrum was limited to 0.1 Hz.

5.4.2.2 Transition Regime

During transition, the Zircaloy-4 specimen showed a rapid decrease of cell impedance, also a decrease of phase angle at intermediate frequencies. Zircaloy-4 behave similarly to ZIRLOTM, but transition point for ZIRLOTM is earlier (150 days), where as Zircaloy-4 has a transition point about 166 days. The time evolution of impedance spectra is very similar during the transition regime (Figure 5.25).

5.4.2.3 Post-transition Regime

Post-transition Zircaloy-4 specimen behaviour is shown in Figure 5.26. A slow increase of modulus was observed at intermediate to low frequencies, however, high frequency modulus remains similar as oxidation progresses. Phase angle variation at intermediate frequency is very small, but a gradual increase over time can still be observed.



(b) Repassivation stage

FIGURE 5.25: Impedance evolution of Zircaloy-4 sheet specimen (Z4RXRR5) during (a) degradation stage of the transition regime from 154 to 166 days and (b) repassivation stage from 167 to 180 days. Electrolyte-resistance-subtracted Bode plot.



FIGURE 5.26: Bode plot of impedance data collected from Zircaloy-4 sheet specimen (Z4RXRR1) in the post-transition regime. Electrolyte-resistance-subtracted Bode plot.

5.5 Ex-situ EIS

The data validity was checked by KK transformation.

5.5.1 Results - ZIRLOTM

5.5.1.1 Pre-transition oxide

ZIRLOTM tube specimens from the in-situ autoclave experiment were used, hence ex-situ measurement can be compared with in-situ data collected on the same specimen with the same exposure time. The impedance response of pre-transition oxide is shown in Figure 5.27, two distinct time constants were observed. Initial impedance response was recorded immediately after the immersion, and two distinct time constants were observed. At high frequencies, impedances response shows a capacitive behaviour, with a phase relaxation peak reaching -80°. A phase minimum was observed at 1 kHz, accompanied by the change of slope for the impedance modulus. At lower frequencies, a second time constant was observed with some dispersive character, and the phase angle decreases with increasing immersion time. The impedance modulus also decreased slightly with increasing immersion time at frequencies below 100 Hz. Impedance responses recorded at 6 hours and longer immersion behaved essentially identically, indicating electrolyte had filled the pores/cracks network.

Ex-situ measurements on 130 days pre-transition oxide has confirmed that all pretransition oxide has two distinct time constants separated by a phase minimum at about 1 kHz. A constant slope of about -0.9 is also observed for the impedance modulus at high and low frequencies in Figure 5.28. The phase angle plot suggested that, at high frequency, the oxide had only shown capacitive behaviour, while at low frequency, a second phase peak was observed with some characteristic of diffusional impedance. These observations suggested that two layers of oxide might



FIGURE 5.27: Impedance response of ZIRLOTM tube specimen at ambient temperature after 93 days of exposure. Ambient temperature impedance is measured in $0.5M \text{ Na}_2\text{SO}_4$.

have different time constants ($\tau = RC$), which indicated that two phase angle peaks in Figure 5.28 could be contributed by different oxide layers. For example, at high frequency, the series capacitance behaviour of the total oxide may be contributed mainly from the porous oxide layer that had the smallest capacitance value. However, at low frequency, the barrier layer in series with the diffusional term may be dominated the overall impedance spectra. SEM examination have confirmed that the outer part of the oxide is porous and cracked, barrier oxide layer is dense and protective, and these two layers are separated by the interfacial cracks that filled with electrolyte. If the outer part of the oxide is porous, the water content within the pores can increase the dielectric constant of this layer, hence the capacitance of the layer is increased.



FIGURE 5.28: Impedance response of ZIRLOTM tube specimen at ambient temperature after 130 days of exposure. Ambient temperature impedance is measured in $0.5M \text{ Na}_2\text{SO}_4$.

In Figure 5.29 and 5.30, the high frequency loop (shown in subfigure of Figure 5.29 and 5.30) is contributed from the total oxide capacitance, while the low frequency response affected by soaking process is contributed from the diffusional mass transport process through porous oxide and it is in series with barrier oxide layer response (i.e., dielectric behaviour).



FIGURE 5.29: Nyquist plot of ambient temperature impedance response of $ZIRLO^{TM}$ tube specimens after 93 days of exposure. Ambient temperature impedance is measured in 0.5M Na₂SO₄. Enlarged high frequency plot is shown in subfigures.



FIGURE 5.30: Nyquist plot of ambient temperature impedance response of $ZIRLO^{TM}$ tube specimens after 130 days exposure. Ambient temperature impedance is measured in 0.5M Na₂SO₄. Enlarged high frequency plot is shown in subfigures.
5.5.1.2 Post-transition Oxide

The post-transition oxide was expected to have a significant amount of porosity and surface cracks. However, the impedance spectra (Figure 5.31) collected from 180 days (post-transition) specimen with increasing immersion time only showed a small effect from the porosity. This suggested that either the volume fraction of the porosity is small or the majority of the pores are very large which can be soaked very quickly. SEM studies had confirmed that large surface cracks exist on 180 days Zircaloy-4 specimen (Figure 5.14).



FIGURE 5.31: Impedance response of ZIRLOTM tube specimen at ambient temperature after 180 days of exposure. Ambient temperature impedance is measured in $0.5M \text{ Na}_2\text{SO}_4$.

The two time constants were observed in Figure 5.31, phase angle vs. frequency plot suggested that two distinct layers were coexisting. High frequency time constant



FIGURE 5.32: Impedance response of Zircaloy-4 sheet specimen at ambient temperature after 130 days of exposure.

could be contributed from the total oxide capacitance, while barrier layer oxide and a diffusional process were dominating the low frequency response (barrier layer oxide response always in series with the diffusion process and reactions which are only occurring at low frequencies.)

5.5.2 Results - Zircaloy-4

5.5.2.1 Pre-transition Oxide

A Zircaloy-4 specimen that had a exposure of 130 days was tested. Similar two time constant response was found (Figure 5.32). Lower phase angle response was recorded at high frequencies compared with 130 days $ZIRLO^{TM}$ specimen. The low



FIGURE 5.33: Impedance response of Zircaloy-4 sheet specimen at ambient temperature after 180 days of exposure.

frequency response is affected by the soaking time. However, no significant different of the phase angle shift was found at low frequency at 6 hours and longer immersion.

5.5.2.2 Post-transition Oxide

A specimen that had been exposed for 180 days was also tested. Initial impedance response is similar to 180 days ZIRLOTM specimen. However, as soaking time increases, the modulus and phase angle were decreased at low frequencies. This suggested that the barrier oxide layer became porous after the kinetic transition, and the volume fraction of the pores may be higher than those found on the 180 days ZIRLOTM specimen.

5.6 Discussion

5.6.1 Weight Gain

The corrosion kinetics of zirconium alloys can be be described reasonably well by cubic or parabolic law, but it is not possible to discriminant between them. More data points during the initial oxidation stage are required in order to make a better judgement on the oxidation kinetics. However, this is not carried out in the current study due to a number of issues.

Firstly, heating up and cooling down an autoclave can be time consuming (e.g., few hours for heating up and maybe a day for cooling down), larger autoclaves (i.e., autoclaves used to weight gain study at EDF research facilities) would take considerably longer. Corrosion may well be happening during these operations, below the required temperature (i.e., 360°C).

Secondly, for the same reason as described above, autoclave tests are usually carried out on the time scale of days instead of hours. For zirconium alloys, the rapid initial growth may only last a few days or even shorter period of time. A 20-day autoclave run would not have had the capability to capture the initial oxidation stage. Lack of data points also leads to the uncertainties of the oxidation kinetics in the post-transition regime due to the expected rapid growth at the beginning of post-transition regime.

5.6.2 Visual Examination

Variation of oxide colours maybe interpreted as variation of oxide thicknesses, only if the oxide was very thin/transparent and colours were due to interference of light. The colour of black and grey oxide is contributed from the oxide structural features (e.g., interfacial cracks) rather than oxide thickness. "Patchy" oxide surface is generally observed on post-transition specimens, but not on pre-transition specimens, which suggests this colour changing phenomenon maybe related to the kinetic transition. The weight gain plot showed a rapid increase of weight gain after the kinetic transition, which can be correlated with the change of appearances of the oxide. The grey regions on the "patchy" oxide could be characterised as post-transition oxide, in contrast, the black regions could be seen as pre-transition oxide.

The non-uniform distribution of the grey oxide indicated that the process of a pretransition oxide turning into post-transition oxide must have taken place locally and subsequently spread out to cover the whole surface, evidence can be found on the remaining black oxide region with a concave shape (Figure 5.4(b)).

SPPs may also contribute to colour variation during corrosion, as described by Tejland et al. (2010), some SPPs are nobler than the zirconium matrix, when the matrix materials (i.e., Zr metal) are oxidised, second phase particles are not immediately oxidised but retain their metallic character for a long time. Zirconium oxide with metallic particles embedded may exhibit absorption of light at UV-visible-NIR wavelengths, which makes the oxide appear to be black. As oxidation progresses, the metallic particles will be oxidised eventually and absorb less light, which increased the reflectance of the oxide and giving it a greyish appearance.

In addition, interfacial cracks parallel to the oxide surface would act as reflecting surfaces, hence further increase the reflectance of the oxide.

5.6.3 Microscopic Characterisation

Lateral interfacial cracks were observed on most of the specimens. The most important question is when these cracks were formed, during oxidation at high temperature or during cooling. The time scale of such event maybe difficult to investigate, due to the limited number of available techniques and the severe experimental conditions.

However, the SEM analysis on the cross section of the oxide layer may give some clues. Interfacial cracks observed in the cross section images are often related to the localised slow oxidation rate. The convex shaped metal substrate underneath the crack is an evidence for the slow oxidation rate, since no ionic or electronic transport can be made through these lateral cracks. Localised cease of growth beneath the crack is a distinct feature while the adjacent oxide kept on growing. This observation suggested that the oxidation front is "pinned" by the interfacial cracks. This supports the hypothesis that lateral cracks were formed during oxidation. On the contrary, if the cracks were formed during cooling period (i.e., few hours to a day), the oxidation rate is largely suppressed by the rapid cooling rate (e.g., 150°C/hour for autoclave used in this study), hence the temperature would be insufficient for any further growth of zirconium oxide.

Rapid oxidation was observed after the kinetic transition, determined from the weight gain plot. In order to support such oxidation kinetics, a faster charge and mass transfer route is required. Surface cracks were observed on the post-transition oxide. Transport of reactants (e.g., water) may have occurred through these surface cracks which may have reduced the mean migration distance (i.e., distance between metal/oxide interface where oxidation reaction take place and oxide/electrolyte interface where water reduction reaction occurred) for both the electrons and oxygen ions.

Mechanistic understanding of such phenomenon is still unclear, however, surface cracks are usually a response to stresses generated by the oxidation process. The growth and thermal stresses generated during corrosion at high temperature could be accommodated by a number of mechanisms, involving cracking of the oxide, spalling of the oxide from the alloy substrate, plastic deformation of the substrate and plastic deformation of the oxide.

No spalling of the oxide was observed in the SEM analysis, however, the oxide surface became rougher as oxidation time was increased. This development of surface roughness may resulted from the plastic deformation of the substrate or the thin oxide. The metal substrate is unlikely to be plastically deformed during oxidation due to the relative dimensions between the oxide and metal substrate. This is true for bulk deformation, but not necessarily for the local deformation that would be associated with surface undulations. Thus, metal substrate adjacent to metal/oxide interface would be susceptible to plastic deformation, and further oxidation would result the interfacial undulation observed at metal/oxide interface shown in Figure 5.6(a).

All specimens had similar surface conditions at the beginning of the oxidation. As exposure time increases, surface features were developed, possibly due to the preferential growth of columnar oxide grains under compressive stresses or the oxide buckling effect in order to relief stresses building up within the oxide. At the buckled regions, metal substrate could be dragged by the buckling oxide and form peak shaped metal/oxide interface (i.e., interface undulations). As oxidation progresses, metal/oxide interface undulation could be influencing the surface oxide roughness.

Some features developed during oxidation has been observed in Figure 5.14, where certain areas of oxide surface appeared to be wavy, morphology of original metal grains were clearly shown on the oxide surface. This indicated that crystallographical orientation of the parent metal substrate could have an influence on the growth rate of oxide grains, which maybe significant over long oxidation time.

5.6.4 Equivalent Circuit Modelling

The analysis of the oxide layer suggests the scheme presented in Figure 5.34 for corrosion of zirconium alloys. A two layer structure of the oxide is proposed in this study, a porous outer oxide and a dense barrier oxide layer. Macropores are present in the outer part of the porous oxide and micro- or nanopores may present in the inner part. The barrier oxide layer is dense and free of any porosity. Interfacial cracks may develop during oxidation at the metal/oxide interface, however, these cracks can be linked with the electrolyte if connected with porosity.



FIGURE 5.34: Schematic representation of the zirconium oxide, relative layers and various interfaces.

From the physical model, an electrical model can be developed. Corrosion is associated with anodic and cathodic reactions that take place at various interfaces. Therefore, the total impedance at open circuit potential can be described as the anodic impedance in parallel with the cathodic impedance with a solution resistance R_e added in series for a metal surface. For an oxide covered metal, the anodic impedance can be expressed as a charge transfer resistance in parallel with a space-charge capacitance and usually takes place at metal/oxide interface. Generally, in an electrochemical system that the electrode surface is covered with an oxide, the double layer capacitance is normally neglected. The double layer normally would have a value in the order of μ F for every cm² of electrode area. For an insulating oxide film (e.g., ZrO₂ that is ~1 μ m thick), oxide capacitance value of 10⁻⁸ to 10⁻¹² F/cm² would be expected. Since double layer capacitance would exist in series with oxide capacitance, the overall capacitance that is measured by the instrument will be dominated by the smallest capacitance value. For this reason, anodic impedance is usually negligibly small compared with oxide impedance.

The cathodic reaction normally takes place where anodic reaction happens, however, in the case of an oxide layer present in between the base metal and corrosive environment, the two reactions are often assumed to be separated by the non-penetrable oxide (i.e., for ZrO_2 system, barrier layer oxide can be seen as a non-penetrable oxide). As a result, the anodic reaction would occur at the metal/oxide interface, and the cathodic water reduction reaction would take place at oxide/electrolyte interface (i.e., at the end of micropores, which are located at the walls of the macropores) where water reduction is facilitated with electron transfer through the barrier oxide. A method developed by de Levie (1967) was used, which is a distributed impedance term (i.e., usually known as transmission line), Z_D , to describe the response in the micropores.

A proposed equivalent circuit for modelling the impedance response of zirconium oxide during in-situ EIS measurement is shown in Figure 5.35

A porous outer oxide is generally considered during development of the equivalent circuit model. Cylindrical pores were used as a basic model to describe the porous



FIGURE 5.35: Equivalent circuit model for impedance response measured during in-situ EIS measurement, where a two layer oxide had been considered in this model.

behaviour of zirconium oxide. Macropores may be connected in series with micropores to described the soaking characteristics observed during the ex-situ EIS experiment. The impedance response of the cathodic reaction can be described by a distributed impedance in space as a transmission line in the conducting macropores. The interfacial impedance of the micropores can be expressed as a cathodic double layer capacitance C_{dl} in parallel with the Faradaic branch of a cathodic charge transfer resistance R_{ct} in series with a transmission line impedance term Z_D , which is the diffusion analog of the impedance of a semi-infinite length, uniformly distributed RC transmission line. A resistance term R_p represents the ohmic resistance of the electrolyte through the porous oxide, and the term C_p represents the capacitance of the porous oxide.

Thus, the anodic surface is at the metal/oxide interface, and cathodic interface is at the end of the micropores, which are located at the walls of macropores.

5.6.4.1 Fitting Procedures Example

A fitting example is given below to illustrate the fitting procedures and in relation to develop an adequate equivalent circuit model for further data analysis. A representative experimental data set is shown in Figure 5.36. Impedance spectra was acquired in-situ from ZIRLOTM specimen at 200 days of exposure.



FIGURE 5.36: Bode plot of impedance spectra collected from the 200 days $ZIRLO^{TM}$ sample during in-situ experiment at 360°C.

By a close examine of the impedance data shown in Figure 5.36, a diffusional term at the frequency range of 10^{-1} - 10 Hz can be identified. At higher frequency end, the impedance response can be identified as the oxide response which can be described by the circuit in Figure 5.37.



FIGURE 5.37: Electrical circuit that describes the impedance response of an oxide layer, the equivalent circuit consists of a solution resistance R_e in series with an oxide resistance R_{ox} in parallel with a capacitor C_{ox} representing the dielectric response of the oxide at high frequencies.

A Randles circuit shown in Figure 5.38 was proposed for the initial fitting procedure, which describes the high frequency oxide response and low frequency mass transport behaviour (i.e., diffusional). In Figure 5.39, by comparing the fitting result with the experimental data, the basic equivalent circuit can be established as it shown in Figure 5.38. However, at intermediate frequency, the equivalent circuit does not describe the experimental impedance response.



FIGURE 5.38: The Randles circuit that describes the impedance response of an oxide layer with diffusional influence.



FIGURE 5.39: Fitting results and experimental data from the 200 days ZIRLOTM sample during in-situ experiment at 360°C.

At this point, it is useful to review some of other corrosion systems that may have similar impedance response. For example, a coated metal which share the similarity as the Zr-ZrO_2 system, since ZrO_2 can be seen as a coating materials that has been applied to the zirconium substrate. The impedance response for an impermeable coating can be described by a pure capacitor in series with a solution resistance. However, most paint coatings degrade with time, and water penetrates into the coating and forms a new liquid metal interface under the coating, and corrosion can occur at this freshly formed interface.



FIGURE 5.40: Equivalent circuit model for the impedance response measured on a failed coating system.

The equivalent circuit in Figure 5.40 can be used to describe the impedance response of a failed coating. The capacitance of the intact coatings is represented by C_i , which has a much small capacitance value than double layer capacitance. Units for these coating usually in the order of nF, due to the thickness of the coating (usually in the order of μ m). R_p is the resistance of ion conducting paths (i.e., resistance of the electrolyte inside the pore) that developed in the coating. The actual paths can be porosities, cracks or grain boundaries, it may not be physical pores filled with electrolyte. The failed coating system, where a pocket of electrolyte is formed once the coating is penetrated, the bare metal would be in contact with the electrolyte. In this case, the electrolyte inside this pocket can be very different from the bulk electrolyte (e.g., pH level, resistivity, ionic concentration, etc). In addition, a kinetically controlled charge transfer reaction can be present between the pocket of electrolyte and the bare metal. R_{ct} and C_{dl} are the interface components that



FIGURE 5.41: Fitting results obtained using the equivalent circuit shown in Figure 5.40.

describes this interfacial reaction that take place at the metal/electrolyte interface. The fitting result is shown in Figure 5.41 using the failed coating model (Figure 5.40). The results seems in good agreement with the experimental data, however, the circuit parameters values determined by the fitting cannot make sensible justification of the real system (a table of the fitting parameters and determined values is shown in Table 5.1). The R_{ct} value is much smaller than expected, which means the corrosion rate is much higher than the observed value from weight gain experiment.

TABLE 5.1: Fitting results for the experimental data collected from the 200 days $ZIRLO^{TM}$ sample during in-situ experiment at 360°C.

R_p	W_R	W_T	W_P	R_{ct}	C_{dl}	C_i
92 k Ω	$1.58~\mathrm{M}\Omega$	40 k	0.17	$1.2 \text{ k}\Omega$	$1 \times 10^{-8} {\rm F}$	$1.1 \times 10^{-9} \text{ F}$

The model to describe the zirconium oxide system would be similar to the failed coating model (shown in Figure 5.40. However, instead of a kinetic controlled charge transfer process and a diffusion process, an oxide layer maybe always present at the metal surface (i.e., the barrier oxide layer) if it was exposed to electrolyte.

In addition to the failed coating model, there are certain modifications should be considered according to an adequate physical model of the zirconium corrosion system under investigation. The direct access of the metal substrate is absent in the case of zirconium oxidation compared with a metal covered with a failed coating, due to zirconium's high oxygen affinity in water, a thin layer of barrier oxide would always be present in between the electrolyte and bare metal. The barrier oxide layer that can be described with an oxide resistance R_b and capacitance C_b . The oxide/metal interface response may be neglected due to its very small contribution to the overall resistance and capacitance (i.e., oxide/metal interfacial transfer resistance is considered very small compared with oxide electrical resistance, so it has very small effect on the total oxide electrical resistance; the interfacial capacitance is very large, however, when it is in series with other capacitances, the largest capacitor has very small contribution towards the total capacitance according to Equation 3.37).

As a result, a modified equivalent circuit (Figure 5.35) based on the failed coating model was developed and illustrated in Section 5.6.4. An addition oxide layer was introduced to model the barrier oxide response of the system. The fitted impedance curve is shown in Figure 5.42 using the modified equivalent circuit (Figure 5.35) and the fitting results are shown in Table 5.2.

TABLE 5.2: Fitting results using equivalent circuit shown in Figure 5.35 for the experimental data collected from the 200 days ZIRLOTM sample during in-situ experiment at 360° C.

R_p	W_R	W_T	W_P	R_{ct}	C_{dl}	C_p	R_b	C_b
$62 \text{ k}\Omega$	$552~\mathrm{k}\Omega$	50	0.29	$53 \text{ k}\Omega$	42 nF	$1.3 \mathrm{nF}$	$69 \text{ k}\Omega$	9.5 nF



FIGURE 5.42: Fitting results obtained using the equivalent circuit shown in Figure 5.35.

By further examine the fitting results, the total oxide capacitance and oxide resistance would dominate the high frequency response in the frequency range between 1 k - 100 k Hz. From the fitting results shown in Table 5.2, the total oxide resistance can be expressed as $(R_{total} = R_{ct} + R_b \approx 120 \text{ k}\Omega)$ at high frequency range; and the total oxide capacitance can be expressed as $(C_{total} = [C_p^{-1} + C_b^{-1}]^{-1} \approx 1$ nF). The corresponding characteristic frequency for the total oxide response at high frequency can be calculated as $f_{RC} = (2\pi R_{total}C_{total}) \approx 1.3 \text{ kHz}$. The characteristic frequency of barrier layer oxide response can be calculated as $f_{RC} = (2\pi R_b C_b) \approx 240$ Hz which is indicated in Figure 5.42. The characteristic frequency of the cathodic reaction which take place at the oxide/electrolyte interface can also be calculated as $f_{RC} = (2\pi R_{ct}C_{dl}) \approx 72$ Hz. Although the characteristic frequencies for each time constant are very close to each other, the changing of gradient of the |Z| plot in Figure 5.42 can be interpreted as dispersion of the impedance response due to the appearing of transmission line behaviour as the frequency decreases.

5.6.5 Fitted Electrical Parameters

In-situ EIS data collected on a number of specimens over a long period of time were fitted to the equivalent circuit model illustrated in Figure 5.35, using complex non-linear least square regression (CNLS) program built into $ZView^{\textcircled{R}}$.

Time evolution of the fitted parameters is represented as a function of exposure time. The impedance spectra were collected from six samples for each alloy with different pre-oxidation times (e.g., pre-oxidation was performed at EDF autoclave, see Table 4.3 for detail).

The standard score plot in Figure 5.43(b) (also known as "z-score" plot), is a dimensionless quantity derived by Equation 5.2,

$$z = \frac{|x - \mu|}{\sigma} \tag{5.2}$$

where x is individual data value, μ is the mean of the data set and σ is the standard deviation. In this instance, the use of z-score is not as a test statistic for a significance test, but rather as a numerical guide to finding subsets of data which might show different trends than others.

5.6.5.1 C_b Barrier Oxide Layer Capacitance

Time evolution of barrier oxide capacitance in Figure 5.43(a) had shown that ZIRLOTM tube specimen experienced a maximum in capacitance at about 160 days exposure. This is consistent with the weight gain data in Figure 5.1, where a sudden increase of weight gain was observed. Zircaloy-4 specimen had shown a similar time evolution of the barrier oxide layer capacitance in Figure 5.43(b), with a local maximum at

about 160 days exposure. This suggests that barrier oxide layer is thinned during the kinetic transition. This suggests that the sudden increase of weight gain of the sample during transition maybe controlled by the barrier oxide layer thickness.

In the pre-transition regime, the capacitance value on both alloys were almost identical, despite some discrepancies at initial oxidation stage where regression method may have difficulty distinguish between the capacitance contribution from barrier and porous oxide. However, in the post-transition regime, the capacitance value for Zircaloy-4 is much lower than ZIRLOTM, indicating that the barrier oxide layer for Zircaloy-4 is thicker compare to ZIRLOTM, if the same oxide dielectric constant for both materials alloys were assumed.

The z-score plot in Figure 5.43(a) showed very little deviation from the mean ($\leq 0.5z$) in pre- and post-transition region, but large deviation ($\approx 2z$) was observed at initial oxidation and kinetic transition, suggesting that these two events behaved similarly. For Zircaloy-4 specimen, large deviation ($\approx 1z$) was observed in the post-transition regime, which compared with $\leq 0.5z$ for pre-transition regime.

5.6.5.2 R_b Barrier Oxide Layer Resistance

Time evolution of the resistance term for the barrier oxide layer is shown in Figure 5.44(a) for ZIRLOTM tube. A local minimum of barrier oxide layer resistance is shown at about 160 days of exposure, indicating the kinetic transition also has effect on the barrier oxide layer resistance, which is consistent with the barrier oxide layer capacitance observation and weight gain data. From a charge transfer point of view, the electrons created by the anodic half-cell reaction can be transported faster to the cathodic site through a thinner barrier oxide layer, hence, a higher oxidation rate is expected.



FIGURE 5.43: Fitted results for capacitance of barrier oxide layer as a function of oxidation time.



FIGURE 5.44: Fitted results for resistance of barrier oxide layer as a function of oxidation time.

Two large deviation ($\approx 2z$) were observed in the z-score plot, the initial oxidation stage and the beginning of post-transition stage (about 150 days) indicating these two regions has dissimilar rate of change in terms of oxide resistance. Notes that the trend of data points at the initial stage and repassivation stage after the first transition looks almost identical in Figure 5.44(a).

Figure 5.44(b) had shown similar time evolution of the barrier oxide layer resistance for Zircaloy-4 specimens, however, fitted parameter at the initial oxidation stage has some discrepancies, this could be accounted for by the variations of each individual specimen, interruption of autoclave test (e.g., autoclave seal failure, introducing new samples into the autoclave would require new weld being made between the sample and electrical feedthrough wire, which would temporarily decrease the cell impedance by exposing the fresh weld to the electrolyte), effect from electrolyte and effect from regression process. Despite all the small discrepancies, a general trend of the parameter can still be obtained in the time evolution plot.

5.6.5.3 C_p Porous Oxide Layer Capacitance

Time evolution of porous oxide capacitance in Figure 5.45(a) for ZIRLOTM tube is less clear than Figure 5.45(b) for Zircaloy-4. In Figure 5.45(a), however, a general trend of constant capacitance before transition (160 days) and followed by a decrease of capacitance after transition was observed. Similar trend is observed on Zircaloy-4 specimen in Figure 5.45(b). From the weight gain data shown in Figure 5.1, pre-transition oxide doubled its weight gain in the time period of 20 ~ 140 days, which means the oxide thickness also doubled accordingly. The observation from Figure 5.43(a), also indicated that barrier oxide thickness remains almost constant during the pre-transition regime (from 80 - 140 days). This suggests oxide thickness increases while relative capacitance remains constant, which indicates possible oxide dielectric losses occurred during the formation of porous oxide.



FIGURE 5.45: Fitted results for capacitance of porous oxide layer as a function of oxidation time.

It should be noted that electrical properties of the porous oxide maybe different from the barrier oxide, due to the electrolyte filled pores. Large time constant dispersion can arise as a result of the nonuniform mass transfer (i.e., mass transfer through the porous oxide with different pore geometries). Thus, analysis on the porous oxide capacitance maybe less quantitative than the barrier oxide layer.

5.6.5.4 C_{dl} Cathodic Double-layer Capacitance

An electric double-layer exists at the electrode/electrolyte interface where cathodic reaction (i.e., water reduction) take place, and its relative capacitance value can be affected by many variables, including electrode potential, temperature, ionic concentration of the electrolyte, types of ions, electrode roughness, etc. In the case of zirconium oxide, the cathodic reaction and its conditions are unlikely to change throughout the test, however, field strength across the barrier oxide layer may subject to changes during kinetic transition, due to thinning of the barrier oxide layer.

As shown in Figure 5.46(a), C_{dl} of ZIRLOTM tube, was relatively constant during the pre- and post-transition regime, while large increase of capacitance was observed at transition period. For a potentiostatic measurement (i.e., EIS), electrode potential is usually fixed, however, the electric field across an oxide can vary if oxide thickness was changed. This finding is consistent with C_b at transition point, indicated that double layer capacitance associated with cathodic reaction is affected by the barrier oxide layer thickness.

Time evolution of C_{dl} (Figure 5.46(b)) for Zircaloy-4 has shown linear decrease in the pre-transition regime (from 15 - 140 days) and relatively constant behaviour in the post-transition regime. The linear decrease in the pre-transition regime indicated that the high frequency capacitance effect is decreased, because C_{dl} is related to the double layer that formed at the cathodic reaction interface, it indicated that the field strength across the developing oxide was dropping and this decreasing field strength



FIGURE 5.46: Fitted results for double-layer capacitance associated with cathodic half-cell reaction as a function of oxidation time.

has an impact on the thickness of the electrochemical double layer. As field strength decreases, the double layer thickness increases, hence the double layer capacitance decreases.

5.6.5.5 R_{ct} Cathodic Charge Transfer Resistance

Cathodic charge transfer resistance can be related to the rate of the cathodic reaction. A gradual increase of R_{ct} was observed in Figure 5.47(a) for ZIRLOTM tube in the pre-transition regime. During kinetic transition (about 160 days), a sudden decrease of resistance was observed, which R_{ct} value had dropped almost an order of magnitude within few days. An exponential increase of R_{ct} was observed in the post-transition regime. Due to the similar time-constant value of $R_{ct}C_{dl}$ and R_bC_b , a scattering of R_{ct} data at the initial oxidation stage may be introduced by the regression method.

Large data scattering was observed at the initial oxidation stage of Figure 5.47(b) for Zircaloy-4 samples. A steeper increase of R_{ct} was observed in the pre-transition regime. Zircaloy-4 samples also has a higher R_{ct} value compared with ZIRLOTM, which suggests it has a lower oxidation rate, hence, thinner oxide would be expected. This interpretation is consistent with the weight gain plot shown in Figure 5.1, where a lower weight gain was observed for Zircaloy-4 material.

5.6.5.6 W_R Warburg R Parameter

The Warburg impedance arises from diffusion of species to the interface where reaction take place. In the case of zirconium oxide, the actual interface refers to the metal/electrolyte interface at the end of micropores located on the walls of the macropores in the porous oxide. A simple approach was used which involved transmission line model assuming the pores are cylindrical, uniform and infinite in



FIGURE 5.47: Fitted results for charge transfer resistance associated with cathodic half-cell reaction as a function of oxidation time.

length. The generalised finite length Warburg impedance form for an infinite-length diffusion with transmissive boundary can be expressed as

$$Z_w = W_R \frac{\tanh\left[(jT_w\omega)^{p_w}\right]}{\left[(jT_w\omega)^{p_w}\right]}$$
(5.3)

where W_R is the limiting diffusion resistance at very low frequency, also referred as Warburg resistance. Hence, Z_w approaches W_R at low frequencies. W_T the time constant of diffusion. W_P is the Warburg exponent, it has a value of 0.5 for planar electrode which resulting in a 45° straight line in the Nyquist representation. However, for the impedance of a porous electrode, W_P is half of the value as it for the planar electrode, the W_P for the radial diffusion impedance in a pore is 0.25 instead of 0.5 (Scolnik et al. 1991). Thus, a phase angle of 22.5° would be expected.

Time evolution of Warburg diffusion resistance is shown in Figure 5.48(a) and 5.48(b) for ZIRLOTM and Zircaloy-4 respectively. Small variations of W_R at initial stage and transition period were observed. W_R values for Zircaloy-4 are generally higher than ZIRLOTM, indicating that mass transfer was more difficult in the oxide formed on Zircaloy-4 than ZIRLOTM. W_R can also be interpreted as a rate limiting factor for corrosion process, as it has an influence on the rate of which reactant was delivered to the cathodic interface.

5.6.5.7 W_T Warburg T Parameter

The W_T parameter is known as the time constant of diffusion, it can also be described by

$$W_T = \frac{\delta^2}{D} \tag{5.4}$$

where δ is the thickness of diffusion layer (in the order of a few μ m), and D the diffusivity (or diffusion coefficient) of the diffusing species (μ m²/s). A higher W_T



FIGURE 5.48: Fitted results for Warburg R parameter associated with diffusion in pores as a function of oxidation time.

value can be interpreted as a longer diffusion path if D is constant for a specific species.

Considering the cathodic reaction that took place in the micropores, the reactants (i.e., H_2O) and products (i.e., H_2 , OH^-) are present in the pores, small amount of solute (i.e., $B(OH)_4^-$, Li^+) may also be present. However, Warburg impedance is only associated with species that are involved in the interfacial reactions (i.e., H_2O and H_2).

The W_T data seemed to be randomly distributed for both ZIRLOTM and Zircaloy-4 specimens. Most of the data points were in the range of 1 - 10⁴ s. From the SEM examination, porous oxide thickness is in the order of 100 nm to 1 μ m range. As a result, the calculated self-diffusion coefficient of water at 360°C, $D_{H_2O,360°C}$, would be in the range of 10⁻⁸ - 10⁻¹² cm²/s, which is much smaller than bulk water diffusion coefficient at 360°C, 5×10^{-4} cm²/s (i.e., calculated value from room temperature water bulk diffusion coefficient $D_{H_2O,25°C} \approx 10^{-5}$ cm²/s (Xu et al. 2009) using Stokes-Einstein Equation (calculation is shown in Appendix A.2).

Hydrogen gas diffusion in water could also be present in the pores, but no such diffusion coefficient at experimental conditions has been reported elsewhere.

5.6.5.8 W_P Warburg P Parameter

The W_P parameter can be used as indication for pore character. In the classic Warburg impedance, a W_P value of 0.5 (i.e., slope of -0.5 for the |Z| on Bode plot) is observed which corresponds to a 45° straight line with respect to the real axis on the Nyquist plot. Warburg impedance experiences a 45° phase angle, can be characterised as the diffusional impedance response for a planar electrode. However, this flat electrode response was only observed for both materials at initial stage of corrosion. As oxidation progresses, the W_P parameter decreases to about 0.25



FIGURE 5.49: Fitted results for Warburg T parameter associated with diffusion in pores as a function of oxidation time.

for ZIRLOTM shown in Figure 5.50(a), and a $\sim 22.5^{\circ}$ angle on the Nyquist plot was observed in Figure 5.21. The 22.5° angle with respect to the real axis is the characteristic of the "semi-infinite/finite" length diffusion in a porous electrode, which is in good agreement with the de Levie theory.

This W_P can also be interpreted as geometric factors of the pores, a 45° angle tail on the Nyquist plot implies that the mean length of the pores can be fully penetrated by the electric signal (signal penetration depth is equal/larger than the mean length of the pores). On the other hand, when the mean length of pores is much larger than the penetration depth of electric signal (depending on the frequency of the signal, usually at low frequencies, since diffusion process only happens at low frequencies), the Warburg impedance would give a 22.5° angle, suggesting the signal can only penetrate part of the pore depth.

5.6.5.9 R_p Pore Electrolyte Resistance

 R_p describes the Ohmic resistance of electrolyte in porous oxide, which is in series with the cathodic reaction terms (i.e., C_{dl} , R_{ct} and W). For a cylindrical pore, R_p maybe influenced by the length (l) and diameter (d) of the pores,

$$R_p = \rho \frac{4l}{\pi d^2} \tag{5.5}$$

where ρ is the electrolyte resistance.

For ZIRLOTM specimens, there was a sudden decrease at the kinetic transition, which could be caused by the electrical conductivity increase of the electrolyte inside the pores after the kinetic transition. This could also imply that the total number of pores with the same pore length has increased during transition. This interpretation is consistent with SEM observation in Section 5.3 which relatively isolated cracks became interlinked with the nearby cracks and surface cracks after kinetic transition.



FIGURE 5.50: Fitted results for Warburg P parameter associated with diffusion in pores as a function of oxidation time.

However, kinetic transition seemed to have very little effect on R_p for Zircaloy-4 specimens. Although a trend of increasing R_p was observed, the change of R_p before and after the transition period is insignificant.

A method of estimating the volume fraction of the porosity was proposed in this study, by comparing the R_p and electrolyte resistance, R_e .

$$vol\% = \frac{A_{pore}}{A_{total}} = \frac{\rho_p l_p}{R_p} \frac{R_e}{\rho_e l_e} = \frac{l_p R_e}{l_e R_p}$$
(5.6)

where l_e and l_p are the relative thicknesses of bulk electrolyte and porous layer, respectively. l_e can be defined as the distance between the counter electrode and the top surface of the oxide, which is in the order of mm; l_p can be considered as the thickness of the porous layer, which is in the order of 100 nm to 1 μ m. The ratio of relative distance can be expressed as $l_p/l_e \approx 1/1000$. ρ_e and ρ_p are the resistivity of the electrolyte, in this case, ρ is assumed to be the same in bulk and in pores.

For in-situ EIS measurement, the estimated electrolyte resistance R_e is about 5000 Ω (e.g., conductivity of primary water is about 200 μ S·cm at 360°C, see detail in Section 4.4.2) and R_p value of 10⁵ Ω is generally observed. For ex-situ EIS measurement, a higher conductivity electrolyte, 0.5 M Na_2SO_4 (i.e., $R_e \approx 600 \Omega$) was used, and the calculated volume fraction of the oxide is shown in Table 5.3. Oxide porosity was also estimated by calculating the fractions of area which was occupied by cracks with respect to total oxide area in a cross-section image of the oxide (detail of calculation is shown in Appendix A.4).

The porosity value determined from in-situ and ex-situ EIS experiment are consistent with each other, however, little discrepancies remains between the two methods, which could be an effect from the large differences in electrolyte resistivities. The SEM analysis of porosity turned out to have a porosity value much greater than the impedance methods, this result suggested that even though large porosities



FIGURE 5.51: Fitted results for electrolyte resistance in pores as a function of oxidation time.

Time	Method	Soaking Time	R_e / Ω	R_p / Ω	Vol. %				
ZIRLO TM									
130 days	SEM	-	-	-	3.77				
(pre-transition)	in-situ EIS	-	5000	77 k	0.0065				
	ex-situ EIS	0 hours	600	106 k	0.0006				
	ex-situ EIS	24 hours	600	112 k	0.0005				
180 days	SEM	-	-	-	3.62				
(post-transition)	in-situ EIS	-	5000	52 k	0.0097				
	ex-situ EIS	0 hours	600	54 k	0.0011				
	ex-situ EIS	24 hours	600	$53 \mathrm{k}$	0.0011				
Zircaloy-4									
130 days	SEM	-	-	-	3.98				
(pre-transition)	in-situ EIS	-	5000	83 k	0.0060				
	ex-situ EIS	0 hours	600	32 k	0.0019				
	ex-situ EIS	24 hours	600	51 k	0.0012				
180 days SEM		-	-	-	4.24				
(post-transition) in-situ EIS		-	5000	52 k	0.0057				
	ex-situ EIS	0 hours	600	34 k	0.0018				
	ex-situ EIS	24 hours	600	35 k	0.0017				

TABLE 5.3: Oxide porosity (vol. %) estimation of pre- and post-transition oxideusing different methods.

are present in the oxide as lateral interfacial cracks, the interfacial cracks has very limited effects on the impedance behaviour of the oxide. The most likely contributor of the diffusional impedance behaviour would be the surface cracks observed by SEM analysis on oxide surface shown in Figure 5.12 and 5.13 which are directly connected with the electrolyte and can be penetrated by the electrical signal.

Although the interfacial cracks may not be the origin for the diffusional impedance response, however, the cracks could still be filled with electrolyte and cathodic water reduction reaction would be expected to occur at such locations. This has been confirmed by the study led by Pecheur et al. (1996), which had investigated the lithium profile of the Zircaloy-4 oxide. The lithium profile in the porous oxide layer suggested that higher concentration (i.e., 3 times higher than lithium concentration in electrolyte) of lithium could be the result of electrolyte infiltrated the outer oxide during corrosion due to its porous nature.

5.6.6 Oxide Thickness Evolution

Oxide thickness, in principle, dominates the capacitance of the oxide, which can be calculated from the classical parallel plate capacitor formula in Equation 5.7. The dielectric function ε is assumed to be an intrinsic property of the material and often independent with oxidation time. However, this may not be the case for porous oxide, since water can be found in the pores, and dielectric constant of water (i.e., $\varepsilon_{H_2O} = 11$ at 600 K and water density of 0.5 g·cm⁻³, Pitzer (1983)) is comparably smaller than ZrO₂ (i.e., $\varepsilon \approx 20$, Schefold et al. (2003)) at 360°C.

5.6.6.1 Barrier Oxide Layer Thickness

Estimation of barrier oxide layer thickness $(d_{barrier})$ can be done via calculation using parallel plate capacitor formula,

$$d_{barrier} = \frac{\varepsilon_r \varepsilon_0 A}{C} \tag{5.7}$$

where ε_r and C are the relative dielectric constant and capacitance respectively, ε_0 is the permittivity of vacuum, and A is the area of the electrode. A relative dielectric constant of $\varepsilon_r \approx 15$ is used for zirconium oxide.

As shown in Figure 5.52(a) and 5.52(b), similar barrier oxide layer thickness was observed in the pre-transition regime for both alloys. During kinetic transition (i.e., around 150 days), Figure 5.52(a) and Figure 5.52(b) suggested a partial loss of barrier oxide for ZIRLOTM and Zircaloy-4, later regrowth resulted in a thicker barrier oxide. Note that there might be a second kinetic transition at about 250 days, indicated by the shift of barrier oxide layer thickness in Figure 5.52(b).


(b) Zircaloy-4

FIGURE 5.52: Barrier oxide thickness evolution as a function of oxidation time.

Time constant $\tau = RC$ is an intrinsic property of an oxide, in a parallel configuration RC circuit, τ is the product of multiplying oxide resistance R_b and capacitance C_b . A time-constant R_bC_b plot of the barrier oxide layer is shown in Figure 5.53. ZIRLOTM has shown a constant behaviour for the barrier oxide layer in pre- and post-transition regime, however, the post-transition R_bC_b value is slightly attenuated. Large variations of R_bC_b were observed at the transition phases, probably due to the development of dispersive terms during transition. R_bC_b response for the Zircaloy-4 specimens was more scattered than ZIRLOTM, However, a trend of R_bC_b $\approx 10^{-3}$ s can be obtained. Large variation at transition phase was also observed.

 R_bC_b response obtained from both alloys had shown similar values which suggests the barrier oxide layer on both alloys are consistent, although dispersive terms arise from the geometry of the electrode, porosities of the oxide and oxide thickness may contributed to the final R_bC_b values.

According to the definition of resistance $(R = \rho l/A)$ and parallel plate capacitance $(C = \varepsilon_r \varepsilon_0 A/d), \tau = RC$ can be expressed in term of resistivity (ρ) , relative dielectric constant (ε_r) and dielectric permittivity (ε_0) .

$$\tau = RC = \frac{\rho l}{A} \frac{\varepsilon_r \varepsilon_0 A}{d} = \rho \varepsilon_r \varepsilon_0 \tag{5.8}$$

where A is the area of the oxide and d = l is the oxide thickness.

The calculated resistivity of zirconium oxide barrier oxide layer is approximately $7.5 \times 10^8 \ \Omega \cdot cm$ at 360°C. However, no such data has been reported elsewhere in the literature.

5.6.6.2 Total Oxide Thickness

As shown in Figure 5.35, as the influence of the parallel conduction term in impedance decreases with increasing frequency, porous oxide capacitance (C_p) in series with the



(b) Zircaloy-4

FIGURE 5.53: Time-constant (R_bC_b) evolution for the barrier oxide layer as a function of oxidation time.

barrier oxide layer capacitance (C_b) may well approximate the total oxide capacitance, and capacitance of the total oxide layer (C_{total}) can be expressed as,

$$\frac{1}{C_{total}} = \frac{1}{C_p} + \frac{1}{C_b} \tag{5.9}$$

Time evolution of the C_{total} is shown in Figure 5.54. Small discrepancies were present in Figure 5.54(a), however, a general trend of decreasing of oxide capacitance was observed in the post-transition regime. In the pre-transition region the oxide capacitance remains relatively constant, this discrepancy can be accounted for the dielectric loss during formation of porous oxide, and later infiltration of the pores by electrolyte (i.e., at 360°C, $\varepsilon_{H_2O,25^\circ C} \approx 11$). Upon transition, oxide capacitance increases rapidly, possibly due to the enhanced penetration of electrolyte through the porous outer layer under the influence of stress relief process that occurred during transition.

A consistent trend of decreasing of C_{total} is observed for Zircaloy-4 specimens in Figure 5.54(b).

The oxide thickness can then be calculated using Equation 5.7. However, there are discrepancies between the time evolution of oxide capacitance and weight gain data, this discrepancy can be accounted for by the uncertainty of porous oxide dielectric properties. Dielectric constant of zirconium oxide might be changed during the kinetic transition, due to the physical changes of the oxide structure.

For this reason, the oxide thickness estimated by total oxide capacitance C_{total} is considered to be less accurate than the weight gain measurement and SEM analysis.



(b) Zircaloy-4

FIGURE 5.54: Time evolution of the total oxide capacitance as a function of oxidation time.

5.6.7 Porosity Development

It has been confirmed by the SEM analysis carried out on a number of samples which had different oxidation times, that cracking started at the early stage of oxidation (e.g. 25 days) and continuous formation was seen throughout the entire oxidation process. It may be inappropriate to assume that the appearance of cracks at metal/oxide interface causes the transition to occur. Cracks on the surface of the oxide were also observed by SEM analysis on both pre- and post-transition specimens, interfacial cracks formed during the pre-transition regime were interconnected with surface cracks. This is confirmed by the ex-situ soaking experiment, as evidenced by the decreasing phase angle upon increased soaking time.

The grain structure in zirconium oxide is primarily characterised as columnar grains lined up to the oxide growth direction which is perpendicular to the metal/oxide interface, due to the compressive stresses building up within the oxide (i.e. Pilling-Bedworth ratio for zirconia ~ 1.56). A diffusion process can occur through these columnar grain boundaries, creating a pathway for mass transfer (i.e. ionic species). This ionic pathway is distinct to the mass transfer pathway formed by interlinking the cracks. As the compressive stress within the oxide layer accumulating as the oxide thickens, the ionic transfer along the grain boundaries can no longer efficiently delivering the ionic species to the reactive sites (i.e. metal/oxide interface) due to closing up of these paths. Hence, a plateau can be observed after the initial rapid growth in the pre-transition regime in the weight gain plot.

During the transition regime, stress relief is possibly caused by the tetragonal to monoclinic phase transformation. Tetragonal zirconia may arrest propagating cracks through a martensitic phase transformation from tetragonal to monoclinic zirconia. Hence, a propagating crack originated in the monoclinic phase entering a region of tetragonal phase, would relieve the compressive stresses close to the level that was required to maintain the meta-stable tetragonal phase. Consequently, the tetragonal phase will undergo a phase transformation to a monoclinic phase with a resulting volume expansion. This volume expansion will put the surrounding oxide matrix in tension which will result in further cracking of the oxide. Surface morphology analysis also suggests grain boundary sliding and oxide buckling may have occurred after the kinetic transition.

On the other hand, formation of interfacial cracks, would introduced a circumferential empty space, that slows down the electric and mass transport through the oxide, due to the blocking effect of these lateral cracks. Slow oxidation was observed from weight gain and SEM oxide thickness analysis for pre-transition oxide. However, during the transition regime, more interfacial cracks were observed using SEM, but the contrary occurred, high oxidation rate was determined from weight gain measurement. This indicates that interfacial cracks were penetrated by electrolyte, thus enhanced electrical and mass transfer would occur.

Liquid transport through the cracks occurred across the outer layer, which limits the length of the oxygen ion transport path to the thickness of barrier oxide layer. This explains the rapid repassivation phase during transition regime. The structural implication of this phenomenon is that outer oxide conductance is similar to the liquid phase, which is the reason that in repassivation phase, the impedance spectra shares similar features with initial oxide growth spectra. Furthermore, electrolyte front could be shifted into the porous oxide, due to the existence of interlinked interfacial cracks and surface cracks that were filled with electrolyte.

Chapter 6

Conclusion

6.1 Conclusion

The most important contribution of this electrochemical study is the establishment of autoclave EIS technique and demonstration of the in-situ EIS measurement under the condition of pressurised primary coolant at 360°C.

The cyclic corrosion process of zirconium alloys is demonstrated as a stress relief triggered event that results in porosity development, hence influencing electrical and mass transfer through the oxide. A two layer oxide structure was observed, a barrier oxide layer in series with a porous outer oxide layer, with distinctive structural and electrical properties.

Equivalent circuit modelling and fitting results provides electrical data for various oxide layers and reactions, which can be used as references for further oxide modelling studies. The equivalent circuit element can also be used to estimate relative oxide layer thicknesses. Time evolution of the regressed parameters (e.g., C_b , R_b and C_{dl} , etc.) also confirms the changes of electrical properties during transition period. A degradation and repassivation phase during transition regime were observed in the time evolution of barrier oxide layer capacitance.

The rate-determining factor for the oxidation process was found to be the interlinking process of interfacial and surface cracks followed by electrolyte infiltration rather than the formation of interfacial cracks during the transition regime. Lateral crack formation at the metal/oxide interface can be considered beneficial, since isolated voids/cracks act as barriers to stop the electronic and mass transfer. Thus, strategies to improve corrosion resistance of zirconium alloys can aim at prevention of surface crack formation. A relatively thicker barrier oxide layer was interpreted for Zircaloy-4 from the time evolution of regressed C_b element, which can be correlated with the lower weight gain data, suggesting that oxidation rate maybe controlled by the thickness of the barrier oxide layer.

Porosity in the outer oxide structure was confirmed by ambient temperature soaking experiment (i.e., ex-situ EIS). Nearly every specimens showed a bilayer oxide response, indicating that porosity is a common feature throughout the oxidation of zirconium alloys in the high temperature water environment.

Macro-porosity was found on the post-transition oxide which can be immediately soaked by the high conductivity electrolyte (e.g., $0.5 \text{ M Na}_2\text{SO}_4$ solution). As a result, the impedance response for a post-transition oxide may only show the response of newly formed micro-porous and barrier oxide layer.

6.2 Overview of the contribution of this work

This work mainly focused on the impedance technique for zirconium oxide characterisation in a high temperature water environment. Impedance spectroscopy is a very efficient tool to characterise the electrical response of a particular system nondestructively. Hence, a transient process of the system can be investigated without interrupting its course. Impedance technique is also very sensitive to changes in the system that might have an influence on the electrical properties. This has been illustrated with the barrier oxide evolution process during the kinetic transition, which conventional techniques would have difficulty observing.

Due to the fact that impedance spectroscopy does not supply all the answers, SEM was used as a complementary technique to elucidate the interfacial processes and structural characters. With SEM examination carried out on specimens with different exposure times, a correlation between oxide structure and electric properties was obtained.

By understanding the impedance response of the zirconium oxide system, a more detailed corrosion mechanism was revealed, not only from a micrographic point of view, but also from an electrical point of view. Nevertheless, the oxidation process is an electrochemical process, which involves charge and mass transfer through the oxide layer, and the oxidation mechanism is closely related to these transfer processes. With the knowledge gained from this project, in parallel with researches from others, a thorough understanding of the zirconium corrosion system can be achieved, and by further applying this knowledge to developing better materials, an improved performance of the new alloy would be expected.

6.3 Future Directions

During the course of this project only two alloys were tested, the reason for choosing these materials is based on other work that had been conducted elsewhere within the project. The variety of materials under study involves many more alloy compositions and heat treatment conditions. A comparison of these materials would help us to understand the corrosion mechanisms with respect to their unique chemical composition and processing route (e.g. SPPs sizes and distribution and textures) and their oxide electrical properties. By isolating these parameters which would affect its corrosion behaviour, development of new alloys with better corrosion properties would be possible.

Hence, some systematic in-situ EIS experiments are needed, in order to determine the effects from the material parameters. Due to the large number of specimens, a more efficient testing equipment would need to be designed (i.e. modifications would be needed for the autoclave, which would enable it to accommodate multiple samples and have multiple electrical feeds).

Furthermore, only the material parameters have been considered in this study, it would be sensible to know the effects of the water chemistry. Because, knowing the corrosion environment is equally important as knowing the corroding metal. Number of parameters regarding the water chemistry may affect the outcome of materials corrosion performance (i.e. pH values, dissolved hydrogen concentration, lithium concentrations, etc.). The electrical properties of the oxide formed in these media could also be affected by the incorporation of ionic species from the solution (i.e. lithium doping, proton doping, etc.). Hence, controlling the water chemistry also would have an effect on the oxide formation and failure behaviour during service life.

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Appendix A

Calculation

A.1 Calculation of dissolved hydrogen concentration

We can assume that the water vapour pressure above the liquid is the equilibrium vapour pressure of water at 25°C, i.e. 3.17kPa (Lewis Evans 2006).

The pressure of the gas mixture is 50 psi, we need to convert the psi unit into kPa in order to subtract the vapour pressure, since 1 psi ≈ 6.895 kPa

50 psi = 50 \times 6.895 = 344.75 kPa

the pressure of the gas mixture on the liquid is

(total gas pressure) - (water vapour pressure) = 344.75 - 3.17 = 341.58 kPa

and the gas mixture consist of 5%H₂ and 95%N₂, the partial pressure of hydrogen gas is calculated as

341.58 Kpa × 5% = 17.079 kPa

we need to convert the kPa unit to atmosphere in order to calculate the dissolved hydrogen concentration, since 101.325 kPa ≈ 1 atm

17.079 kPa = 17.079/101.325 = 0.168 atm

Applying Henry's law, where $K_H(H_2) = 7.9 \times 10^{-4} \ mol \cdot dm^{-3} \cdot atm^{-1}$,

 $c_{H_2} = 7.9 \times 10^{-4} \times 0.168 = 1.327 \times 10^{-4} \ mol \cdot dm^{-3}$

To convert this to $mg \cdot dm^{-3}$, we multiply by the factor:

molar mass of hydrogen \times 1000

since $M_{H_2} = 2g \cdot mol^{-1}$

 $c(H_2) = 1.327 \times 10^{-4} \times 2 = 0.2654 \ mg \cdot dm^{-3}(ppm)$

if we want to convert to the standard temperature and pressure (STP) unit $[cm^3(STP) \cdot kg^{-1}]^1$, we need to consider the STP hydrogen density, a mole of any gas occupies 22.4 litre at STP, and 1 mole of hydrogen is 2.0158 g.

Density of hydrogen = mass / volume = 2.0158/22.4 = 0.089g/L or $0.089mg/cm^3$.

so $0.2654 \ mg \cdot dm^{-3}(ppm) = 0.2654/0.089 = 2.98 \ cm^3(STP) \cdot kg^{-1}$.

¹For dissolved hydrogen, $1cm^3(STP) \cdot kg^{-1} \approx 0.089$ ppm

A.2 Bulk Water Diffusion Coefficient Calculation

Stokes-Einstein Equation, that describes the temperature dependence of the diffusion coefficient in liquids.

$$D = \frac{kT}{6\pi r\eta} \tag{A.1}$$

where k is the Boltzman constant (i.e., 1.38×10^{-23} J/K), η is the dynamic viscosity of water (Pa·s), T is the absolute temperature and r is solute molecule radius (i.e., in the case of self-diffusion of water, r refers to water molecule radius).

According to Equation A.1, the relative diffusion coefficient $D_{H_2O,633K}$ at experimental conditions can be estimated using the expression,

$$\frac{D_{H_2O,298K}}{D_{H_2O,633K}} = \frac{T_{H_2O,298K}}{T_{H_2O,633K}} \cdot \frac{\eta_{H_2O,633K}}{\eta_{H_2O,298K}}$$
(A.2)

where $\eta_{H_2O,633K}/\eta_{H_2O,298K}\approx 0.1$ which was estimated from water dynamic viscosity vs. temperature plot (DDB 1973) and $D_{H_2O,298K}\approx 10^{-6}$ cm²/s has been used as the self-diffusion coefficient of water at room temperature (Xu et al. 2009).

A.3 Fitting Error Affecting the Calculated Results

The experimental data was fitted using CNLS regression technique (Section 3.7.1), which is a standard built-in fitting function in ZView^(R). The error estimates are calculated by testing several solutions near the 'best fit'. For example, if the best value for a particular resistor is 100 Ω , the value is increased until the goodness of fit (i.e., Chi-Squared) starts to decrease. If Chi-Squared value remain unchanged until reaching a solution that is $\pm 2 \Omega$ away from the best fit value (e.g., 100 Ω), then the error estimate would be 2% of the best fit. Often the complexity of the equivalent circuit would have large influence on the error estimates of the elements, since each individual element has its own influence on the fitting results at all frequencies. By minimising the necessary number of circuit elements used, and controlling the degree of freedom of each element, fitting error can be reduced.



FIGURE A.1: Reproduction of the equivalent circuit model shown in Figure 5.35.

An example is shown in Table A.1 for data collected from the in-situ EIS measurement on ZIRLOTM using the equvalent circuit model shown in Figure A.1. The error percentage of the fitting results remained less than $\pm 5\%$. C_p and C_b , which were used in the oxide thickness calculation remained less than $\pm 2.5\%$. Since the thickness is directly calculated from the capacitance values, the results would have the same percentage error.

Circuit Element	Fitting Result	Error	Error $\%$	
100 days				
R_b	60104 Ω	$452 \ \Omega$	0.750	
C_b	$8.385 \times 10^{-9} \text{ F}$	$8.934 \times 10^{-11} \text{ F}$	1.065	
R_{ct}	24236 Ω	725 Ω	2.990	
C_{dl}	2.771×10^{-8} F	$4.985 \times 10^{-10} \text{ F}$	1.799	
W_R	437600 Ω	$3756~\Omega$	0.858	
W_T	17.76	0.6423	3.617	
W_P	0.2364	0.001	0.522	
R_p	83399 Ω	$309 \ \Omega$	0.371	
$\dot{C_p}$	$9.331 \times 10^{-10} \text{ F}$	$2.835 \times 10^{-12} \text{ F}$	0.304	
120 days				
R_b	$40395 \ \Omega$	311 Ω	0.770	
C_b	$1.253 \times 10^{-8} \text{ F}$	$1.246 \times 10^{-10} \text{ F}$	0.994	
R_{ct}	14056 Ω	498 Ω	3.548	
C_{dl}	$2.431 \times 10^{-8} \text{ F}$	$3.431 \times 10^{-10} \text{ F}$	1.411	
W_R	990070 Ω	5626 Ω	0.568	
W_T	341	8	2.358	
W_P	0.241	0.001	0.237	
R_p	61445 Ω	218 Ω	0.356	
C_p	$1.777 \times 10^{-9} \text{ F}$	$4.738 \times 10^{-12} \text{ F}$	0.267	
160 days				
R_b	16804 Ω	$177 \ \Omega$	1.056	
C_b	$3.744 \times 10^{-8} \text{ F}$	$8.952 \times 10^{-10} \text{ F}$	2.375	
R_{ct}	9402 Ω	$265 \ \Omega$	2.829	
C_{dl}	$3.803 \times 10^{-7} \text{ F}$	$1.901 \times 10^{-8} \text{ F}$	5.004	
W_R	5.788 M Ω	$0.127~\mathrm{M}\Omega$	2.208	
W_T	21363	957	4.482	
W_P	0.492	0.002	0.367	
R_p	45011 Ω	$134 \ \Omega$	0.298	
C_p	$2.001 \times 10^{-9} \text{ F}$	$6.424 \times 10^{-12} \text{ F}$	0.319	
180 days				
R_b	40714 Ω	$262 \ \Omega$	0.644	
C_b	8.385×10^{-9} F	$8.934 \times 10^{-11} \text{ F}$	1.065	
R_{ct}	$24236~\Omega$	725 Ω	2.990	
C_{dl}	2.771×10^{-8} F	$4.985 \times 10^{-10} \text{ F}$	1.799	
W_R	437600 Ω	$3756 \ \Omega$	0.858	
W_T	17.76	0.6423	3.617	
W_P	0.2364	0.001	0.522	
R_p	83399 Ω	$309 \ \Omega$	0.371	
C_p	9.331×10^{-10} F	$2.835 \times 10^{-12} \text{ F}$	0.304	

TABLE A.1: Representative fitting results using equivalent circuit shown in Figure 5.35 for the in-situ EIS experimental data collected from the ZIRLOTM sample at 360° C.

A.4 Oxide Porosity Estimation from SEM Images

Original cross-section oxide SEM images collected using different microscope were set to the same exposure settings, and converted into binary images by applying the same image threshold setting, in which the areas representing the cracks can then be calculated as volume fraction with respect to the total oxide area, using image analysing software, ImageJ^(R). The original and binary images of each oxide studied was shown in Figure A.2 to A.5, and the calculated volume fraction is presented in Table A.2.



FIGURE A.2: Oxide porosity estimation for the 130 days $ZIRLO^{TM}$.

Exposure Time /days	vol. %		
ZIRLO TM			
130	3.77		
180	3.62		
Zircaloy-4			
130	3.98		
180	4.24		

TABLE A.2: Oxide porosity calculated from SEM images.



FIGURE A.3: Oxide porosity estimation for the 180 days ZIRLOTM.



FIGURE A.4: Oxide porosity estimation for the 130 days Zircaloy-4.



(a) SEM Image



FIGURE A.5: Oxide porosity estimation for the 180 days Zircaloy-4.

Appendix B

Electroless Nickel Plating

B.1 Solutions and Procedures

B.1.1 Applications

Chemically produce a uniform thickness nickel-phosphorus alloy layer on the substrate, providing good adhesion and protection when doing sample preparation.

B.1.2 Solution Recipe

Solution A: Surface Activator

Pd/Sn colloidal is used, which contains the following ingredients:

- 100 mg $SnCl_2$
- 25 mg PdCl₂
- 7.5 ml of 37% HCl
- $\bullet~15~\mathrm{ml}$ of DI water

Solution B: Nickel Source

• 38g/L Nickel Sulphate (Generally, a Nickel salt will do.)

Solution C: Reducing Agent

Reducing nickel from the source solution, with aid from the Pd/Sn colloidal particles which deposited on the substrate.

- 26g/L Sodium Hypophosphite
- 16g/L Sodium Acetate anhydrous
- 5 drop of 0.5 M hydrochloric acid to control the pH

B.1.3 Procedure

Make sure all three solutions are ready.

- Clean the specimens with some organic solvent to remove any oil or dirt
- Rinse with DI water
- Immerse the specimens into 0.5M nitric acid solution to remove any contamination
- Rinse with DI water and blow dry
- Immerse the specimens into solution A (activator) for 2 mins
- Rinse with DI water thoroughly
- Mix solution B and C (both solution needs to be at 85° C) and keep stirring
- Immerse the specimens into the plating bath (mixture of solution B and C) for 2 hours (depending on the coating thickness required, $2h \sim 10\mu m$)
B.1.4 Extra Information

Plating solution needs to be filtered during the process, because deposits of nickel metal will appear after 30 mins, making the plating result less satisfactory. By filtering the deposited metal out of solution, a better surface finish can be achieved. A simple way to achieve this is by keep passing the solution through a filter directly above the plating bath.