Effect of pH on Coatings Used to Protect Aluminum Beverage Cans

by

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Abstract

This study investigated the performance of epoxy-free coatings used to protect aluminum beverage cans from corrosion in acidic solutions. Electrochemical Impedance Spectroscopy and cyclic voltammetry tests were used to distinguish good and bad coatings by monitoring the corrosion of the underlying aluminum. The goal of this work was to understand how coatings protect the aluminum in spite of holes and holidays in the coating. Bad coatings were made by introducing pinholes. Three scenarios were found to hinder or stop corrosion: change from neutral to acidic pH, de-aeration using carbon dioxide gas, and the formation of bubbles. This study concluded that the formation of bubbles on the exposed surface of the aluminum, in concert with the coating, protects the aluminum from corrosion in acidic solution.

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Chapter 1 Introduction

1.1 Background

Aluminum used to make beverage cans is coated inside and outside with a resin to protect from corrosion. Beverage cans made with aluminum alloy are favoured due to them being lightweight and their ability to be recycled [1]. They are also easier to transport and store compared to beverage containers made of glass. Aluminum beverage cans have good anti-corrosion properties in neutral solutions, however, in the presence of acidic solutions aluminum corrodes [1]. For instance, Coke™ has a pH 2.38 and Diet Coke™ has a pH 2.92 [2]. Epoxy resins are commonly used as coatings to protect aluminum from corrosion [3]. A resin starts as a liquid which changes to a solid with a hard finish when set [3]. Two types of resins exist: natural, also called oleoresins, and synthetic. Traditionally synthetic epoxy resins are used to coat beverage cans. These resins contain bisphenol A (BPA), which is introduced into the coating during production [4]. There is a concern that BPA may leach into the liquid contained inside beverage cans.

BPA is included in the Domestic Substances List (DSL), which identifies substances used in Canadian commerce [5]. This list is updated by the Chemicals Management Plan (CMP), managed by Environment Canada and Health Canada [5] [6]. CMP assesses chemicals to determine if they are harmful to human health. If a chemical is found to be harmful, the CMP takes action to protect consumers [6]. The CMP identified BPA as a chemical of concern [4].

1.2 Problem

Health Canada has decided to focus on BPA intake in infants because baby formula is often stored in cans coated with resins containing BPA or in plastic bottles that contain BPA [4]. The decision was based on the possibility of formula being the only nutrition an infant receives. Health Canada reviewed reports, submitted by the Plastic Industry (SPI), on the effects BPA had on human health. Toxicology studies submitted before 1979 were also reviewed. It was found that BPA may affect the reproduction system in high doses (139 times higher than the probable intake for the general public and 9.5 times higher for infants). This was due to it behaving similarly to estrogen and possibly acting as an endocrine disruptor [4]. Reports, with dates ranging from 2004 to 2007, describe the effects of high doses of BPA on rats and mice. These reports showed that very high doses were capable of causing side effects such as behavioural changes (mice became more anxious), and an increase in certain hormones in rats during early puberty (testosterone in males and estradiol in females). These very high doses, however, ranged from over 1 thousand to 11 million times the probable intake for the general public, and 76 to 76 thousand times the probable intake for infants [4].

Health Canada determined that at current levels of BPA consumption for the general public and infants, BPA does not pose a health risk, because of the extreme doses required to see side effects in rats and mice [4]. Japan, the United States, the European Union, and other health agencies published the same conclusion. Health Canada, however, stated that further research must be conducted on the effects of BPA, especially in infants, to address several drawbacks found in reports from 2004 to 2007. Some of these drawbacks include certain tests using only single doses of BPA, not being able to

reproduce results in other laboratories, and lack of consistency. In the meantime, Health Canada has recommended that exposure to BPA from food packaging should be lowered [4]. The US Food and Drug Administration (US FDA) has also stated that they would support the exposure of BPA being lowered or eliminated in can coatings [3]. Industries have started to look for alternatives to epoxy resins that would not contain BPA, but would be able to protect the food, maintain the same quality, and not cause health risks greater than that of BPA [3] [4].

In spite of the unrealistically high doses required to produce side effects, the perception of the general population is that BPA is bad for human health. Thus, removing BPA is a priority for the food and beverage industry.

1.3 Thesis Objective and Scope

The objective of this thesis was to answer the following question:

- How can beverage can coatings work in low pH solutions despite the presence of holidays?

We want to understand how the coatings work to aid in the development of BPA-free coatings because BPA is a safety concern for the public.

The scope of this thesis was to conduct short-term tests on beverage can material using Electrochemical Impedance Spectroscopy (EIS) and cyclic voltammetry. Tests were conducted in solutions that simulated soft drinks, and in solutions with pH of 0 and 7 to understand the effect of aluminum oxide formation. Acidity of commercial soft drinks varies greatly; the pH of beverages are typically between pH 2.3 to pH 4 [2] [7]. For instance, Coke™ is pH 2.38, and Barq's Root Beer is pH 4 [2] [7].

Beverage can coatings are thought to provide a barrier between the liquid and the aluminum, however, these coatings have pores, flaws, defects and holidays¹. In addition, aluminum is not protected by an adherent oxide layer at low pH because aluminum oxide is not stable (Section 2.3.1). Hence, if the coating is not a perfect barrier, and low pH solution is able to reach the underlying aluminum, then the can should fail rapidly from corrosion. Even though these coatings have holidays, the cans can last for years. Initially, it was believed that the coatings would perform better in neutral solutions than in acidic solutions because a protective plug of stable aluminum oxide would fill the pathways that exist between holidays and pores that lead to the aluminum surface. Figure 1-1 shows the pores connecting to create pathways to the aluminum surface.

Figure 1-1: Schematic of a Coating Containing Linked Pores

Contrary to this expectation, previous experiments have shown that beverage can coatings performed better in acidic pH than neutral [8]. The goal of this work is to understand how a coating with holidays can perform better in acidic solution than neutral,

¹ Holidays are defects in a coating; they are small holes in a coating where the base metal is unprotected [23] [57]

and the implications for new BPA-free coatings. The work in this thesis is a continuation of the work presented in the thesis by M. Ali [8].

1.4 Organization of Thesis

This thesis contains 5 chapters. Chapter 1 discusses background information on beverage cans, as well as the problem definition and objective of this thesis. Chapter 2 introduces the reader to the concept of EIS, as well as a literature review of the latest research related to this thesis. The experimental setup and the equipment used are described in Chapter 3. Chapter 4 covers the test results and Chapter 5 the discussion of these results. Chapter 6 presents the conclusions and recommendations for future experiments.

1.5 Methodology

The research in this thesis was conducted using EIS and cyclic voltammetry. A pinhole through the coating was created in aluminum beverage can samples to represent a holiday. The pinhole was then tested to examine the behaviour of the coating when it was exposed to three different effects: change of pH, de-aeration of the solution, and bubble formation. The methodology is discussed in greater depth in Chapter 3.

Chapter 2 Literature Review

2.1 Electrochemical Impedance Spectroscopy

An EIS experiment uses a sinusoidal voltage or current perturbation [9]. The perturbation is applied over a range of frequencies, which makes it possible to measure and analyze the electrochemical response over a wide frequency range. EIS is widely used due to the large amount of data and information that it provides. It is used in many fields including: corrosion, fuel cell development, paint characterization, and battery development [9]. EIS was created in the 1880s by Oliver Heaviside [10]. Soon after A. E. Kennelly and C. P. Steinmetz generated complex number equations and vector diagrams that made it possible to better present EIS data [10].

2.1.1 Basis of Impedance

In an electrical circuit, impedance, Z , is related to voltage and current by Ohm's Law:

$$Z = \frac{V(t)}{I(t)} \quad 2-1$$

where $V(t)$ and $I(t)$ are the time dependent voltage and current, respectively [10]. In the special case where there is no time dependence, the impedance is known as resistance and is given the symbol R . In this case Ohm's Law becomes:

$$R = \frac{V}{I} \quad 2-2$$

Voltage (or potential) is measured in volts [V], current is measured in amperes [A], and resistance and impedance are measured in ohms [Ω] [10].

Impedance includes information on the phase difference that occurs between voltage and current. Impedance can be separated into a real portion, which is the in-phase component associated with energy loss, and an imaginary portion which is the 90° out-of-phase component associated with storing electrical energy [10].

In this thesis, sinusoidal voltages are applied across coatings and the resulting time-dependent currents are measured [11]. The voltage can be expressed as [10]:

$$V(t) = V_A \sin(2\pi ft) = V_A \sin(\omega t) \quad 2-3$$

where V_A is the amplitude [V], f is the frequency [Hz], t is the time [s], and ω is the radial frequency [rad/s]. In this thesis, for the voltage amplitudes used, the current response was linear, with the same shape and frequency, but with a phase shift between 0 to $-\pi/2$ rads (0° to -90°). The equation for the current response is [10]:

$$I(t) = I_A \sin(\omega t + \theta) \quad 2-4$$

where I_A is the current amplitude [A] and θ is the shift in phase [rads]. Figure 2-1 shows a plot of the current response to a sinusoidal voltage input. Depending on the circuit, the current will either lead or lag the voltage [10]. In Figure 2-1 the current is leading the voltage by the phase shift θ .

Figure 2-1: Current Response to a Sinusoidal Voltage Input at a Given Frequency
[10]

The voltage function and current function can be expressed as a complex relationship [10]:

$$V(t) = V_A e^{j\omega t} \quad 2-5$$

$$I(t) = I_A e^{j\omega t - j\theta} \quad 2-6$$

where j is equal to $\sqrt{-1}$. Using equations 2-1, 2-5 and 2-6, the impedance equation can be written as [10]:

$$Z = Z_A e^{j\theta} = Z_A (\cos \theta + j \sin \theta) \quad 2-7$$

where the last relationship is determined using Euler's equation. Equation 2-7 can be separated into real and imaginary components as follows [10]:

$$Z_{real} = Z_A \cos \theta = Z' \quad 2-8$$

$$Z_{img} = Z_A \sin \theta = Z'' \quad 2-9$$

$$Z = Z' + jZ'' \quad 2-10$$

Impedance can also be expressed equivalently by using its magnitude [10]:

$$|Z| = \sqrt{(Z')^2 + (Z'')^2} \quad 2-11$$

and a phase angle [10]:

$$\theta = \tan^{-1} \frac{Z''}{Z'} \quad 2-12$$

In this thesis, impedance will be described in terms of its real and imaginary components and/or its magnitude and phase angle.

2.1.2 Circuit Elements

The electrical responses of coatings used to protect beverage cans can also be described in terms of passive linear circuit elements. Table 2-1 lists the typical circuit elements that are used when modelling EIS results.

Table 2-1: Circuit Elements [10]

Component	Equivalent Element	Impedance
Resistor	R [ohm]	R
Capacitor	C [F, or ohm ⁻¹ s]	$1/j\omega C$
Inductor	L [H, or ohm s]	$j\omega L$
Constant Phase Element	Q [ohm ⁻¹ s ^{α}]	$1/Q(j\omega)^\alpha$

Table 2-1 shows that the impedance of a resistor is independent of frequency [10]. There is only a real component to the impedance of a resistor. Hence, the voltage and current are always in phase with each other.

A capacitor is another passive electric circuit element [11] [12]. A typical configuration of a capacitor consists of a material, known as a dielectric, sandwiched on two sides by conducting plates. A capacitor can store energy. For a capacitor, the impedance decreases as the frequency increases [10]. A capacitor only has an imaginary impedance component. Unlike a resistor, the current of a capacitor is shifted -90° to its voltage. The capacitance can be calculated using the following equation:

$$C = \frac{\epsilon_o \epsilon A}{d} \quad \mathbf{2-13}$$

where C is the capacitance [F], A is the area of the electrodes, d is the distance between the electrodes, ϵ_o is the constant electrical permittivity of a vacuum ($8.85 \cdot 10^{-14}$ F/cm) and ϵ is the relative permittivity of the material between the electrodes (which reflects the ability of the material that is being analyzed to store electrical energy) [10]. In this thesis, the dielectric material will be the coating, which is attached on one side to the aluminium beverage can alloy. The alloy acts like one of the plates of a capacitor. The other side of the dielectric coating is exposed to solution containing electrolytes, which behaves like the second plate of the capacitor.

An inductor is another passive electric circuit element [10]. While it also has only an imaginary impedance like a capacitor, its impedance increases as frequency increases and its current is shifted $+90^\circ$ compared to its voltage [10].

A fourth passive circuit element used in modelling EIS spectra is the constant phase element (CPE). The equation for the impedance of a CPE contains a parameter α ,

which can be used when the dielectric is fractal or as a fitting parameter [13] [14]. As an example, the double-layer capacitor, discussed in Section 2.2 , is described as a CPE [10]. There exist special cases for values of α . When α is equal to 1, then the CPE coefficient, Q , is equal to C , and the CPE impedance is equivalent to the impedance of a pure capacitor. If α equals 0 the CPE impedance becomes the impedance of an ideal resistor, where R is equal to $1/Q$. If α equals -1 the CPE impedance becomes equivalent to the impedance of an inductor. There also exists another special case when α is equal to 0.5, where the CPE impedance becomes the Warburg impedance for homogenous semi-infinite diffusion [10].

Passive circuit elements can be combined to create equivalent circuits which model electrochemical systems. Two simple circuits are shown below. A resistor and capacitor in series, known as a R|C circuit, is shown in Figure 2-2.

Figure 2-2: A Resistor and Capacitor in Series (R|C Circuit) [11]

The impedance of a R|C circuit can be calculated as [11]:

$$Z = R + \frac{1}{j\omega C} \quad \mathbf{2-14}$$

When a resistor and a capacitor are in parallel with each other a R||C circuit is formed, shown in Figure 2-3.

Figure 2-3: A Resistor and Capacitor in Parallel (R||C Circuit) [10]

The impedance of a R||C circuit can be calculated as [10]:

$$\frac{1}{Z} = \frac{1}{R} + \frac{1}{j\omega C} \quad 2-15$$

$$Z = \frac{\frac{1}{R} - j\omega C}{\left(\frac{1}{R}\right)^2 + (\omega C)^2} \quad 2-16$$

2.1.3 Nyquist Plots

A Nyquist plot, also called a complex plane impedance diagram, is created when the negative imaginary portion of the impedance equation (Equation 2-10) is plotted on the vertical axis and the real portion is plotted on the horizontal axis [10] [15]. Each point on the Nyquist plot is the impedance at one frequency. Figure 2-4 shows a Nyquist plot for a typical R||C circuit. The impedance can be expressed as a vector on the Nyquist plot [11] [15]. This vector has a length equal to the magnitude of the impedance (Equation 2-11). The phase angle can also be expressed as the angle between the impedance magnitude vector and the horizontal axis (Equation 2-12).

Figure 2-4: Nyquist Plot for a R||C Circuit Showing Impedance Vector and Other Major Features [11]

In Figure 2-4 the frequencies are implicit in the plot. Following the curve from right to left the frequency increases, as shown by the arrow. This does not occur for all circuits or at all AC frequencies but is usually the case when impedance increases as frequency decreases [10] [15].

An advantage of a Nyquist plot is that if a dielectric has multiple components with different time constants, it will be readily seen in the plot [10] [12]. A plot with a single semi-circle will have one time constant. For each additional semi-circle there exists another time constant. In general, the time constant can be expressed as:

$$\tau = RC \quad \quad \quad \mathbf{2-17}$$

where the R and C depend on the components. The magnitude of the resistor is the diameter of the semi-circle in a Nyquist plot. This thought to be due to the impedance being purely capacitive at the highest frequency but purely resistive at the lowest frequency. As the frequency approaches zero, the impedance approaches the value of the

resistor. Examples of processes with single time constants are charge-transfer and activation-energy-controlled mechanisms [10].

A Nyquist plot does not always have a single full semi-circle with the center of the semi-circle on the real axis [13]. There are several reasons for why the center of the semi-circle may be located in the complex plane. One scenario is where the arc does not pass through the origin. This may be caused by R_{∞} having a value greater than zero and/or the plot containing more arcs at higher frequencies. Another scenario is when the material-electrode system contains distributed elements. This will cause the time constant to no longer equal a single value, but instead be distributed continuously or discretely around a mean time constant. The width of the distribution of a time constant is related to the angle by which a semi-circle arc has been depressed below the real axis. Another reason for distorted semi-circle is the presence of other mean time constants that have values within two orders of magnitude or less of the semi-circle being analyzed. Overlapping semi-circles may be observed if this occurs [13].

The inductive loop is another feature of a Nyquist plot [10] [16] [17] [18]. It appears as a loop with a positive imaginary component at lower frequencies². Strictly speaking these are pseudo-inductances that occur because of chemistry on the surface. For instance, the appearance of an inductive loop has been associated with weakening of the protective aluminum oxide layer by the dissolution of the aluminum alloy [10] [16] [17] [18].

The shape of a Nyquist plot can reveal if a coating is functioning well or if it has failed [10]. An ideal perfect coating would appear as a vertical line in the Nyquist plot, similar to the one shown in Figure 2-5 [10].

² Can also occur at higher frequencies due to mutual inductance [56].

Figure 2-5: Nyquist Plot for an Ideal Coating [11]

The corrosion process involves transfer of electrons. *If the coating performs well as an electrical barrier, it will also perform well as a corrosion barrier.*

2.1.4 Bode Plots

Another common way to represent EIS data is to use a Bode plot, in which the frequency dependence is shown explicitly [10] [15]. In the Bode plot, the phase angle and the logarithm of the impedance magnitude are plotted against the logarithm of the frequency. Figure 2-6 shows a Bode plot for an ideal coating. The impedance of an ideal coating behaves like a capacitor; it is very high at low frequencies (*i.e.*, greater than $10^{10} \Omega$ at 0.1 Hz for the coatings used in this work), the impedance plot is a straight line with a slope of -1, and the phase angle is -90° [11]³. In this thesis, positive phase angles and impedances with a positive slope are indications of a bad coating; when these features are present the underlying aluminum is corroding. This interpretation is supported by the

³ The rise in phase angle at high frequencies is due to inductance of the cables. See footnote 2.

observation that when cathodic protection is applied, positive phase angles and impedances with positive slopes disappear [8].

Figure 2-6: Bode Plot of an Ideal Coating [11]

2.2 Test Cell and Electrodes

An EIS experimental setup consists of an electrolyte, a working electrode, a counter electrode, and a reference electrode [19]. The working electrode is where the corrosion reactions occur in the electrochemical system. In this study, the working electrodes are the coated aluminum samples. The counter electrode is usually an inert material, like graphite, that is used to complete the current path in the test cell, and to act as a current source and current sink. A reference electrode provides an offset potential relative to a standard [19].

The three common experimental setups for studying coatings use 2 or 3 electrodes [19]. Generally, electrodes are solids immersed in electrolyte [19]. Figure 2-7 shows a schematic of a typical test cell. The reference and counter electrodes are inserted into the electrolyte [20]. The working electrode is held flush against one side of the cell. The

right end of the cell contains a through hole that allow electrolyte to make contact with the working electrode [20].

Figure 2-7: Schematic of a Typical Test Cell

In a typical experiment electrical connections are made between the measuring instrument and electrodes using 4 leads: working, counter, working-sense, and reference [19]. Figure 2-8 shows schematics for 2 and 3 electrode setups. The working and counter leads carry the current, while the working-sense and reference leads measure the potential. A reference electrode is capable of maintaining a constant potential. Ideally it experiences only minimal current flow so that its voltage is unaffected by the current flowing in the cell. When the currents are low in the test cell (less than or equal to μA) the counter electrode can be used as the reference electrode since the potential drops are miniscule; this is a 2 electrode setup [19]. In this type of setup the working and working-sense electrodes are connected together, and the counter and reference electrodes are

connected together. In this case the inert material of the counter electrode is acting as a reference point for the measured potential, as well as the counter electrode [19].

Figure 2-8: 2 Electrode Setup (Left) and 3 Electrode Setup (Right) [19]

A 3 electrode cell also has the working and working sense electrodes connected together, but has separate counter and reference electrodes [19]. The potential of the counter electrode can change without affecting the potential between the working electrode and reference electrode. Using an independent reference electrode in this way allows accurate measurement of the potential of the working electrode [19].

An electrode and an electrolyte form an electrical double layer at their interface [11]. When ions from the electrolyte attach themselves to the electrode surface the double layer is formed. The double layer causes the charged electrode to be separated from the charged ions in the electrolyte. This separation, which is usually on the order of 0.1 nanometers (10^{-10} m), causes a double layer capacitance to form. The double layer capacitor is influenced by many factors including: temperature, oxide layers, electrode roughness, and electrode potential [11]. The double layer capacitor creates an energy barrier between the metal and the electrolyte [21].

2.3 Corrosion

Corrosion is defined as the reaction, either chemical or electrochemical, of a material with its environment which causes the material to deteriorate [22]. Corrosion characteristically occurs in electrolyte solutions. An electrolyte may be alkaline, neutral or acidic. When a metal is immersed in an electrolyte and begins to corrode there is a transfer of electrons between two different areas on the metal. An area of a metal that is giving up electrons is called an anode. An area where the electrons are being absorbed is called a cathode. An electrical circuit forms since there exists a potential difference between the anode and cathode. Electrons flow through the metal from the anode to the cathode and ions diffuse through the solution, in particular positively charged ions and solutes, *e.g.*, H^+ and O_2 , flow from the electrolyte solution to the cathode, where they are reduced by electrons [23].

An anodic reaction occurs when electrons are produced. It also called an oxidation [22]. The general anodic reaction is:

The anodic reaction for aluminum is [24]:

A cathodic reaction, or a reduction, occurs when electrons are consumed. Several cathodic reactions can occur during metallic corrosion [22]. More than one cathodic reaction and one anodic reaction can occur simultaneously. When a metal is exposed to an acidic solution, hydrogen reduction is the cathodic reaction. The hydrogen reduction reaction equation is:

Hydrogen gas is produced when hydrogen ions react with the electrons produced by the anodic reaction.

Oxygen reduction is another cathodic reaction. It can occur in a mildly acidic solution in the presence of air. If the solution is exposed to air the following reaction may occur [22]:

In neutral or basic solutions the cathodic reaction is also called an oxygen reduction reaction. The oxygen reduction equation for basic or neutral solutions is as follows:

During corrosion, both cathodic and anodic reactions must occur simultaneously. They must also occur at the same rate to conserve charge. There must be equal production and consumption of electrons [22].

2.3.1 Aluminum

A thin protective corrosion product film forms on the surface of most metals and alloys [25]. The thin film is a result of the metal or alloy reacting with its environment. Without the thin film on its surface a metal would return to its thermodynamically stable condition. Some metals and alloys produce a film that creates a corrosion resistant surface. These films are called passive films and are the cause of passivity of a metal or alloy. [25]

Passivity is difficult to define but can be considered as a metal or alloy losing its chemical reactivity when placed in certain environments [22]. A metal or alloy that has become passive can be thought of as becoming inert and acting as a noble metal [22].

The ability of aluminum to resist corrosion is caused by its capacity to passivate under certain conditions [25]. The passivity of aluminum is caused by the formation of a barrier oxide layer that protects the underlying aluminum from particular corrosive environments. The formation of a protective oxide film in solutions of different pH can be predicted approximately by using a Pourbaix diagram, which can be used to determine at which thermodynamic conditions the oxide layer may form. Figure 2-9 gives the Pourbaix diagram for aluminum in 25 °C water [25].

Figure 2-9: Pourbaix Diagram for Aluminum and Water System at 25°C [25]

The diagram contains three types of regions: an immunity region, a passivation region, and two corrosion regions [26]. The immunity region, where the metal is immune to corrosion, is bounded above by lines 1, 2, and 3. Line 1 corresponds to the equilibrium reaction [24]:

Line 2 corresponds to the equilibrium reaction:

Line 3 corresponds to the equilibrium reaction:

In the passivation region, the oxide that forms depends on the environmental conditions [24] [25]. At lower temperatures, aluminum trihydroxide, $Al(OH)_3$, tends to form. At higher temperatures, boehmite, $Al_2O_3 \cdot H_2O$, tends to form. Hydrargilite, $Al_2O_3 \cdot 3H_2O$, may form if aluminum hydroxide is aged. At very high temperatures, above approximately 230 °C, a protective oxide no longer forms. The pH at which the oxide is considered most stable is approximately 5, shown as line *c* [24] [25].

There are two corrosion regions in Figure 2-9, at high and low pH. Soluble Al^{3+} ions form at low pH values using equation 2-23. The soluble ions are in equilibrium with the insoluble oxide shown by the vertical concentration lines on the left of the Pourbaix diagram:

At high pH values, the soluble AlO_2^{-} ions are in equilibrium with the insoluble oxide shown by the vertical lines on the right of the Pourbaix diagram:

Lines *a* and *b* in Figure 2-9 give the thermodynamic stability of water. These limits are for water at 1 atmosphere and at 298 K. For the area below line *a*, water becomes unstable due to the formation of hydrogen gas, which corresponds to the following half reaction:

In the area above line *b*, water is unstable due to the formation of oxygen gas. Oxygen gas formation corresponds to the following half reaction:

Between lines *a* and *b* water is stable relative to oxygen and hydrogen gas.

It is important to define the ionic activity that will be used to determine if significant corrosion is occurring. An allowable amount of metal dissolution must be decided upon to determine if there is corrosion. A solubility of 10^{-6} g atoms of soluble ion per litre is customarily used as a threshold for the metal to be immune to corrosion. The horizontal and vertical lines labelled 0 to -6 in Figure 2-9 are marked with the logarithm of the activity and are used to determine the concentration.

Using this potential versus pH diagram, aluminum is passivated between approximately pH 4 and 9 where stable aluminum oxide can form. The passivity of aluminum is also influenced by the temperature of the aqueous solution, the type of oxide that develops, and the assumption that there is a low dissolution of aluminum. Multiple types of oxides show very little solubility at approximately pH 5 [25].

When placed in water or in atmospheres that are at ambient temperature the oxide layer that develops to protect the aluminum is amorphous and has a thickness of a few

nanometers. However, when the temperature is increased, the thickness of the protective oxide that is formed is also higher [25].

Using Figure 2-9 it can be seen that aluminum will corrode in alkaline and acidic solutions due to the fact that no protective oxide forms in these solutions. When it corrodes in alkaline solutions aluminum forms AlO_2^- ions. In acidic solutions Al^{3+} ions form. There are cases where the oxide layer is insoluble in solution or where it is stable due to the oxidizing characteristics of a solution; acetic acid and sodium disilicate are two examples. Due to the possibility of several different ions that can be present depending on the environment, and due to the large influence ions have on the corrosion of aluminum, there is no general relationship between corrosion rate and pH [25].

2.3.2 Polarization

A polarization curve, also known as an Evans diagram, is useful since it demonstrates the kinetics of corrosion and not just the thermodynamic condition given by the Pourbaix diagram [25]. The curve can be presented with potential (V) on the vertical axis and the current density (I) on the horizontal axis, or vice versa [26]. The current density is usually graphed on a logarithmic scale and with units of A/cm^2 or A/mm^2 depending on the sample size. The current is a direct measure of the corrosion rate at that particular voltage [26].

The two main polarization test procedures are galvanostatic and potentiodynamic [26]. In the galvanostatic procedure, current is controlled by the instrument while the potential is recorded. Using the potentiodynamic procedure, the potential is controlled while the current is measured [26].

During a potentiodynamic polarization test the voltage is first increased in the anodic direction, which is known as a forward scan [25]. After reaching a pre-set voltage, the voltage is decreased in the cathodic direction, which is known as a reverse scan. A cyclic voltammetry test is a type of potentiodynamic test where there can be one or several forward and reverse scans. The corrosion potential is the potential at which the anodic current, also called the corrosion current, and cathodic currents are equal [27]. The corrosion potential is usually the voltage selected as the starting point of a test [25].

A hysteresis loop is a common feature [25]. It occurs when the curve does not follow the same path during the reverse scan as it did during the forward scan. A hysteresis is created when there is a difference in current density between the two scans at the same potential. A change in the chemical condition at the surface is responsible for this feature. This may be passivation or the formation of permanent pits, which have the opposite effects [25].

If the current density is greater on the reverse scan than on the forward scan, then the corrosion rate has increased [25]. This can be symptomatic of localized corrosion, such as pitting, that was induced during the forward scan. This clockwise loop is called a positive hysteresis. A counter clockwise loop negative hysteresis occurs when the current density is lower during the reverse scan than it was during the forward scan at the same potential. This implies that re-passivation is occurring more readily than during the forward scan. It can indicate that the sample is resistant to localized corrosion. Figure 2-10 shows the forward scan of an active-passive metal [25].

Figure 2-10: Evans Diagram for Active-Passive Metal [28]

An increase in metal corrosion rate is responsible for the increase in current density above the corrosion potential [25]. At a maximum in current density, known as the critical current, a high corrosion rate is observed. The potential at the critical current is known as the passivation potential. Between the corrosion potential and the passivation potential the metal is in an active state. The passivation potential is the beginning of a transition between the active and the passive state, when a passive oxide film begins to form on the surface of the metal, limiting the corrosion current. Since the system is entering a passive state, the current density decreases. The passive current is a constant current and is no longer dependent on the potential. At this time the rate of formation and the rate of dissolution of the oxide are equal, resulting in a dynamic

equilibrium. The current density can once again increase if the oxide film that formed during passivation breaks down. The break down can be caused by weak points within the film, and often marks the start of pitting, in which case the potential at which this occurs is called the pitting potential. Figure 2-11 shows some of the major features that occur on a potentiodynamic polarization curve [25].

Figure 2-11: Polarization Curve Displaying Common Features

In this thesis, the underlying metal in the samples produced polarization curves similar to Figure 2-11. When the coating was behaving as a good coating, the current density would not increase or decrease with a change in potential, and would have a value near the low-current limit of the equipment. When the coating was behaving as a bad coating, the cyclic voltammetry test was able to detect the corrosion of the underlying aluminum.

2.3.3 Environmental Variables

The presence of oxygen in a solution has an influence on the corrosion of aluminum [25]. In a de-aerated solution, the corrosion of aluminum can be very slow. When there is O_2 present, however, corrosion occurs much faster. As the concentration of dissolved oxygen in solution is increased, the corrosion rate also increases since oxygen encourages attack. In particular this can be observed in acidic solutions [25]. Chloride ions have been suggested to hinder the motion of oxygen vacancies located in the oxide [29]. Hydrogen and nitrogen gases do not influence the rate of corrosion [25]. Hydrogen sulphide and carbon dioxide have been observed to minimally slow down the corrosion rate. This occurs even when their concentrations are high.

The concentration and nature of an acid affects the corrosion rate of aluminum [25]. At room temperature a dilute sulphuric acid solution with a concentration approximately 40% to 95% causes aluminum to corrode rapidly. If the concentration is reduced to approximately 10% then the speed of the attack on the aluminum is greatly reduced. A reduction in the corrosion rate also occurs at very high concentrations. A dilute solution of phosphoric acid, with a concentration of less than 1%, does cause corrosion in aluminum by etching the surface. When raised to an intermediate concentration, the phosphoric acid no longer etches the surface of the aluminum but instead attacks it more severely. Above approximately 0.1% concentration hydrobromic, hydrofluoric and hydrochloric solutions cause aluminum to corrode [25].

The concentration of an alkaline solution also affects the corrosion of aluminum [25]. Above 0.01% concentration sodium hydroxide and potassium hydroxide solutions are highly corrosive to aluminum. Nearly neutral solutions, pH ranging from

approximately 5 to 8.5, of inorganic salts cause very little, or even a negligible amount of corrosion at room temperature. If inorganic salts at this pH range do cause corrosion to occur in aluminum it is usually highly localized in the form of pitting [25].

2.3.4 Corrosion of Aluminum

Pitting is a localized form of corrosion that causes a loss of metal [23]. It can be a deep hole in a metal with a small opening on the surface. Pitting corrosion is difficult to detect. As corrosion progresses the depth of the pit can increase significantly while the opening increases very little. Frequently the opening may be covered in corrosion product making it even more difficult to detect. It is also difficult to detect since pitting does not cause a decrease in thickness of the metal or a large loss in weight. If a pit is allowed to continue to grow it may eventually penetrate the thickness of the material and may cause the component to fail [23].

The reaction within a corrosion pit is an anodic reaction that is a unique autocatalytic process [22]. An autocatalytic process within the pit means that the corrosion process that occurs does not only stimulate corrosion to continue but also empowers the pit to keep growing. Figure 2-12 shows the autocatalytic process that occurs within a corrosion pit in a metal. In this figure the metal is exposed to aerated sodium chloride [22].

Figure 2-12: Corrosion Pit in Metal M Displaying Autocatalytic Process in Aerated NaCl [22]

Within the pit there is a rapid dissolution of the metal [22]. On the surface of the metal adjacent to the pit a cathodic reaction takes place, in this case oxygen reduction. Since the rate of dissolution of the metal within the pit is very fast, a positive charge is produced in this area. The positive charge draws the negatively charged chloride ions into the pit. There is therefore a high concentration of MCl inside the pit. There is also a high concentration of hydrogen ions caused by hydrolysis. In this case this reaction is [22]:

The high concentrations of hydrogen ions and chloride ions accelerate the dissolution of metal and cause the pit to grow [22].

There are four major stages of pitting [30]. The first stage includes processes that occur at the boundary between the passive film and the solution. The second stage includes the processes that occur within the passive film. At this stage no visible microscopic changes have occurred. During the third stage metastable pits initiate and grow. They grow for a short amount of time and stay below the critical pitting potential. The metastable pits are small. The pits then repassivate. The time it takes for a metastable pit to grow and repassivate can be only a few seconds. At the fourth stage the pits experience stable growth. This occurs above a potential called the critical pitting potential. Figure 2-13 shows a sample polarization curve which shows the formation of pits [30].

Figure 2-13: Polarization Curve Showing Pit Formation [31]

E_{cp} is the critical pitting potential in this figure. The figure shows the metastable pits forming below the critical pitting potential. When the metastable pits form, the current oscillates. It increases when the pits form and grow [30]. After a short amount of time the current decreases due to the pits repassivating. Figure 2-13 shows how this behaviour appears as a zigzag pattern on a polarization curve. Metastable pits occur most often at potentials close to the critical pitting potential. The amount of metastable pits on pure aluminum can increase for two reasons when in contact with chloride ions. One condition that causes metastable pits is an increase in anodic potential with a constant

concentration of chloride ions. Metastable pits can also occur when there is a constant potential but the concentration of chloride ions is increased [30].

During the propagation stage of a pit in aluminum, aluminum within the pit is dissolved into Al^{3+} ions [23]. Outside the pit or at the mouth of the pit a cathodic reaction occurs. The cathodic reaction causes the reduction of H^+ or oxygen ions. The cathodic reaction may destroy the protective oxide layer locally. This reaction often causes hydrogen liberation. The pH of the solution within the pit is lowered due to the hydrolysis of water by Al^{3+} ions and the production of protons. A corrosion product made of $\text{Al}(\text{OH})_3$ or Al_2O_3 forms at the mouth of the pit and may eventually block the pit [23] [32]. Figure 2-14 shows the pitting process of aluminum.

Figure 2-14: Pit Propagation of Aluminum [25]

Models that simulate pit initiation exist. An unverified electrode kinetic model for pit initiation has been developed by McCafferty [33]. This model uses the charge on the oxide surface, as well as the pH of zero charge parameter. The model also takes into account the penetration of chloride ions into the oxide film using oxygen vacancies, the

absorption of chloride ions on the oxide surface, and pit initiation at the metal/oxide interface caused by the dissolution of the underlying substrate.

2.4 Wetting

It is important to understand the wetting behaviour of thin polymer films, especially when the polymer is used as a coating [34]. The stability of the film is affected by wetting and dewetting. The field of biophysics has studied “smart” surfaces which are polymers that respond to a change in properties. These properties include a change in pH, ion concentration, or temperature.

Wetting is the adhesion of a fluid to a solid surface [35]. Wettability is the tendency of the fluids to adhere to, or wet, the surface of a solid. The fluid can be water, oil, air, or any other liquid. A surface that is wettable is called hydrophilic or water-wet. A surface that is non-wettable is called hydrophobic or oil-wet. The contact angle between a drop of water and a horizontal surface of a solid object can be observed to determine if a polymer is hydrophilic or hydrophobic. When the drop of water is spread out, with a contact angle of less than 90° , the polymer is hydrophilic. An infinitely hydrophilic polymer would theoretically have a contact angle of 0° . When the contact angle is greater than 90° the polymer is hydrophobic, with an infinitely hydrophobic polymer having a contact angle of 180° . If the contact angle is exactly 90° then the polymer is naturally wet [35]. Figure 2-15 shows two droplets of water on a solid surface; one droplet is considered to be hydrophilic and the other one is considered to be hydrophobic.

Figure 2-15: Hydrophilic and Hydrophobic Contact Angles [36]

2.5 Polymer Chemistry

Cross-linked polymers will swell when they are immersed in a suitable solvent [37]. The amount of swelling that occurs is caused by two opposing forces. These opposing forces are known as solvation and retraction. Solvation forces the solvent to enter the polymer and then dilute the bulk polymer. This causes the chains to elongate. An elastic retractive force is created because of the chains elongating. The elastic retractive force also opposes the elongation of the polymer. The polymer will reach equilibrium between the solvation and retraction forces. Polymers can swell in response to numerous factors including: change in temperature, glucose concentration, and change in pH. The amount of liquid a polymer can absorb is called hydration [38].

Hydrogels are one polymer that have been studied [38] for their swelling. Hydrogels are cross-linked polymers that are hydrophilic. They are able to absorb and

maintain water in their structure without being dissolved. The hydration of hydrogels is driven and caused by their hydrophilic nature. The cross-linked network structure limits the amount of hydration of a polymer. Non-ionic swelling of a polymer decreases as the degree of cross-linking increases [37]. The swelling of polymer particles in a hydrogel membrane has also been studied. The membrane must be optically transparent, inert to the solvents used, permeable, and allow for the polymer particle to swell in a uniform manner. Turbidimetry is used to measure the swelling of particles since there is a change in their refractive index when they swell.

In the 1970s, polymer swelling was tested by placing the polymer in dyed solvent and then examining its cross section using a microscope [39]. The sample was weighed before and after being placed in the solvent, as well as recording its dimensions before and after. The measurement of small changes in the surface of the polymer caused by a weak solvent and the measurement of thin films are not reliable because of the very small changes that occur in the polymer. Polymer swelling has been measured using: quartz crystal micro balance, ellipsometry, electrical conductivity, laser interferometry, surface plasmon resonance spectroscopy, and combinations of micro-mechanical cantilever sensors and surface plasmon resonance spectroscopy.

2.6 Testing Methods

This section will discuss the corrosion testing methods related to beverage cans.

2.6.1 Conventional Methods

Corrosion tests in sealed cabinets have been used to determine the corrosion performance of coatings since the 1900s [40]. They can be used to accelerate corrosion of coatings and reduce the time it takes to obtain results. A cabinet corrosion test consists of placing a sample within a cabinet containing a corrosive environment. The corrosive environment depends on the sample and may include the use of one or more of the following: salt fog, hot and cold temperatures, corrosive gas, humidity and exposure to ultraviolet light [40].

The salt fog test, also called a salt spray test, is the most used common cabinet corrosion test [40]. There exist American Society for Testing and Materials (ASTM) standards for this test which dictate the setup and procedure [40]. Typically, a 5% sodium chloride solution is formed into a fine aerosol fog and a steady 35 °C temperature is kept within the cabinet, however, some industries use a 20% sodium chloride solution and higher temperatures. A typical salt fog test can last for months or years. During the test, the samples are often periodically inspected. The salt fog test is useful as a process control test; for instance, time-to-failure in the salt fog can be used to determine the relative benefits of changing process/manufacturing variables. However, standalone salt fog tests do not necessarily correlate well with in-service performance because of the different chemical reactions and circumstances that occur in service [40].

There exist variations to the salt fog test [40]. Tests on decorative chromium plating on steel, lasting for a few hundred hours, use a 5% sodium chloride salt fog spray that has been acidified with acetic acid to pH 3.2. Exfoliation testing on some aluminum alloys is done using a 5% sodium chloride solution that has been acidified using acetic

acid to pH 2.9, and at 49 °C. The test consists of 0.75 hours of spray, 2 hours of dry air purge, and then 3.25 hours of soaking at a high humidity, making the test duration 6 hours. There exist other variations including a salt/SO₂ spray fog test, acidified synthetic sea water fog test, cyclic salt fog and UV exposure test, and dilute electrolyte cyclic fog and dry test. Salt fog tests are also used in conjunction with other tests. For instance, a filiform test consists of a salt spray followed by an exposure to 70% to 90% relative humidity. Filiform corrosion, which appears as threadlike strands, forms under finishes. Filiform corrosion can occur in powder-clear-coated aluminum and only forms when the relative humidity is between 70% and 95% [40].

Electrochemical methods, using alternating currents (AC) and direct current (DC), are also used to test coatings [40]. Anodized aluminum can be tested using the Ford anodized aluminum corrosion test, also known as FACT. A cylindrical glass cell is clamped onto the surface of the sample and filled with a 5% sodium chloride solution containing cupric chloride, which is acidified with acetic acid. The sample is cathodically polarized by applying a DC voltage between the sample and an electrode immersed in the solution for 3 minutes. The resistance of the coating can decrease over this time, leading to a larger current. This test is no longer an ASTM standard due to certain aluminum alloys failing the test but performing well in service. FACT is also known as cathodic breakdown test when the DC polarization is -1.6 V versus a saturated calomel electrode [40].

Electrochemical noise methods (ENM) are non-destructive tests that appraise the susceptibility of a material to localized corrosion. In an electrochemical system, potential and current fluctuations/noise occur [41]. ENM record these fluctuations as a function of

time. No artificial noise or fluctuations are imposed on the system when using ENM [42]. ENM can produce results that provide information on corrosion rates and mechanisms. While the instruments used to collect data for ENM are inexpensive and simple to use, ENM is not widely used because the data can be difficult to interpret and associate with in service performance. There exist three main approaches to interpret ENM data. These are the statistical, spectral, and chaos theory-based methods [42].

2.6.2 EIS Methods used with Coatings

Equivalent electrical circuits are a popular method used by researchers and authors to analyze measured EIS data [43] [44]. This method assumes a relationship between electrical circuit components and physical features in the EIS data. The Randles circuit is a common model that is used to represent a metal coated with a polymer [21] (Figure 2-16).

Figure 2-16: Randles Circuit [21]

R_{sol} is the solution resistance, C_c is the coating capacitance, and R_p is the pore or flaw/parallel resistance, which represents all the conductive paths which exist through the coating [43] [45]. The impedance of the Randles circuit is given by [21]:

$$Z_{Randles} = R_{sol} + \frac{R_p}{1 + (\omega C_C R_p)^2} - j \frac{\omega C_C R_p}{1 + (\omega C_C R_p)^2} \quad 2-31$$

At high frequencies the impedance of the Randles circuit is equal to the solution resistance, because the impedance of the capacitor is smaller than the solution resistance (the impedance of a capacitor varies as one over the frequency (Table 2-1)) [10]. At mid frequencies, the capacitive component dominates, and at low frequencies the pore/parallel resistance is the least resistive path.

An intact coating demonstrates a capacitive behaviour and high impedance at low frequencies. In this study, the impedance ranged from $10^7 \Omega$ to $10^{10} \Omega$ at frequencies lower than 10 Hz. Depending on the data acquisition equipment used, measurements of the impedance at the higher end of the range were more-or-less unreliable (Section 3.5). As a coating degrades, the low-frequency impedance decreases. In this study, when the impedance was lower than $10^7 \Omega$ below 10 Hz, the coating was no longer protective. Generally, a good coating does not contain conductive paths through pores and/or flaws, and can be represented as a capacitor [43]. As the coating begins to fail, the pores and/or flaws in the coating are filled with electrolyte solution, which create conductive paths [43].

Figure 2-17 shows the coating model commonly used for a failed coating. In this figure, C_{dl} is the double layer capacitance and R_{pol} is the polarization resistance [21]. Polarization resistance represents the impedance of the electrode in the system having its potential changed from its corrosion potential [46]. The change in the potential of the electrode causes current flow, which is caused by electrochemical reactions at the surface of the electrode. The magnitude of the current flow is controlled by the diffusion of reactants moving away from and towards the electrode, and reaction kinetics [46].

Figure 2-17: Circuit Model for a Failed Coating [21]

Figure 2-18 shows a simulation of the Bode plot for a good/intact coating, Curve 1, and a breached/failed coating, Curve 2. Curve 1 was modelled with a Randles circuit and Curve 2 with the failed coating circuit model [21]. In this figure, R_p ranges from $10^6 \Omega$ to $10^8 \Omega$. In this thesis, R_p for good/intact coatings was over $10^{10} \Omega$. The figure shows how the shape of a Bode plot might change when the coating degrades [47].

Figure 2-18: Bode Plot for Intact Coating (Curve 1) and Failed Coating (Curve 2).
Curve 1: $R_{sol} = 5 \Omega$, $R_p = 1 \cdot 10^8 \Omega$, $C = 5 \cdot 10^{-11} F$. **Curve 2:** $R_{sol} = 5 \Omega$, $R_{pol} = 1 \cdot 10^7 \Omega$, $C_c = 5 \cdot 10^{-11} F$, $R_p = 1 \cdot 10^6 \Omega$, $C_{dl} = 5 \cdot 10^{-8} F$, $A = 1 cm^2$. [21]

It is not always possible to use an ideal capacitor to model experimental data [47]. When the coating is non-uniform, has a rough surface, or has an inhomogeneous distribution of current, a constant-phase element (CPE) is used instead of a capacitor for the model in

Figure 2-17. The Warburg impedance is used when the corrosion rate is controlled by the diffusion through electrolyte or the pores of the coating. An indication of Warburg impedance is a 45° tail in the low frequency region in the Nyquist plot. Figure 2-19 shows simulations for the Bode plots and Nyquist plots for: an intact coating; a damaged coating modeled with an ideal capacitor; a damaged coating modeled with a CPE; and a damaged coating modeled with a Warburg impedance [47]. In this thesis, an ideal/intact coating does not display the same behaviour as the simulation shown in Figure 2-19. An ideal coating in this thesis shows the behaviour described in Section 2.1.3 and Section 2.1.4.

Figure 2-19: Bode Plots and Nyquist Plots of Typical Intact, Damaged, Damaged (CPE) and Diffusion (Warburg) Coatings [47]

2.7 Previous Studies

This section will focus on previous studies on beverage can corrosion as well as studies on coating properties.

2.7.1 Beverage Can Corrosion

The two year pack-test is an industry standard [48]. It requires the use of visual examination, which causes this method to not always be reliable. To increase the speed of testing, aggressive solutions like acidic solutions or an applied voltage have been used. Using an acidic solution or an applied voltage during a two year pack-test causes the test to no longer be food product specific. F.S. Bovard et al [48] conducted a test where food cans underwent a two year pack-test. The food cans were then examined both visually and with EIS. To evaluate the coatings quantitatively they reduced the impedance spectrum to a single numerical performance indicator. They used three different methods to find a numerical performance indicator. The three methods were: using low frequency impedance [$\log(Z)$ at 0.04 Hz], using break-point frequency ($\theta = 45^\circ$), and percent ideal behaviour [48].

The low frequency impedance method assumed a Randles equivalent circuit [48]. F.S. Bovard et al [48] found that the low frequency impedance, taken at 0.04 Hz, was approximately equal to the sum of the charge transfer resistance, the solution resistance, and the coating resistance. The low frequency impedance was also found to correspond to the coating degradation that was visually observed, which appeared as blisters [48].

The break-point frequency method also assumed a Randles equivalent circuit [48]. This method focused at the point where there is a change from capacitive to resistive behaviour in the impedance response, at a phase angle of $\theta = 45^\circ$. This method

was used when the charge transfer resistance could not be determined because of too much noise at the lower frequencies. A Randles circuit with two time constants can have two break-point frequencies [48]. A Bode plot showing two break-point frequencies can be seen in Figure 2-20.

Figure 2-20: Typical impedance Bode plot showing the low and high break-point frequencies [48]

The high break-point frequency occurs when the impedance of the coating is changing to the solution resistance (which can be negligible) plus the pore resistance [48]. The low break-point frequency occurs when the impedance is changing to the solution resistance, plus the pore resistance, plus the charge transfer resistance. The high

break-point frequency was the primary break-point frequency used when comparing data in this study [48], however, it was not always measurable by the researchers. The low break-point frequency was used when the high break-point frequency was not available [48].

The percent ideal behaviour method reduced EIS data to a single numerical performance indicator [48]. This method used the ratio of the area under a Bode magnitude curve versus the area under an ideal capacitive curve. A coating is evaluated depending on how close its curve is to the ideal capacitive curve; the closer this curve is to the ideal capacitive curve, the better the coating is. This method gives it an advantage over the other two methods as it uses the entire frequency spectrum [48].

The paper concluded that EIS can be used to inspect coatings when using food product as the electrolyte [48]. All three methods correlated well with the traditional visual inspection. It was found that the low frequency impedance method worked well when there was no noise. It was also the easiest to use since the data was obtained straight from the Bode plot. The break-point frequency method was not always accurate since the high break-point frequency was not always measurable. Lastly, while the percent ideal method used the whole frequency spectrum, the drawback found was that it had to be calculated [48].

A two part study by Grandle and Taylor [49] [50] acknowledged that there is a need to replace current beverage can coatings due to proposed changes in regulations concerning volatile organic compounds, as well as a need to store more aggressive materials inside polymer coated aluminum cans. The first part of the study focused on finding an EIS parameter, which will be discussed, that is easy to obtain and can also be

used to evaluate the performance of coatings [49] [50]. The second part of the study took the parameter that was found and evaluated samples of coatings.

Before an EIS parameter could be found, the authors first compared the impedance responses of an uncoated aluminum alloy sample to the impedance response of a coated aluminum alloy sample without any defects and a coated aluminum alloy sample with a defect [49] [50], which can be seen in Figure 2-22. This made it possible to determine the parts of the impedance spectrum related to the coating and the solution-oxide-metal interface. Three different thicknesses of a proprietary epoxy-acrylic polymer were used. The intentional defect was approximately 0.1 mm in diameter and was made using a carbide scribe [49] [50].

Figure 2-21 shows the EIS results for a sample before and after a defect was made [49] [50]. It was observed that prior to the defect the EIS response of the intact coating was almost purely capacitive. After the defect was made the EIS response became more complex, with more than one time constant becoming visible. The impedance also began to decrease at the low frequency end of the spectrum [49] [50].

Figure 2-21: Impedance Spectra for Coated Aluminum Alloy at Times Before and After Intentional Defect [49]

The sample used in Figure 2-21 was compared to an uncoated aluminum alloy sample [49] [50]. It was determined that the phase angle peak that occurred at 96 hours and 5 Hz was due to water and ion ingress into the defect, which caused reactions to occur with the metal and/or oxide. By comparing the damaged coated sample, shown in Figure 2-22, with the uncoated sample it was also determined that the second time

constant for the damaged coated sample occurred at the same frequency as the time constant for the uncoated sample [49] [50].

Figure 2-22: Comparison of the Bode Phase Plots for Coated and Uncoated Aluminum Samples in Acidic Chloride Solution [49]

The authors suggest that this time constant therefore contained information about the reactions such as charge transfer occurring at the metal surface, and/or information about the oxide [49] [50]. The high frequency time constant was believed to provide information on the coating, including the overall coating capacitance. An increase in the size of the defect, caused by new defects forming or the original defect increasing in size, was thought to have caused the decrease in interfacial impedance that was observed after 96 hours [49] [50].

The study also included EIS results for coated and uncoated samples placed under DC polarization [49] [50]. When the potential was in the transition region (Section 2.3.2)

the data was scattered at low frequencies. It was suggested that the scatter was caused by the current fluctuating as metastable pits formed [49] [50].

Figure 2-23 shows a very complex proposed circuit model for a coated aluminum sample in chloride solution [49] [50]. The change in coating capacitance with time was used to study water content in the film, however, Brasher's equation assumes that the change in coating capacitance was caused only by water permeating into the coating. It also assumes that the distribution of water in the coating is uniform but random. *Failure due to the coating blistering or spot corrosion could not be predicted using the change in coating capacitance* [49] [50].

Figure 2-23: Proposed Equivalent Circuit Model for Coated Aluminum in Chloride Solution [49]

Data was fitted to the model in Figure 2-23 and the coating capacitance values were obtained [49] [50]. The coating capacitance was then plotted versus time. After five

months of exposure the coating capacitances of the samples increased approximately 5% or less with time. The samples were not all failing, due to spot corrosion, at the same rate. Only the sample with the intentional defect showed a large change in coating capacitance which may have been caused by water ingress into the intentional defect. *It was determined that observing changes in coating capacitance cannot be used to predict failure or as a parameter to measure performance* [49] [50].

Pore resistance was also considered a possible parameter [49] [50]. It was determined that, while short term observations of the pore resistance did well in correlating to the changes observed after 5 months, it could not be used as a parameter in a large test. This is due to the pore resistance requiring fitting to the circuit in Figure 2-23 which can be difficult and time consuming. The pore resistance decreased by orders of magnitude when the coating was severely degraded and was impossible to obtain when the pore resistance became low [49] [50].

The magnitude of the low frequency impedance, between 0.01 and 0.05 Hz, was used as the parameter to evaluate the performance of coatings [49] [50]. This parameter could be easily obtained from a Bode plot or a Nyquist plot. While it gave information on how the coating was failing, it was also found to correlate with the performance of the coating. The average low frequency impedance was plotted on a log scale versus time of exposure in days. If the log average low frequency impedance remained the same the coating was not considered degrading. The performances of different coatings were ranked by comparing their log average low frequency impedance at specified exposure times. A coating with a higher parameter magnitude at the same exposure time as other coatings was considered to be performing better. The magnitude of the low frequency

impedance was found to reflect the change in defect area and the charge transfer response [49] [50]. Gui and Kelly [51] went on to analyze the performance of corrosion prevention compounds using the method described by Grandle and Taylor [49] [50]. They suggested that the double layer capacitance could also be used as a performance parameter, where a lower double layer capacitance represented a coating that was performing better [51].

2.7.2 Coating Properties

A study conducted by M. Shon and H. Kwon [52] observed the effects of modifying an epoxy coating. The epoxy coating was modified with amino branched polydimethylsiloxane (ABP) to give the coating a hydrophobic property on its surface instead of its original hydrophilic property. They were able to show that the modified epoxy coating had a lower water diffusivity and water uptake when compared to a pure epoxy coating. The modified epoxy coating also showed a decrease in corrosion spot size and occurrence density, which signified that the performance of the coating was correlated with its water transport behaviour [52].

Waterborne epoxy/amine coatings are an alternative to epoxy coatings containing BPA [53]. They have poor long term chemical resistance to acids. The chemical resistance of waterborne epoxy/amine coatings was believed to be influenced by hydrophilic emulsifiers that remain in the coating after curing and cause the coating to be more susceptible to attacks from water, solvents, and other chemicals. A. Wegmann [53] found that hydrophilic curing agents have no effect on the chemical resistance of

waterborne epoxy/amine coatings. It was also found that hydrophilic surfactants have a slight effect on the chemical resistance.

Zhang et al. [54] have observed that corrosion protection can be improved with the formation of a hydrophobic layer. Two epoxy resins were tested, EP and EPA. EP resin contains hydroxyl groups which are hydrophilic. EPA resin has the hydroxyl groups replaced with acetoxy groups, which are less hydrophilic than hydroxyl. A cross-sectional area of water passage was observed at the coating/metal interface, and was compared to the cross-sectional area of water passage in the resin matrix (the solution/coating interface). EPA was found to have a narrowing passage which was caused by a hydrophobic layer forming at the coating/metal interface. The hydrophobic layer was suggested to greatly improve the performance of the coating.

Chapter 3 Equipment and Experimental Setup

3.1 Introduction

This chapter provides information on the equipment used and the experimental setups.

3.2 Aluminum Samples

The samples used were an unknown aluminum alloy coated with a waterborne epoxy-free polymer. BPA enters current epoxy coatings used to protect aluminum beverage cans during the manufacturing process. The coating studied cannot be called BPA-free because BPA may have entered the coating unintentionally during manufacturing or other processes. Information on the chemical composition of the polymer was not provided by the company sponsoring this research because it was proprietary. The material was provided as a flat sheet of aluminum coated on both sides. On one side the coating thickness was 2 μm , and on the other side the coating thickness was 8 μm . These coatings are the same as those found in beverage cans, with the thinner coating on the public side and the thicker coating on the beverage side. The aluminum was the same alloy used in beverage cans.

3.3 Test Cell

A Horizontal Cell (Model# K0235) was used for all the corrosion tests [20]. This is a standard electrochemical cell used to test coatings and paints in electrolyte solutions. Figure 3-1 shows the test cell. The body is made of PyrexTM, and end caps and end plates are made of polypropylene. The exposed surface of the sample was circular in shape with an area of $1.0 \pm 0.1 \text{ cm}^2$. A flat rubber o-ring was used to ensure a leak-tight seal

between the end caps and sample. A graphite counter electrode and a reference electrode (Section 3.4) (the reference electrode is not shown in the figure) were inserted through the openings in the top of the test cell [20]. Figure 3-1 shows the graphite counter electrode in one of the holes. The three holes in the foreground were used for the reference electrode and bubbler (Section 3.4).

Figure 3-1: Horizontal Test Cell

3.4 Reference Electrode, pH Reader, and De-aerating Setup

A saturated calomel reference electrode (Accumet 12-520-259 SN 5060376P) was used during most of the tests performed. It had a value of 0.24 V relative to the standard hydrogen electrode [55]. An Orion 2 Star pH reader was used to measure pH.

All de-aeration was completed using carbon dioxide gas (CO_2) or a combination of CO_2 and dry ice. In this thesis, de-aeration means to displace the dissolved oxygen within a solution with CO_2 . The CO_2 cylinder was connected by a tube to a sintered glass frit. The sintered glass frit was placed in a flask containing water. The flask had two openings. The first opening had a tube that lead from the cylinder to the flask. The second opening had a tube that lead from the flask to the test cell. The end of this tube was also attached to a sintered glass frit. Sintered glass frits were used as bubblers because they create small bubbles with large surface areas; they de-aerate a solution faster compared to a tube without a sintered glass frit. The intermediate beaker, placed between the canister and test cell, was necessary. The initial gas from the canister was dry. The intermediate beaker was used to moisten the initial gas from the canister. A dry gas entering the test cell would remove moisture from the solution, which would cause the volume of the solution to decrease and alter the concentration.

CO_2 was bubbled for a minimum of 10 minutes, after which the CO_2 gas was turned off and test cell was sealed. Some tests were performed with CO_2 bubbling during the measurement, as indicated. Aerated solutions in this thesis were exposed to the atmosphere so that the dissolved gases in solution were in equilibrium with the atmosphere. De-aerated solutions were aerated by pouring the solution in and out of the test cell three times; additional mixing did not alter the results.

3.5 Data Acquisition Equipment

Two different data acquisitions systems were used. The first system was a Solartron 1287 potentiostat with a Solartron 1255 gain/phase analyzer. Different

software was used depending on the type of experiment and the equipment used. For EIS tests using the Solartron, Zplot (version 3.2c) was used to run the test and ZView (version 3.2d) to view the results. When the Solartron was used for DC polarization tests (specifically cyclic voltammetry tests), CorrWare (3.2c) was used to run the tests and CorrView (3.2d) to view the results. The second system was a Gamry PC4/300. Gamry Framework (4.35) was used to run both EIS and DC polarization (specifically cyclic voltammetry) tests and EchemAnalyst (5.3) was used for viewing.

The Gamry system had an upper impedance limit (open circuit) of $10^{12} \Omega$ at 100 mHz. The Solartron system had an upper impedance limit of $10^9 \Omega$ at 100 mHz. In general, the impedance and phase angle measurements would vary slowly with frequency, however, below 200 Hz the measurements would sometimes vary rapidly, appearing as noise and spikes in the spectra [8].

The explanation for the noise and spikes depends on how close the impedance measurements were to the limits of the data acquisition equipment. When the impedance measurements were close to the limit of detection, the spikes were considered to be noise, otherwise, the spikes were considered to be real. In addition, when phase angles spiked into positive values, this was interpreted as an indication that the underlying aluminum was corroding (Section 2.1.4). The spikes do not appear at higher frequencies, but do appear at lower frequencies, consistent with the rates of corrosion reactions [49].

3.6 Solutions

Hydrochloric acid solutions (HCl) (Anachemia, UN# 1789, CAS# 7647-01-0, Lot# 210187), potassium chloride (KCl) (Bioshop, CAS# 7447-40-7, Lot# 1b19806), and

distilled water solutions were used. During testing samples were exposed to one or more of the following conditions:

- Aerated distilled water (pH 5-7)
- Aerated HCl (pH 0-4)
- Aerated KCl (pH 4)
- De-aerated distilled water (pH 5-7)
- De-aerated HCl (pH 0-4)
- De-aerated KCl (pH 4)

3.7 Experimental Procedure

The material used to make blank samples was provided by an industry partner and was received as large sheets. Blank samples were cut using scissors. The sample sizes were 9.5 cm by 4.0 cm. A height of 9.5 cm was chosen to match the height of the end plates (Section 3.3). The width was chosen to be wider than the end caps so that when a blank sample was attached to the test cell, a permanent marker could be used to trace around the end cap on the public side. This was done to assist repositioning the sample in the same location. The public side was labelled with the name of the sample, the sheet it was cut from, and the date of the experiment.

After a blank sample was removed from the test cell, a non-permanent indication of the o-ring could be seen on the surface. This indication was used to determine the area where the sample was exposed to solution. The pinhole was made within this area. The traced lines of the end cap on the back of the sample were used to reposition the sample in the test cell, thus ensuring that the pinhole was exposed to solution.

Pinholes were created with a mathematical compass or sewing needle. The following sewing needle sizes were used: 70/10, 80/12, 90/14. The first number in sewing needle sizes is the approximate diameter of the needle shaft (before any reinforcements to the needle shaft). A needle designated as 70 would mean the diameter of the needle is 0.7 mm. Needle sizes do not include the diameter of the needle tip.

The force required to create a pinhole depended on the instrument used. A sharper instrument, like a sewing needle, damaged a sample more readily than a blunter instrument, such as the mathematical compass. All pinholes were created by hand. It was relatively easy to scratch the surface of a sample with a sewing needle. Care had to be taken to use enough force to go through the coating, but not enough to go too deep into the metal. The pinhole could be seen with the naked eye. The force used ranged from 3.4 N to 6.9 N, which was determined by placing samples on a balance and recording the force required to make a pinhole without visible damage to the metal underneath the coating.

The samples were easily scratched and damaged by other objects, including other samples. Care had to be taken while handling and storing samples. Samples were carried by holding the edges. A tissue was used to wipe the surface of a sample clean. When not in use, samples were stored individually in a plastic sleeve (photo album).

Only enough liquid to cover the exposed surface of a sample was poured into the test cell. A test cell filled close to the top would have caused the liquid to overflow when the solution was de-aerated (Section 3.4).

The first few steps were the same for all samples. A blank sample was placed in distilled water. An EIS test was used to determine if there was any existing damage. If

there were signs of pre-existing defects, *e.g.*, scratches caused by poor handling or storage, the sample was discarded or a different area of the same sample was tested.

Figure 3-2 shows the results for a sample that was considered to not have any major pre-existing defects which would alter the results of future tests. In these results the impedance appeared as a relatively straight line, with a slope of -1, which reached approximately $10^{10} \Omega$ at low frequencies. The phase angle stayed at approximately -90° , except at frequencies below a few Hertz.

Figure 3-2: A Good Blank Sample Containing No Measurable Pre-existing Defects

Figure 3-3 shows the EIS test results for a blank sample that was considered to have pre-existing defects. The impedance at low frequencies is resistive and not capacitive; the slope in the impedance plot is closer to 0 than -1. In addition, the impedance falls short of $10^{10} \Omega$ seen in Figure 3-2 for a good blank sample. The departure of the phase angle from -90° is much more apparent at low frequencies.

Figure 3-3: A Poor Blank Sample Containing Pre-existing Defects

Once a blank sample was tested and determined to have no measurable pre-existing defects, a pinhole was created. The next step was another EIS test in distilled water to determine if the pinhole penetrated the coating. If the EIS results were similar to

the results for a good blank sample, the sample was discarded, or the pinhole was reworked. If the EIS results were different, the sample was considered for further study with EIS or cyclic voltammetry.

EIS tests used a frequency range from 10^5 Hz to 10^{-1} Hz. Tests were performed using an AC excitation voltage of 20 mV [8]. Sample area size was set to 1 cm^2 . The DC polarization test used was a cyclic potentiodynamic test, also known as cyclic voltammetry. The DC tests used a scan rate of 20 mV/s and a rate of 50 mV/point, which were determined by maximizing the number of data points and minimizing the duration of the test to minimize the degradation of the sample during the test. The potential range for a cyclic voltammetry test was based on the Pourbaix diagram for aluminum. Potential ranges were selected to ensure the major characteristics of an Evans diagram were seen, if they were to occur (Section 2.3.2). The largest range used was -3 V to 2.5 V, and the smallest was -1 V to 1 V.

Chapter 4 Results of Experiments

This section will go over the major results observed throughout the conducted tests. All figure captions state which data acquisition equipment was used to obtain the results; for results obtained using the Gamry, the figure caption will include (Gamry) at the end, and for the Solartron, (Solartron) will appear at the end.

4.1 Effect of pH on Corrosion

This section will describe a series of tests where pH was altered, back and forth between neutral and acidic conditions; it is divided by sample, Sample A and Sample B, where each section describes the series of tests using its respective sample.

4.1.1 Sample A

Distilled Water (pH 7)

The pinhole in Sample A was created using the point of a mathematical compass, as described in Section 3.7. The Bode plot and Nyquist plot results in distilled water (pH 7) can be seen in Figure 4-1 and Figure 4-2. The plots suggest that the pinhole through the coating was sufficiently large to cause the underlying aluminum to corrode; for instance, the Bode plot contains positive phase angles and an impedance with a positive slope at low frequencies (Section 2.1.4). Similarly, the Nyquist plot shows positive imaginary impedance (Section 2.1.3). Positive phase angles, imaginary impedance, and slopes at low frequencies are indications of active corrosion. In addition, the Bode plot in Figure 4-1 resembles Figure 3-3 more than Figure 3-2; for instance, the impedance of the coating is not capacitive below 20 Hz and the impedance at lower frequencies is below

$10^7 \Omega$, which is indicative of a bad coating (Section 2.6.2). The lack of integrity of the coating can also be seen in the cyclic voltammetry results shown in Figure 4-3. If the coating were good, then the corrosion of the underlying aluminum would not be visible and the current would not increase with applied DC voltage (Section 2.3.2). In Figure 4-3, as the DC potential is increased above the corrosion potential, the current density increases initially, then it slows down, suggesting passivation. With further increase in the potential, pitting occurs in the transpassive region. As the potential is decreased, the current density decreases as the passivation potential is reached (Section 2.3.2). This behaviour with applied DC potential is consistent with the corrosion of aluminum and not the behaviour expected of a good coating (Section 2.3.2).

Figure 4-1: EIS Bode Plot Results in Distilled Water (pH 7) for Sample A Containing a Pinhole (Gamry)

Figure 4-2: EIS Nyquist Plot Results in Distilled Water (pH 7) for Sample A Containing a Pinhole (Gamry)

**Figure 4-3: Cyclic Voltammetry Results for Sample A in Distilled Water (pH 7).
Potential Range: -2 V to +2 V (Gamry)**

Distilled Water (pH 7) → HCl (pH 0)

When the solution in the test cell was changed to HCl (pH 0), Figure 4-4 shows that the coating is now behaving as a good coating: the coating is capacitive and goes to high impedances at low frequencies, no positive phase angles, and no positive slopes. The Nyquist plot, seen in Figure 4-5, appears as an almost vertical line along the axis, with no positive imaginary impedance. In contrast to Figure 4-3, Figure 4-6 shows currents at the limit of detection of the instrument that are independent of the applied DC voltage (Section 2.3.2). The implication is that changing the pH from 7 to 0 transformed a bad coating, with a pinhole, into a good coating.

Figure 4-4: EIS Bode Plot Results in HCl (pH 0) for Sample A Containing a Pinhole (Gamry)

Figure 4-5: EIS Nyquist Plot Results in HCl (pH 0) for Sample A Containing a Pinhole (Gamry)

Figure 4-6: Cyclic Voltammetry Results for Sample A in HCl (pH 0). Potential Range: -2 V to +2 V (Gamry)

HCl (pH 0) → HCl (pH 3.8)

An HCl solution with a pH of 3.8 (distilled water acidified with HCl) was used to investigate the behaviour of the coating between the ‘bad’ pH 7 results seen in Figure 4-3 and the ‘good’ pH 0 results seen in Figure 4-6. A cyclic voltammetry test was performed and the results can be seen in Figure 4-7. The sample started off with the same current density as in HCl (pH 0) (10^{-11} A/cm²), and began to increase by two orders of magnitude at -0.5 V. On the return scan, after reaching 0.9 V, the current density increased by five orders of magnitude (this point has been highlighted by a red circle in the Figure). As the voltage was reduced further, the polarization plot had the characteristics of corroding metal, including a passivation potential, similar to those shown in Figure 4-3.

The test was repeated with the same sample under the same conditions. The results are shown in Figure 4-8. This time the sample only briefly stayed at a current density of 10^{-11} A/cm² and then began behaving like corroding aluminum.

Figure 4-7: Cyclic Voltammetry Results for Sample A in HCl (pH 3.8). Potential Range: -2 V to +2 V (Gamry)

Figure 4-8: Second Cyclic Voltammetry Results for Sample A in HCl (pH 3.8). Potential Range: -2 V to +2 V (Gamry)

HCl (pH 3.8) → HCl (pH 0)

In the next test, the pH was changed from 3.8, which was the value in previous test, to 0.

Cyclic voltammetry results are shown in Figure 4-9. The current density started at 10^{-11} A/cm² and increased by factor of 6 on the upward scan. The curve also returned on the passivation side, which is the behaviour of an intact sample.

**Figure 4-9: Second Cyclic Voltammetry Results for Sample A in HCl (pH 0).
Potential Range: -2 V to +2 V (Gamry)**

HCl (pH 0) → HCl (pH 3.8)

The solution in the test cell was changed to HCl (pH 3.8). Another cyclic voltammetry test was performed, and the results are shown in Figure 4-10. At the beginning of the test, corrosion of the underlying aluminum was recorded; the corrosion potential can be seen. The aluminum was able to passivate, after reaching the corrosion potential, until 0.7 V on the forward scan. After this point in the test, the aluminum appeared to go through stages of corrosion and passivation as the current density jumped between high values (10^{-7} A/cm²) and low values closer to the limit of detection of the equipment (10^{-10} A/cm²). On the return scan, at 0.5 V the current density began to increase and the polarization curve began to resemble corroding aluminum again; a passivation potential appeared on the return sweep. Based on the Pourbaix diagram, it

was possible the aluminum was able to passivate at pH 3.8, or the coating had some influence on impeding the corrosion of aluminum.

Figure 4-10: Third Cyclic Voltammetry Results for Sample A in HCl (pH 3.8). Potential Range: -2 V to +2 V (Gamry)

HCl (pH 3.8) → Distilled Water (pH 7)

The solution was switched to distilled water (pH 7). A cyclic voltammetry test was performed, with the results shown in Figure 4-11. The polarization curve was similar to the results expected when the underlying aluminum was corroding; a corrosion potential appeared on the forward scan, followed by passivation between -0.9V and 1 V, pitting from 1 V until the return scan where the aluminum passivated again. The aluminum appeared to corrode again after 0.3 V on the return scan, and the passivation

potential appeared. The results had typical features of aluminum corrosion and passivation at pH 7.

Figure 4-11: Second Cyclic Voltammetry Results for Sample A in Distilled Water (pH 7). Potential Range: -2 V to +2 V (Gamry)

Distilled Water (pH 7) → Distilled Water (pH 7) 9 Days Later

After the previous test, Sample A was cleaned with distilled water, dried, and left exposed to air for 9 days. The first test conducted upon returning was an EIS test. Figure 4-12 shows the Bode plot. The results show that the underlying aluminum was corroding and that the coating was behaving as a bad coating; positive angles and an impedance below $10^7 \Omega$ at low frequencies can be seen in the Bode plot. Figure 4-13 shows the Nyquist plot for the EIS test; two semi-circles can be seen, as well as positive imaginary

impedance at low frequencies. Two cyclic voltammetry tests were performed next, the results can be seen in Figure 4-14 and Figure 4-15.

Figure 4-12: EIS Bode Plot Results in Distilled Water (pH 7) for Sample A Containing a Pinhole. Performed 9 days after Initial Tests (Solartron)

Figure 4-13: EIS Nyquist Plot Results in Distilled Water (pH 7) for Sample A Containing a Pinhole. Performed 9 days after Initial Tests (Solartron)

Figure 4-14: Cyclic Voltammetry Results for Sample A in Distilled Water (pH 7). Performed 9 days after Initial Tests. Potential Range: -2 V to +2 V (Solartron)

Figure 4-15: Cyclic Voltammetry Test Results for Sample A in Distilled Water (pH 7). Performed 9 days after Initial Tests. Potential Range: -3 V to +3 (Solartron)

Both tests showed that the underlying aluminum was corroding; corrosion potential, pitting, and passivation potential can all be seen. The current density changed with a change in voltage, indicative of the coating behaving as a bad coating. Pitting that occurred in the first cyclic voltammetry test, results shown in Figure 4-14, may have damaged the sample enough so that the second cyclic voltammetry test results differed slightly, seen in Figure 4-15. The second test began at a higher current density ($5 \cdot 10^{-7}$ A/cm² versus $2.5 \cdot 10^{-7}$ A/cm²), and also the during pitting a higher current density was reached ($2 \cdot 10^{-6}$ A/cm² versus $3 \cdot 10^{-7}$ A/cm²).

Distilled Water (pH 7) → HCl (pH 0)

The distilled water (pH 7) was switched to HCl (pH 0). An EIS test was completed, and the Bode plot can be seen in Figure 4-16. The coating was now behaving as a good coating, even after being left exposed to air for 9 days; the coating was capacitive, the impedance reached high values (above $10^9 \Omega$) at low frequencies, and there were no positive phase angles (excluding noise). The Nyquist plot, shown in Figure 4-17, also implied that Sample A had a good coating again; no positive imaginary impedance can be seen, and the curve follows a vertical path along the axis.

Figure 4-16: EIS Bode Plot Results in HCl (pH 0) for Sample A Containing a Pinhole. Performed 9 days after Initial Tests (Solartron)

Figure 4-17: EIS Nyquist Plot Results in HCl (pH 0) for Sample A Containing a Pinhole. Performed 9 days after Initial Tests (Solartron)

HCl (pH 0) → HCl (pH 5.3)

Another intermediate pH, between 0 and 7, was used to investigate if behaviour between a ‘good’ coating and a ‘bad’ coating could be observed. An EIS test was performed using pH 5.3 HCl (distilled water acidified with HCl). The Bode plot for this test can be seen in Figure 4-18. The results show a coating that is displaying behaviour that is between a ‘good’ and a ‘bad’ coating; there are no positive phase angles, but the phase angles do not remain at -90° . While a high impedance of over $10^9 \Omega$ is reached at

lower frequencies, the coating does not behave as a capacitor since the line does not have a slope of -1 throughout the entire test.

Figure 4-18: EIS Bode Plot Results in HCl (pH 5.3) for Sample A Containing a Pinhole. Performed 9 days after Initial Tests (Solartron)

The same sample was then left overnight in distilled water (pH 7).

HCl (pH 5.3) → Distilled Water (pH 7) Overnight → HCl (pH 2)

The next solution used was HCl (pH 2), after the sample had been left soaking in distilled water (pH 7) overnight. An EIS test was performed, and the Bode plot for this test can be seen in Figure 4-19. The coating was now behaving as a bad coating in low

pH solutions; the underlying aluminum was corroding and could be detected during the EIS test. The phase angles were close to 0° or positive, and the impedance was low at lower frequencies, below $10^7 \Omega$ and indicative of a bad coating. After the sample had been soaked overnight in distilled water (pH 7), all tests (no matter which pH solution was used) produced results where the underlying aluminum was corroding.

Figure 4-19: EIS Bode Plot Results in HCl (pH 2) for Sample A Containing a Pinhole, Left Overnight in Distilled Water (pH 7) (Solartron)

An optical microscope was used to find the size of the pinhole after all testing was complete. Figure 4-20 shows the microscopic image of the pinhole in Sample A taken at 200x magnification. The pinhole had a size of $250 \mu\text{m}$ by $290 \mu\text{m}$.

Figure 4-20: Microscopic Image of Sample A Pinhole (Post-experiments, 200x Magnification)

4.1.2 Sample B

Sample B contained a pinhole which was made with a 70/10 sewing needle (Section 3.7). A microscopic image was taken of the pinhole before conducting any experiments. The pinhole, seen in Figure 4-21, measured approximately 85 μm by 53 μm . The image shows that the sewing needle had penetrated the coating, but also that the needle had created a lip around the pinhole by pushing the coating back.

Figure 4-21: Microscopic Image of Sample B Pinhole (Pre-experiments, 200x Magnification)

Distilled Water (pH 7)

The first solution used was distilled water (pH 7). A Bode plot for an EIS test can be seen in Figure 4-22. The results are indicative of corroding aluminum; for instance, the phase angles are not at -90° , and the impedance is low (less than $10^7 \Omega$) at low frequencies. This suggests that the coating is behaving like a bad coating.

Figure 4-22: EIS Bode Plot Results in Distilled Water (pH 7) for Sample B Containing a Pinhole (Solartron)

Distilled Water (pH 7) → HCl (pH 1)

The solution was then switched to HCl (pH 1). The Bode plot for an EIS test is shown in Figure 4-23. The coating was now behaving as a good coating; the impedance reached over $10^9 \Omega$ at lower frequencies, and there were no positive phase angles.

Figure 4-23: EIS Bode Plot Results in HCl (pH 1) for Sample B Containing a Pinhole (Solartron)

Further testing (EIS and cyclic voltammetry) was conducted on Sample B by switching back and forth between distilled water (pH 7) and HCl (pH 1).

HCl (pH 1) → Distilled Water (pH 7) → HCl (pH 1)

Figure 4-24 shows two other tests that were conducted. The solution was switched from HCl (pH 1), to distilled water (pH 7), and then back to HCl (pH 1). The figure shows that the aluminum was corroding (impedance below $10^7 \Omega$ at low

frequencies) in distilled water (pH 7), but then the coating began to behave as a good coating (impedance near the limit of the equipment at low frequencies) in HCl (pH 1).

Figure 4-24: Two EIS Bode Plot Results for Sample B Containing a Pinhole in (Solartron): Distilled Water (pH 7) (Left) and HCl (pH 1) (Right)

Spikes in impedance and phase angle appeared in both test results shown in Figure 4-24. For the test conducted in distilled water (pH 7), the spikes were considered to be real (corrosion) due to the low impedance at low frequencies (Section 3.5). For the test conducted in HCl (pH 1), the spikes that appeared where the impedance was capacitive (-1 slope) were considered to be noise. Between 0.5 Hz and 0.1 Hz, the spikes in impedance and phase angle appeared to no longer be noise, but signs of the underlying aluminum corroding (the impedance is not at the limit of detection of the equipment at low frequencies). To verify that the underlying aluminum was now corroding, several EIS and cyclic voltammetry tests were conducted. These tests were performed using both the Solartron and the Gamry to verify that one of the machines was not malfunctioning.

As an aside, it is important to note the difference in impedance at high frequencies between the two results shown in Figure 4-24. The resistive behaviour of the impedance at high frequencies in distilled water (pH 7) is the resistance of the solution, R_{sol} . R_{sol} does not depend on frequency. The appearance of R_{sol} in the plot can be explained using the Randles circuit model (Figure 2-16) and the circuit model for a failed coating (Figure 2-17). At high frequencies, the impedance of a capacitor is low (Table 2-1). Current follows the path of least resistance, which in Figure 2-16 and Figure 2-17 at high frequencies would be the path containing R_{sol} and coating capacitance, C_c . Since the magnitude of R_{sol} of distilled water dominates the magnitude of C_c , R_{sol} of distilled water is visible at high frequencies in the results. R_{sol} of HCl is lower than the R_{sol} of distilled water because the HCl solution contains more ions in solution; these ions create a path of least resistance for the current in solution. R_{sol} of HCl is dominated by C_c and cannot be seen in the results.

The last EIS test on Sample B in HCl (pH 1) was performed after several EIS and cyclic voltammetry tests showed that the Solartron was not malfunctioning and the aluminum was now corroding. Figure 4-25 shows the results of the next test. The coating started to behaving as a bad coating in HCl (pH 1), allowing the underlying aluminum to corrode; for instance, phase angles close to 0° , and the impedance becoming independent of frequency starting at $2 \cdot 10^8$ Hz (resistive behaviour) are indications that the aluminum is now corroding.

Figure 4-25: Third EIS Bode Plot Results in HCl (pH 1) for Sample B Containing a Pinhole (Solartron)

The sample was visually examined and a second pinhole was observed to have formed next to the one that was created. The sample was examined using a microscope. The created pinhole, seen in Figure 4-26, now measured approximately 63 μm by 59 μm . Overall, the pinhole did not increase in size.

Figure 4-26: Microscopic Image of Sample B Pinhole (Post-experiments, 200x Magnification)

The damage that was observed, the new pinhole that had formed during testing, was also observed with a microscope. The microscopic image can be seen in Figure 4-27. The damage that had formed, which measured approximately 110 μm by 100 μm, was almost double the size of the created pinhole, both before and after testing.

Figure 4-27: Microscopic Image of Sample B Damage (Post-experiment, 200x Magnification)

4.2 Effect of De-Aeration of Solution Using Carbon Dioxide

This section will describe tests where the solution in the test cell was aerated, and de-aerated using carbon dioxide gas (CO_2). Aerated solutions have their dissolved gases in equilibrium with atmospheric air. In the de-aerated solutions, the aerated dissolved gases have been replaced with CO_2 (Section 3.4). Unless otherwise stated, the same sample was used during testing. The pH of solution was not altered during these tests.

4.2.1 Sample C

Aerated Distilled Water (pH 7)

A pinhole was made in Sample C using a mathematical compass (Section 3.7). Figure 4-28 shows the Bode plot for an EIS test conducted in aerated distilled water (pH 7). The results are indicative of corroding aluminum and a bad coating; there are positive phase angles, and the impedance at lower frequencies is below $10^7 \Omega$. The Nyquist plot can be seen in Figure 4-29; it can be used to infer that the underlying aluminum was corroding because of the appearance of positive imaginary impedances (Section 2.1.3).

Figure 4-28: EIS Bode Plot Results in Distilled Water (pH 7) for Sample C Containing a Pinhole (Solartron)

Figure 4-29: EIS Nyquist Plot Results in Distilled Water (pH 7) for Sample C Containing a Pinhole (Solartron)

Aerated Distilled Water (pH 7) → De-aerated Distilled Water (pH 7)

The distilled water in the test cell was de-aerated using dry ice and by bubbling carbon dioxide gas through the solution for 30 minutes (Section 3.4). An EIS test was completed. Figure 4-30 shows the Bode plot. The coating is now behaving better than it did in aerated distilled water (pH 7); compared to Figure 4-28, there are no more positive phase angles and the impedance at lower frequencies went above $10^7 \Omega$ (reaching $10^9 \Omega$). It is not considered to be behaving as a good coating because the phase angles do not stay at -90° and the impedance curve does not have a slope of -1 (capacitive behaviour). The

Nyquist plot, seen in Figure 4-31, also can be used to infer that the coating was behaving better than before; compared to Figure 4-29, there are no more full semi-circles or positive imaginary impedances, but the curve does not follow the vertical axis and begins to form part of a semi-circle.

Figure 4-30: EIS Bode Plot Results for Sample C Containing a Pinhole in De-aerated Distilled Water (pH 7) (Solartron)

Figure 4-31: EIS Nyquist Plot Results in De-aerated Distilled Water (pH 7) for Sample C Containing a Pinhole (Solartron)

4.2.2 Sample D

Aerated KCl (pH 4)

A pinhole was made in Sample D using a mathematical compass, as described in Section 3.7 . The Bode plot result, for an EIS test completed in aerated KCl (pH 4), can be seen in Figure 4-32. The coating is considered to be behaving as a bad coating because the underlying aluminum is corroding; for instance, positive phase angles, and impedance with a positive slope at low frequencies are features seen in Bode plots for corroding aluminum.

Figure 4-32: EIS Bode Plot Results for Sample D Containing a Pinhole in KCl (pH 4) (Solartron)

Aerated KCl (pH 4) → De-aerated KCl (pH 4)

The KCl solution in the test cell was de-aerated using carbon dioxide gas for 10 minutes, as described in Section 3.4 . An EIS test was conducted on this sample after de-aerating the solution. The carbon dioxide gas was left bubbling into the solution during the test. Figure 4-33 shows the Bode plot. From the Bode plot it can be inferred that the coating is now behaving as a good coating, even with a pinhole exposing the underlying aluminum. Compared to the previous results, seen in Figure 4-32, the Bode plot shown in Figure 4-33 has features indicative of a good coating; for instance, the impedance is

high at low frequencies (almost reaching $10^{10} \Omega$ at 0.1 Hz), and the phase angles are close to -90° , except at low frequencies where the limit of detection for the equipment (Section 3.6) was reached and the data became noisy (large peaks).

Figure 4-33: EIS Bode Plot Results for Sample D Containing a Pinhole in De-aerated KCl (pH 4) (Solartron)

4.3 Formation of Bubbles

This section will describe results where a bubble formed over the pinhole, stopping the underlying aluminum from corroding. Unlike in the previous sections, the pH was kept constant during these tests. Both aerated and de-aerated solutions were used for these tests.

4.3.1 Sample E

KCl (pH 4)

The pinhole in Sample E was created using a mathematical compass. An EIS test was conducted using KCl (pH 4). The Bode plot showing the results for this test can be seen in Figure 4-34. At the beginning of the test, starting at the high frequencies, the underlying aluminum was corroding and the coating was behaving as a bad coating. The impedance magnitude curve started with a slope of -1 at high frequencies, until it began to roll over starting at $2 \cdot 10^3$ Hz until 40 Hz. The phase angle, between $2 \cdot 10^3$ Hz and 40 Hz, began to increase from -90° to -10° . When the test reached 40 Hz, the phase angle dropped to -90° and the impedance resumed a -1 slope. At this time, a bubble had formed over the pinhole on the surface of the sample, and could be seen visually. When the test reached 1 Hz, this point during the test is shown as a dotted ellipse in the Bode plot shown in Figure 4-34, the surface of the sample was quickly exposed to air by shaking and tilting the test cell. After the bubble was removed, the Bode plot began to resemble a plot for corroding aluminum; for instance, the impedance at low frequencies dropped from above $10^8 \Omega$ to below $10^5 \Omega$.

Figure 4-34: EIS Bode Plot Results for Sample E Containing a Pinhole in KCl (pH 4) (Solartron)

The results for a cyclic voltammetry test, shown in Figure 4-35, also demonstrate a bubble forming over a pinhole and preventing the underlying aluminum from corroding. After the corrosion potential was reached, the current density stayed at $4 \cdot 10^{-10}$ A/cm². During the test, shown as a dotted circle in the figure, a bubble had formed on the surface of the sample and over the pinhole. When -0.6 V was reached on the forward scan, the bubble was removed from the surface of the sample by shaking and tilting the test cell. Once the bubble was removed, the cyclic voltammetry results began to

resemble corroding aluminum again; pitting and the passivation potential can be seen in the results.

Figure 4-35: Cyclic Voltammetry Results for Sample E in KCl (pH 4). Potential Range: -2.5 V to +3 V (Solartron)

4.3.2 Sample F

De-aerated Distilled Water (pH 7)

The pinhole in Sample F was made with a mathematical compass, as described in Section 3.7. The results for a cyclic voltammetry test in de-aerated distilled water (pH 7) are shown in Figure 4-36. The solution was de-aerated for 30 minutes using CO₂. The results resemble typical corroding aluminum results (Section 2.3.2). During the reverse scan, at 0.7 V, the current density decreased by 5 orders of magnitude. At this time during the test, the surface of the sample was observed, without disturbing the test cell,

and a bubble could be seen on the surface of the sample where the pinhole had been made.

Figure 4-36: Cyclic Voltammetry Results for Sample F in De-aerated Distilled Water (pH 7). Potential Range: -2.5 V to +3 V (Solartron)

An EIS test was performed in the same solution, de-aerated distilled water (pH 7), without disturbing the test cell or removing the bubble. The Bode plot results are shown in Figure 4-37. Using the results, it can be inferred that the underlying aluminum is no longer corroding; high impedance at low frequencies (above $10^9 \Omega$ at 0.1 Hz), and phase angles close to -90° are not features of corroding aluminum.

Figure 4-37: EIS Bode Plot Results for Sample F Containing a Pinhole in De-aerated Distilled Water (pH 7) (Solartron)

A second cyclic voltammetry test was performed without disturbing the bubble on the surface of the sample. The results, shown in Figure 4-38, suggest that the underlying aluminum is no longer corroding, and the coating is behaving as a good coating due to the pinhole being blocked; the current density does not change as potential is increased and decreased.

Figure 4-38: Second Cyclic Voltammetry Results for Sample F in De-aerated Distilled Water (pH 7). Potential Range: -2.5 V to +3 V (Solartron)

After the second cyclic voltammetry test, the bubble was removed from the surface of the sample (shaking and tilting the test cell and exposing the surface of the sample to air). An EIS test was performed, and the Bode plot results can be seen in Figure 4-39. The underlying aluminum is now corroding; for instance, the impedance at low frequencies in the Bode plot is below $10^7 \Omega$, phase angles are positive, and the slope of the impedance becomes positive at high frequencies.

Figure 4-39: Second EIS Bode Plot Results for Sample F Containing a Pinhole in De-aerated Distilled Water (pH 7) (Solartron)

A cyclic voltammetry test, with no bubble over the pinhole present, was performed. The results are shown in Figure 4-40. The shape and features of the curve are indicative of corroding aluminum; a corrosion potential occurs during the forward scan, the current density increases as voltage increase during the forward scan, and a passivation potential occurs during the reverse scan.

Figure 4-40: Third Cyclic Voltammetry Results for Sample F in De-aerated Distilled Water (pH 7). Potential Range: -2.5 V to +3 V (Solartron)

The results of two cyclic voltammetry tests, Figure 4-36 and Figure 4-40, were placed on the same graph to show the similarities, seen in Figure 4-41. Both sets of results have the same shape and features, until a bubble formed and blocked the pinhole in the results from Figure 4-36. The shift in current density is caused by the corrosion that occurred during the previous EIS test, results shown in Figure 4-39. The EIS test may have damaged the aluminum enough to increase the current density when another cyclic voltammetry test was performed.

Figure 4-41: Cyclic Voltammetry Results from Figure 4-36 and Figure 4-40 Overlaid to Emphasize the Similarities

Samples C and F experienced different results in de-aerated distilled water (pH 7). This is attributed to the pinholes being different sizes and shapes. Both pinholes were created using the same tool, a mathematical compass, but were made by hand and therefore would be different if the same force and angle were not used.

Chapter 5 Discussion of Results

5.1 Summary: Effect of pH on Corrosion

According to the Pourbaix diagram, a protective oxide barrier cannot form to protect aluminum from corrosion in strongly acidic solutions (Section 2.3.1). In neutral pH (pH 7), oxide can form and impede corrosion, but in strongly acid solutions (pH 0), no protective oxide can form and the aluminum should corrode. In the same way, if there were a holiday in a coating that exposes the underlying aluminum to the solution, then it would be expected that the aluminum would corrode more in strongly acidic solutions than in neutral solutions. In this study, it was found that for large pinholes, where the width may have been more than 80 μm , the underlying aluminum corroded more in acidic solution than in neutral solution, as expected, however, the opposite occurred for small pinholes, where the width may have been less than 80 μm .

Sample A (Section 4.1.1) and Sample B (Section 4.1.2), each one having a pinhole through the coating, both displayed sensitivity to pH. Both samples showed signs of the underlying aluminum corroding in neutral pH. The coating behaved as a good coating once the solution pH was changed from neutral to strongly acidic (pH 0 and pH 1). When placed in a neutral solution again, the coating behaved poorly once more. The coating behaved as a good coating again when placed in strongly acidic solution. Thus, pinholes that were ‘visible’ in neutral pH solution, *i.e.*, there were features of corroding aluminum, became ‘invisible’ in low pH solution, *i.e.*, there would no longer be features that are associated with corroding aluminum. Eventually, the coatings on both of the samples behaved poorly and allowed the aluminum to corrode in both neutral and low pH solutions.

5.2 Summary: Effect of De-aerating Using Carbon Dioxide

De-aeration slowed corrosion in pH 4 and pH 7 solutions (Section 4.2). Sample C changed from a poor coating to a good coating when distilled water (pH 7) was de-aerated using CO₂ (Section 4.2.1). The lowest pH at which corrosion was seen to be impeded with CO₂ de-aeration was pH 4.

Sample D was tested in aerated KCl (pH 4) and de-aerated KCl (pH 4) (Section 4.2.2). In aerated KCl (pH 4), the coating behaved poorly allowing the underlying aluminum to corrode. When the solution was de-aerated, the coating behaved well.

5.3 Summary: Formation of Bubbles

Section 4.3 showed corrosion stopped when a bubble was observed to have formed over the pinhole. Sample E showed that a bubble, large enough to be seen with the naked eye, could form in acidic KCl solution (pH 4). The bubble could not be dislodged easily; shaking the test cell did not remove it, the bubble had to be exposed to air.

It was observed that a large bubble could also form in de-aerated solutions, as seen in the results for Sample F (Section 4.3.2). Even in de-aerated distilled water (pH 7), a bubble formed over the pinhole. The bubble was observed after corrosion of the aluminum had stopped. When the bubble was dislodged, the aluminum began to corrode.

5.4 Interpretations and Explanations

Explanations have been proposed for why samples with pinholes behaved well in strongly acidic pH solutions and behaved poorly in neutral pH solutions. The

explanations are: swelling (Section 2.5), wetting (Section 2.4), and bubble formation. The in-service relevance is discussed with reference to the experiments using solutions de-aerated with CO₂.

Swelling

The chemical formulation of the polymer coating is proprietary, however, the coating is known to be an epoxy-free (Section 3.2). The coating may swell in acidic solution and block the pinhole. If the coating swells, there should be a change in the impedance in the capacitive region of EIS plots when the pH is changed from neutral to acidic [49]. The impedance of a capacitor is proportional to the thickness of the coating divided by the dielectric constant of the coating (Equation 2-13 and the equation for impedance of a capacitor (Table 2-1)). In Figure 4-24, the impedances in the capacitive region, where the impedance slope is -1, did not change when the pH was changed. This indicates that the ratio between thickness of the coating and the dielectric constant of the coating remains the same. For the ratio to remain the same, it would either not change when pH is changed (coating does not swell), or the thickness of the coating and the dielectric constant would change in the same way. It is unlikely that they would change in the same way: for instance, if the change in the dielectric constant depends on the volume of electrolyte absorbed into pores, the thickness would depend on cube root of the volume absorbed. Thus the lack of change in the capacitance as pH is changed is interpreted to mean that the coating does not swell more than the reproducibility associated with the impedance measurements, which is typically a few percent. The

coating thickness is 8 μm , which should require swelling of more than a few percent to close the pinhole in Sample B, which was 85 μm by 53 μm .

A simple experiment to show that swelling on the order of tens of microns is not happening is to compare the heights of surfaces under a drop of acid solution and neutral solution; running a stylus over the surface confirms no difference in height.

Another experiment is to measure if there is a change of resistance as pH is changed [38]. The suggested experiment involves taking a blank sample and measuring the resistance across the coating as pH is decreased from 7 to 0. If there is a change in resistance when pH is decreased, it might signify that the polymer swells. Resistance versus time, and resistance versus pH could be plotted and compared to see if there is a relationship between resistance and pH. A similar experiment was conducted using hydrogel by Lesho et al [38].

Wetting

Wetting may be the reason why the coating is pH-responsive. The polymer may become hydrophobic in strongly acidic solution. A hydrophobic coating might protect the aluminum by repelling acidic solution away from the pinhole. One suggested experiment to determine if the polymer becomes hydrophobic in acidic pH solution is to examine the contact angle. Drops of solutions with different pH could be placed along a blank sample and the contact angle measured as a function of pH. Preliminary experiments showed no difference in contact angle.

Wetting is considered to be another unlikely cause. For wetting to be the only mechanism responsible for the polymer behaving well in low pH solutions, the polymer

would need to prevent solution from reaching the underlying aluminum across the entire pinhole. It is considered unlikely that an 8 μm thick polymer is capable of extending any hydrophobic effect to the middle of a pinhole; in the case of Sample B, the middle of the pinhole would be as far as 42 μm away from the edge of the polymer.

De-aeration Using CO_2

Oxygen promotes and maintains the cathodic reaction (oxygen reduction) in mildly acidic solutions in the presence of air (Section 2.3) [22] [24]. In strongly acidic solution, the cathodic reaction is dominated by hydrogen reduction [22]. The results presented in Section 4.2 are consistent with previous work [8] showing de-aeration impeded corrosion in neutral solution, where oxygen reduction reaction dominates, however, de-aeration did not impede corrosion in strongly acidic solution, where the hydrogen reduction reaction dominates. Samples with large pinholes were not affected by de-aeration when the pH was 1 or 0. The lowest pH in present experiments at which CO_2 reduced corrosion was pH 4 (Section 4.2.2).

While many soft drinks have an acidic pH around 2.5, there are other soft drinks, such as root beer, with a pH of 4 [2] [7]. It is possible that de-aeration aids in impeding corrosion in beverage cans when the pH of the drink is at pH 4 or above, however orange juice, which has a pH of about 3.5 and is also sometimes stored in aluminum beverage cans, is not carbonated. Thus, de-aeration using CO_2 cannot be the only reason coated aluminum beverage cans perform well.

Initially, experiments with CO_2 were conceived to test whether de-aeration would cause the underlying aluminum to stop corroding. If de-aerating a strongly acidic

solution would prevent the aluminum from corroding, then the ability to make a pinhole ‘invisible’ in aerated strongly acidic solution might be interesting, but irrelevant for in-service conditions. For strongly acidic solutions, de-aeration using CO_2 made no difference, therefore being able to ‘heal’ pinholes by making them ‘invisible’ is relevant for the performance of the coating in-service.

Bubble Formation

The explanation for why the coated aluminum system behaves well in acid may be because bubbles form and block access of the electrolyte to the aluminum. When large bubbles were visibly blocking the pinholes, corrosion was observed to stop. It is suggested that for the other instances where corrosion was stopped in strongly acidic solutions, it may be because smaller bubbles likewise formed on the surface of the aluminum. These bubbles may form instantly, due to the aluminum corroding at a high rate in strongly acidic solution. The hydrogen reduction reaction is the dominating cathodic reaction in strongly acidic solutions, and hydrogen gas and bubbles form via Equation 2-29 (Section 2.3). Once the entire surface of the exposed aluminum is covered in tiny bubbles, corrosion can be stopped because the solution can no longer reach the aluminum. The size of the pinhole in the coating may constrain the bubble to be smaller than the critical size needed to leave the surface. In the instances where the samples were polarized anodically, the bubbles on the surface of the exposed aluminum could be oxygen (Equation 2-29) and/or chloride gas bubbles.

This bubble formation process can be related to nucleate boiling. In both cases, bubbles form at nucleation sites (in this thesis, the nucleation site would be in the

pinhole). Figure 5-1 shows the bubble formation process in liquid when a metal is placed on a heated surface. There are three major steps in nucleate boiling: nucleation, growth, and bubble release [56]. Similar steps are envisioned for hydrogen bubble formation in pinholes, except for bubble release.

Figure 5-1: Three Major Steps of Bubble Formation in Liquid on a Heated Metal Surface: Nucleation, Growth, and Bubble Release [56]

For nucleate boiling, the vapour bubbles will eventually be released because of the heat flux [56], however, for the hydrogen bubble in the pinhole, it may not be released if it shuts down corrosion. In nucleate boiling, the vapour bubble cannot turn the heat flux off, but the hydrogen bubble can cover the surface of the aluminum and stop corrosion, which could stop the growth of the hydrogen bubble before it reaches the critical size to be released from the surface.

The proposed bubble formation process for a coating-aluminum system with a pinhole in strongly acidic solution is shown in Figure 5-2. The four major steps in this bubble formation process are: bubble nucleation (1), bubble growth (2), bubble convergence (3), bubble coalescence (4). Cathodic and anodic reaction sites exist on the surface of the exposed aluminum. The exposed aluminum is corroded as the anodic reaction occurs, shown in the Figure as a curved aluminum surface. Small hydrogen bubbles, too small to see with the naked eye, form at the cathodic reaction sites because of hydrogen reduction reactions (bubble nucleation). The bubbles grow as the anodic and cathodic reactions continue, but still remain too small to be seen by the naked eye (bubble growth). It is possible that a bubble could roll off a cathodic site, because of the curved aluminum surface, and another bubble begin to form at the same cathodic site. The bubbles could eventually cover the entire surface of the exposed aluminum, block all the cathodic and anodic reaction sites, and stop corrosion (bubble convergence). The bubbles could also coalesce and form one large bubble, which might be visible to the naked eye (bubble coalescence). If the bubbles are not stable, they could be released from the surface of the aluminum, and the aluminum would begin to corrode again.

Figure 5-2: Proposed Bubble Formation Process for a Coating-Aluminum System with a Pinhole in Strongly Acidic Solution

The size of a pinhole should determine the probability that a bubble can form and block access of the electrolyte to the aluminum. An experiment could be performed where a range of pinhole sizes and shapes are examined under a microscope to see if formation of bubbles is correlated with corrosion currents.

As an example of how the proposed mechanism can be used to explain the results in this thesis, consider Figure 4-7; a cyclic voltammetry test was conducted on Sample A with a pinhole in HCl (pH 3.8). The results show that the current density was at $4 \cdot 10^{-11}$ A/cm² from -2 V until -0.5 V during the forward scan. The low current density, close to the limit of the equipment, could signify that small bubbles formed over the surface of the aluminum, and prevented the exposed aluminum from corroding. The current density increased to $3 \cdot 10^{-10}$ A/cm², which may be used to infer that the bubbles underwent a change; the increase in current density could be caused by the bubbles moving or coalescing and decreasing the effectiveness of the electrical barrier that the bubbles

created. During the reverse scan, from 2 V to 0.8 V, the current density decreased to $3 \cdot 10^{-10}$ A/cm²; the bubbles may have undergone another change which caused the effectiveness of their electrical barrier to increase. After 0.8 V during the reverse scan, the current density increased significantly from $3 \cdot 10^{-11}$ A/cm² to $4 \cdot 10^{-6}$ A/cm²; the graph began to resemble typical aluminum results until the end of the test. This change may indicate that bubbles left the surface of the aluminum and allowed corrosion.

Chapter 6 Concluding Remarks and Recommendations

Health Canada has determined that BPA could cause detrimental health effects, but only in extreme doses well above average intakes. Health Canada has recommended, but not insisted, that concentrations of BPA be lowered in the food industry when possible. Some members of the general public are quite concerned. Current aluminum beverage cans are protected from their corrosive contents by coatings that contain BPA, and the can industry is concerned about public perception of the safety of their products. The can industry is looking for new BPA-free coatings that will work as well as current coatings. The current coatings are believed to act as barriers, with few holidays connecting the beverage with the aluminum. In spite of these holidays, these coatings work well. Extensive research has been undertaken to reduce holidays, and the expectation is that new BPA-free coatings should be designed to have very few holidays as well. The goal of this thesis was to determine why the coating on aluminum beverage cans work well in acidic solutions despite containing holidays.

The major conclusions are:

- Aluminum samples covered with a coating containing a manufactured pinhole, for example a 50 μm by 80 μm pinhole, corroded in neutral solutions, and did not corrode in acidic solutions, contrary to expectations based on the Pourbaix diagram;
- Corrosion was observed to stop when bubbles visibly blocked pinholes;

- Corrosion was reduced in solutions de-aerated with CO₂ for pH 7 and 4, but not pH 1 and 0. This is consistent with the oxygen reduction reaction being dominant in pH 7 and 4, but the hydrogen reduction reaction dominating in pH 1 and 0.

Several explanations were proposed, but dismissed, for the contrary behaviour of coated aluminum samples in acidic solution. These include:

- Swelling: measurements of the impedances in the capacitive region for samples in acid and neutral solutions were the same, which suggests that the coating does not swell. In addition, it is unlikely that a 8 µm thick coating was able to swell enough to cover a 50 µm pinhole.
- Wetting: preliminary tests showed that contact angle of a drop of solution on the surface of a sample did not increase as pH decreased, indicating no change in wettability of the coating. It is unlikely that a 8 µm thick coating is capable of extending any hydrophobic effect to the middle of a 50 µm pinhole.

Bubble formation is proposed to explain why the coating works well in acidic solution, despite the coating containing holidays. The hydrogen reduction reaction produces hydrogen bubbles in strongly acidic solutions that can cover the exposed surface of the aluminum, rendering it inactive. This explanation is contrary to what might be expected from the aluminum Pourbaix diagram, where protective oxides form in neutral solutions, and do not form in strongly acidic solutions. Contrary to this expectation, the surface of the aluminum is protected from acid by hydrogen bubbles, which are prevented from leaving the surface of the aluminum when the exposed area of

the aluminum is small. Thus, in strong acid, it is not the coating that becomes protective, but the coating-aluminum system.

References

- [1] N. Anyadike, *Aluminium: The Challenges Ahead*. Cambridge, England: Woodhead Publishing, 2002.
- [2] S. Murrell, T.A. Marshall, P.J. Moynihan, F. Qian, and J.S. Wefel, "Comparison of In Vitro Erosion Potentials Between Beverages Available in the United Kingdom and the United States", *Journal of Dentistry*, vol. 38, pp. 284-289, 2010.
- [3] J.S. LaKind, "Can Coatings for Food and Beverages: Issues and Options", *Int. J. Technology, Policy and Management*, vol. 13, no. 1, pp. 80-95, 2013.
- [4] Health Canada. (2008, August) Health Risk Assessment of Bisphenol A from Food Packaging Applications. [Online]. http://www.hc-sc.gc.ca/fn-an/securit/packag-emball/bpa/bpa_hra-ers-eng.php
- [5] Government of Canada. (2012) Domestic Substances List Inventory Update. [Online]. <http://www.hc-sc.gc.ca/chem-chim/dsl-lis/index-eng.php>
- [6] Environment Canada. The Chemicals Management Plan. [Online]. <http://www.ec.gc.ca/toxiques-toxics/default.asp?lang=En&n=49FA6607-1>
- [7] P. Jain, P. Nihill, J. Sobkowski, and M.Z. Agustin, "Commercial Soft Drinks: pH and In Vitro Dissolution of Enamel", *General Dentistry*, vol. 55, no. 2, 2007.
- [8] M. Ali, "Studies of the Use of Electrochemical Impedance Spectroscopy to Characterize and Assess the Performance of Lacquers Used to Protect Aluminum Sheet and Can Ends", M.A.Sc. Thesis Carleton University, Ottawa, Ontario, 2012.
- [9] Gamry Instruments. (2011) A Snapshot of Electrochemical Impedance Spectroscopy. [Online]. <http://www.gamry.com/assets/Application-Notes/A-Snapshot-of-EIS.pdf>
- [10] V.F. Lvovich, *Impedance Spectroscopy: Applications to Electrochemical and Dielectric Phenomena*. Hoboken, New Jersey: John Wiley & Sons, 2012.
- [11] Gamry Instruments. (2012, September) Basics of Electrochemical Impedance Spectroscopy. [Online]. <http://www.gamry.com/assets/Application-Notes/Basics-of-EIS.pdf>

- [12] M.E. Orazem and B. Tribollet, *Electrochemical Impedance Spectroscopy*. Hoboken, New Jersey: John Wiley & Sons, 2008.
- [13] J.R. Macdonald, Ed., *Impedance Spectroscopy: Emphasizing Solid Materials and Systems*. Toronto: John Wiley & Sons, 1987.
- [14] E. Barsoukov and J.R. Macdonald, Eds., *Impedance Spectroscopy: Theory, Experiment, and Applications*, 2nd ed. Hoboken, New Jersey: John Wiley & Sons, 2005.
- [15] D. Loveday, P. Peterson, and B. Rodgers, "Evaluation of Organic Coatings with Electrochemical Impedance Spectroscopy Part 1: Fundamentals of Electrochemical Impedance Spectroscopy", Gamry Instruments, 2004.
- [16] Princeton Applied Research. (2010) Application Note AC-1: Basics of Electrochemical Impedance Spectroscopy. [Online]. <http://www.princetonappliedresearch.com/Literature/index.aspx>
- [17] Gabrielli, C.; Solartron Analytical. (1998, March) Identification of Electrochemical Processes by Frequency Response Analysis. [Online]. <http://www.solartronanalytical.com/Literature/Technical-Notes.aspx>
- [18] M. Keddah, C. Kuntz, H. Takenouti, and D. Schuster, "Exfoliation Aorrosion of Aluminium Alloys Examined by Electrode Impedance", *Electrochimica Acta*, vol. 42, no. 1, pp. 87-97, 1997.
- [19] Gamry Instruments. (2011, April) Two-, Three-, and Four-Electrode Experiments. [Online]. <http://www.gamry.com/assets/Application-Notes/2-3-4-Electrodes.pdf>
- [20] Princeton Applied Research. (2010) Flat Cell. [Online]. <http://www.princetonappliedresearch.com/Our-Products/Accessories/Flat-Cell-Kit.aspx>
- [21] P. Marcus and F. Mansfeld, Eds., *Analytical Methods in Corrosion Science and Engineering*. Boca Raton, Florida: CRC Press, 2006.
- [22] M.G. Fontana, *Corrosion Engineering*. United States of America: McGraw-Hill, Inc., 1986.

- [23] P.A. Schweitzer, *Fundamentals of Corrosion: Mechanisms, Causes, and Preventative Methods*. Boca Raton, Florida: CRC Press, 2010.
- [24] P.R. Roberge, *Corrosion Engineering: Principles and Practice*. Toronto: McGraw-Hill, 2008.
- [25] E. Ghali, "Aluminum and Aluminum Alloys", in *Uhlig's Corrosion Handbook*, 3rd ed., R. W. Revie, Ed. Hoboken, New Jersey: John Wiley & Sons, 2011, pp. 715-746.
- [26] P. Marcus, Ed., *Corrosion Mechanisms in Theory and Practice*, 3rd ed.: CRC Press, 2011.
- [27] D. Talbot and J. Talbot, *Corrosion Science and Technology*. New York: CRC Press, 1998.
- [28] NACE International. (2010) Corrosion - Anodic Protection. [Online]. <http://events.nace.org/library/corrosion/AnodProtect/passivecurve.asp>
- [29] F.J. Martin, G.T. Cheek, W.E. O'Grady, and P.M. Natishan, "Impedance Studies of the Passive Film on Aluminium", *Corrosion Science*, vol. 47, pp. 3187-3201, 2005.
- [30] Z. Szklarska-Smialowska, "Pitting Corrosion of Aluminum", *Corrosion Science*, vol. 41, pp. 1743-1767, 1999.
- [31] G. McRae, "MAAE 4906C - Corrosion and Corrosion Control", , Ottawa, ON, ON, 2012.
- [32] C.M.A. Brett, "On the Electrochemical Behaviour of Aluminium in Acidic Chloride Solution", *Corrosion Science*, vol. 33, no. 2, pp. 203-210, 1992.
- [33] E. McCafferty, "The Electrode Kinetics of Pit Initiation on Aluminum", *Corrosion Science*, vol. 37, no. 3, pp. 481-492, 1995.
- [34] M. Geoghegan and G. Krausch, "Wetting at Polymer Surfaces and Interfaces", *Progress in Polymer Science*, vol. 28, pp. 261-302, 2003.
- [35] E.C. Donaldson and A. Waqi, *Wettability*:. Gulf Publishing Company, 2008.

- [36] Adhesion Bonding. (2012, March) Plastic Surface Energy Wetting Test Methods. [Online]. <http://www.adhesionbonding.com/2012/03/19/plastics-surface-energy-wetting-test-methods/>
- [37] B.K. Lavine, L. Oxenford, M. Kim, N. Kaval, M. Benjamin, and W.R. Seutz, "Novel Turbidimetric Method to Study Polymer Swelling", *Microchemical Journal*, vol. 103, pp. 97-104, 2012.
- [38] M.J. Lesho and N.F. Jr. Shepphard, "A method for Studying Swelling Kinetics Based on Measurement of Electrical Conductivity", *Polymer Gels and Networks* 5, pp. 503-523, 1998.
- [39] G. Gervinskas, D. Day, and S. Juodkazis, "High-precision Interferometric Monitoring of Polymer Swelling using a Simple Optofluidic Sensor", *Sensors and Actuators B*, vol. 159, pp. 39-43, 2011.
- [40] R. Baboian, Ed., *Corrosion Tests and Standards: Application and Interpretation*, 2nd ed.: ASTM International, 2005.
- [41] G.P. Bierwagen, C.S. Jesscoate, J. Li, S. Balbyshev, D.E. Tallman, and D.J. Mills, "The use of electrochemical noise methods (ENM) to study thick, high impedance coatings", *Progress in Organic Coatings*, vol. 29, pp. 21-29, 1996.
- [42] R.-G. Hu, S. Zhang, J.-F. Bu, C.-J. Lin, and G.-L. Song, "Recent progress in corrosion protection of magnesium alloys by organic coatings", *Progress in Organic Coatings*, vol. 73, pp. 129-141, 2012.
- [43] S. Skale, V. Dolecek, and M. Slemnik, "Substitution of the constant phase element by Warburg impedance for protective coatings", *Corrosion Science*, vol. 49, pp. 1045-1055, 2007.
- [44] A.C.A. de Vooys, B. Boelen, and D.H. van der Weijde, "Screening of coated metal packaging cans using EIS", *Progress in Organic Coatings*, vol. 73, pp. 202-210, 2012.
- [45] F. Mansfeld, "Electrochemical Impedance Spectroscopy (EIS) as a New Tool for Investigating Methods of Corrosion Protection", *Electrochimica Acta*, vol. 35, no. 10, pp. 1533-1544, 1990.

- [46] Metrohm Autolab B.V. (2011, July) Autolab Application Note COR03. [Online]. http://www.ecochemie.nl/download/Applicationnotes/Autolab_Application_Note_COR03.pdf
- [47] E. Cano, D. Lafuente, and D.M. Bastidas, "Use of EIS for the Evaluation of the Protective Properties of Coatings for Metallic Cultural Heritage: A Review", *J Solid State Electrochem*, vol. 14, pp. 381-391, 2010.
- [48] F.S. Bovard, T.D. Burleigh, and A.T. Smith, "Electrochemical Impedance Spectroscopy of Electocoated Aluminium Food Cans", *Electrochimica Acta*, vol. 40, no. 2, pp. 201-207, 1995.
- [49] J.A. Grandle and S.R. Taylor, "Electrochemical Impedance Spectroscopy of Coated Aluminum Beverage Containers: Part 1 - Determination of an Optimal Parameter for Large Sample Evaluation", *Corrosion*, vol. 50, no. 10, pp. 792-803, October 1994.
- [50] J.A. Grandle and S.R. Taylor, "Electrochemical Impedance Spectroscopy as a Method to Evaluate Coated Aluminum Beverage Containers - Part 2: Statistical Analysis of Performance", *Corrosion*, vol. 53, no. 5, pp. 347-355, May 1997.
- [51] F. Gui and R.G. Kelly, "Performance Assessment and Prediction of Corrosion Prevention Compounds with Electrochemical Impedance Spectroscopy", *Corrosion*, vol. 61, no. 2, pp. 119-129, 2005.
- [52] M.-Y. Shon and H.-S. Kwon, "Effects of Surface Modification with Amino Branched Polydimethylsiloxane (ABP) on the Corrosion Protection of Epoxy Coating", *Corrosion Science*, vol. 49, pp. 4259-4275, 2007.
- [53] A. Wegmann, "Chemical Resistance of Waterborne Epoxy/Amine Coatings", *Progress in Organic Coatings*, vol. 32, pp. 231-239, 1997.
- [54] S.-Y. Zhang, Y.-F. Ding, S.-J. Li, X.-W. Luo, and W.-F. Zhou, "Effect of Polymeric Structure on the Corrosion Protection of Epoxy Coatings", *Corrosion Science*, vol. 44, pp. 861-869, 2002.
- [55] H.H. Uhlig and R.W. Revie, *Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering*, 3rd ed. Toronto, Canada: John Wiley & Sons, 1985.

- [56] O.E. Dwyer, *Boiling Liquid-Metal Heat Transfer*. Illinois, USA: American Nuclear Society, 1976.
- [57] Gamry Instruments. (2011) EIS Measurement of a Very Low Impedance Lithium Ion Battery. [Online]. <http://www.gamry.com/application-notes/eis-measurement-of-a-very-low-impedance-lithium-ion-battery/>
- [58] L.L. Sheir, R.A. Jarman, and G.T. Burstein, Eds., *Corrosion - Volume 2*, 3rd ed. Woburn, United States of America: Butterworth-Heinemann, 1994, vol. 2.