



DEVELOPMENT OF PROTECTIVE COATINGS FOR METALLIC BIPOLAR PLATES IN PEM FUEL CELL APPLICATIONS.

By

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A thesis submitted to
the University of Birmingham
for the degree of
DOCTOR OF PHILOSOPHY

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January 2023

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ABSTRACT

Polymer electrolyte membrane fuel cells have the potential to progress the worlds energy cycle toward a greener future. PEM fuel cells have the potential to power data centres, drones, auxiliary power units on planes, heavy and light duty vehicles but are still hindered by high costs and low hydrogen supply. For PEM fuel cells to become a mainstream power source, the price of stacks needs to be reduced. In addition, some applications require improvements in the gravimetric power density currently produced by systems.

Metallic bipolar plates have become the standard for modern fuel cell systems but plates often require expensive coatings. For this reason cheaper alternatives to PVD coating were investigated for stainless steel plates. Polyaniline/TiN - TiN bilayer coatings were investigated due to the simple equipment needed for coating and the low cost raw materials. Contact resistance was reduced by increasing TiN surface layer loading. This also improved the corrosion resistance of the sample. The optimised coating however failed to meet DoE contact resistance targets.

Reducing PVD coating thickness is another method to reduce coating costs. PVD coatings have already been shown to achieve DoE contact resistance tar-

gets. To increase gravimetric power density the mass of bipolar plates needs to be reduced. Aluminium was selected as the density is 40% that of stainless steel. Aluminium however readily corrodes in simulated fuel cell conditions, the metal is also covered in an insulating oxide layer which would lead to unacceptable contact resistance values. For this reason the substrate must be coated. In this work, TiN, TiC, CrC and TiAu, PVD coatings were applied to 99.0% pure aluminium and TiC, CrC and TiAu coatings to Alloy Al6082 substrates. All coated samples, except the TiC 99.0% coated sample, possessed excellent contact resistance values that far exceed DoE targets. However all the samples displayed typical aluminium corrosion phenomena. The corrosion resistance of materials was probed by means of linear sweep voltammetry and chronoamperometry, with ICPOES, EDX and SEM analysis characterisation techniques utilised to investigate the corrosion solutions and the samples.

Further investigations on the feasibility of aluminium bipolar plates were carried out by means of *in situ* degradation testing. *In situ* degradation was carried out by a duty cycle whereby the voltage was cycled between 0.9 V and 0.6 V. Polarisation curves and impedance spectroscopy measurements were carried out at the start of tests and every 12 hours to assess the performance degradation. The TiAu coating displayed superior performance to the graphitic bipolar plate at beginning of life but degraded through the test. Further work is required to achieve durability requirements. However PVD coated aluminium bipolar plates show promise in increasing the volumetric power density of PEM fuel cells.

ACKNOWLEDGMENTS

I would like to take this opportunity to recognise my supervisors Dr. Ahmad El-Kharouf and Dr. Neil Rees who have supported and guided me on my journey to submitting this thesis. This work would not be here without them. I would also like to thank Ahmad for giving me this opportunity.

I also cannot overstate the love, care and support I received from my family. Without them I would not be able to complete this thesis. My Mum and brother have been there for me at every turn and I have grown closer to both of them during the course of my PhD. Without them I would have been lost. My Dad has provided many wise words and late night chats that helped me see clearly and kept me grounded. Love you bro! Love you Mum!

During my time at the University of Birmingham I had the opportunity to work with many people. John Hooper ensured there was always a friendly face around to solve any and every issue I faced. Dr. Tzu-Chen who supported my work throughout covid and made it possible to get results during this hard time. Theresa Morris and Dr. Ludwig Schneider were both indispensable, and constantly shared their expertise in electron microscopy. Chynthol Kanhimbe and Manzo Brown both worked tirelessly to keep the labs working smoothly and safely. Dr. James Courtney who would drop everything at a moments notice to help with anything. I also wish to extend my appreciation to all the staff for their work in

getting myself and the other students back to the laboratory during covid.

I would also like to say thank you to my PhD family which formed during our time together, including: Alan Stephen, Peter Mardle, Oliver Fernihough, Abigail Snowden, Bhargav Pandya, Christopher Harrison, Naseruddin Khan, Oujen Hodjat-Pugh, Kun Zhang, Sathish Pandiyan, Zeyu Jiang, Laura Allerston, Bernardo Sarruf, Ahmed Ibrahim, Abdul Hye, Pushpa Patel and Marcus Adams.

To my close friends: Matthew Lewis, Jordan Dann, Harry James, Sam Byrne and brother, I cannot tell you how important you are to my life. I trust that all of you would be there for me at my lowest lows. I have felt so grateful to have you all to turn to through all the stress of my PhD.

I would like to acknowledge the EPSRC for the funding of the CDT in Fuel Cells and their Fuels, EP/L015749/1, which supported the research conducted in this paper.

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Chapter One

Introduction

1.1 Global Warming and the Role of Alternative Fuels

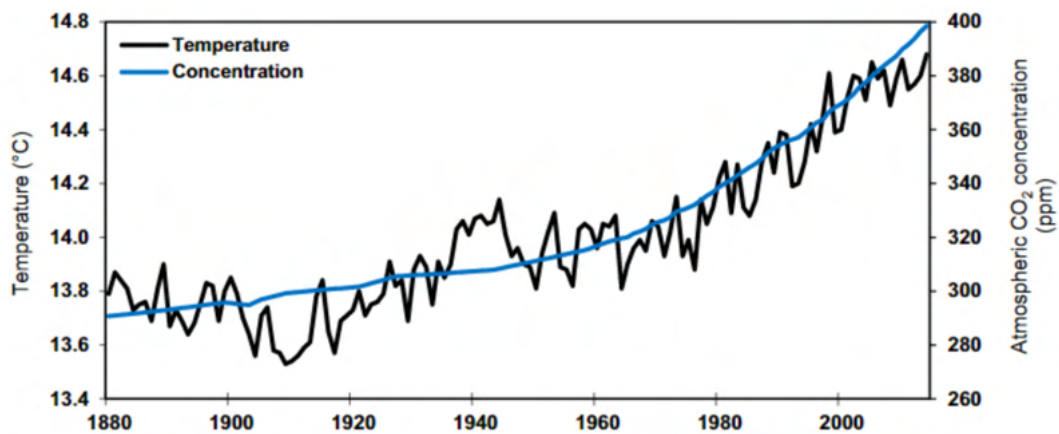


Figure 1.1: Average global temperature and atmospheric CO_2 concentration from pre-industrial era to 2014 (1880-2014) from [1].

The 2015 Paris Agreements pledged to limit global warming to 1.5°C relative to pre-industrial times [5]. The accumulation of CO_2 in the atmosphere is the main driver of global warming [6]. Current trends project an atmospheric CO_2 concentration increasing from the current 410 ppm to between 530 and 980 ppm

by the year 2100. This is far higher than pre-industrial levels of 280 ppm [6]. This increase of CO_2 concentration could cause a global mean temperature increase of 6.1°C [6].

The international community is increasingly concerned with the unrelenting increase in CO_2 emissions and the resulting global warming and climate change [1, 7, 8]. One aspect of climate change includes the increase in sea levels. Sea levels have risen by 19 cm in the 20th century, due to the melting of ice sheets [1]. Global sea and atmospheric temperatures have been reported throughout the last century, with record temperatures being recorded [1]. In 2015 a maximum average temperature rise of 0.93°C was reported [1]. Research has found correlations between average temperature increases and increases in global greenhouse gas emissions, induced by human activities [1]. El-Montasser et al. notes that to alleviate climate change it is imperative that a reduction of atmospheric greenhouse gases occurs [1]. In 2015 atmospheric CO_2 concentrations reached 400 ppm, such values had not occurred in the past 800,000 years [1]. Industrialisation, urbanisation, deforestation and extensive use of fossil fuels are being attributed to the rapid increase in greenhouse gas concentrations [1].

The use of fossil fuels produce CO_2 which accelerate global warming [9]. The present dependence on energy from fossil fuels leads to environmental pollution and global warming, both of which are risks to human health and life [9, 10]. Fossil fuels dominate primary energy supply with a share of 81% of global energy demand [5]. While policy makers are fully aware of the necessity to avert climate change through new sustainable energy sources, they face the dilemma of increasing demand of energy [10]. Greenhouse gases have been associated with

global warming [8]. Welsby et al. concluded that to achieve a 50% probability of limiting global warming to 1.5 °C nearly 60% of oil and natural gas and 90% of coal must remain un-extracted [5]. Consistent rises in carbon emissions are being witnessed [8]. 72% of greenhouse gasses are carbon dioxide emissions (CO_2). Human life is also threatened as natural threats arise from these emissions and risk long droughts, global warming, floods [7]. 2017 was a record year for hurricanes, wildfires, heatwaves and droughts [8]. Furthermore fossil fuels are a non-renewable energy source [7, 9, 10].

Transportation contributes to between 20 - 29% of total world energy consumption, 65% world oil consumption and 24% of global CO_2 emissions for the 10 largest emitters (China, United States, India, Russia, Japan, Germany, South Korea, Iran, Canada and Saudi Arabia [7, 9, 10]). Emissions from the transport sector are expected to grow to 45% of all emissions by 2030 [10]. The transportation sector is also responsible for emissions of harmful (to human health and the environment) gases such as nitrogen oxides, volatile organic compounds, carbon monoxide and carbon dioxide (NO_x , VOC , CO , CO_2) [10]. The European Union had a climate change pact for 2020 to ensure the bloc meets its targets, such as a 20% decrease in GHG emissions, 20% total energy from renewables and increase in energy efficiency [7]. There are also targets for a 10% increase in the share of biofuels in the transportation sector [7]. Changes to the transportation sector are necessary to reduce energy consumption [7].

Renewable energy technologies offer viable simplified solutions for dealing with energy poverty and climate change [8]. Renewable energy sources have low carbon content and therefore are less polluting to the environment [8]. Interna-

tional agencies are promoting the use of renewable energy as a strategy to increase both the access to electricity and to reduce the environmental harm associated with non-renewable technologies [8].

1.2 Hydrogen and Fuel Cells

Fossil fuel alternatives such as biodiesel, methanol, ethanol, butanol, dimethyl ether, diethyl ether, bioethanol, synthetic natural gas (syn gas or SNG) and hydrogen are being investigated as future fuels [10]. From these fuels, hydrogen has established itself as the most viable energy source as a long term renewable alternative to fossil fuels. Hydrogen is a renewable energy carrier that can form part of a cyclic economy [9, 10]. At the point of use, hydrogen does not produce any greenhouse gases, with water and heat the only products (combustion of hydrogen can cause NO_x emissions due to the high flame temperature of hydrogen). H_2 can be used in internal combustion engines [10]. Hydrogen has the potential to transition the world energy mix toward renewable fuels [9].

Hydrogen is the most abundant element in the universe and can readily be found in chemical compounds such as water and the organic compounds of biomass [9]. Hydrogen can be produced from natural gas, however this process continues fossil fuel dependence, geopolitical complications and produces just as much CO_2 as burning the initial gas [9]. Water splitting facilitated by renewable energy through means of electrolytic, photochemical or biological processes offer the most plentiful and climate friendly source of hydrogen [9]. Electrolysis is an

electrolytic method of splitting water. With renewable energy electrolysis can be used to produce renewable green hydrogen. Liquid water is abundant and widely distributed on Earth, therefore hydrogen could potentially avoid the geopolitical issues that arise from the uneven distribution of resources [9, 10]. High purity hydrogen can be produced by the electrolysis of water, the energy required for this process can be supplied through renewable energy sources such as solar, wind and tidal [10]. In addition, hydrogen can be deployed as an energy store for the intermittent energy supply from renewable sources [9].

The clean combustion of hydrogen produces heat and water with no generation of particulates or carbon dioxide; however in air, the combustion of hydrogen can produce nitrous oxides which can be damaging to human health and form acid rain [9, 11, 12]. One way to utilise hydrogen but mitigate nitrous oxide emissions is via an electrochemical reaction facilitated by fuel cells [10]. In these systems electricity, heat and water are produced [9]. The most effective use of hydrogen is the conversion of chemical energy to electrical energy in fuel cells; which offer high conversion efficiencies, in excess of 60% [9]. Hydrogen fuel cells have promising applications in the transportation sector when paired with efficient electric motors (typically above 90% efficiency) [9, 10, 13].

1.3 Polymer Electrolyte Membrane Fuel Cells

Polymer Electrolyte Membrane (PEM) fuel cells are an electrochemical energy conversion system. Within fuel cells a spontaneous reaction occurs between fuel

and oxidant to generate: electricity, heat and the products of the reaction [14]. The reactions occur at the anode and cathode of the system [14]. PEM systems are typically modular and offer a wide window of power from less than 1 kW to MW systems, allowing for a far reaching market diversity [14, 15].

1.3.1 Operation

PEM fuel cells typically operate at 80°C and a relative humidity (RH) of 40% or higher [16]. Humidification of the reactant gas supply and cell, the operating temperature and the gas inlet temperatures were found to be significant parameters in the performance of single cell tests [17]. Membranes typically cannot withstand temperatures higher than 80°C as the chemical and mechanical stability of the ionomer is compromised due to the low glass transition temperatures of the polymer chains of perfluorosulfonic acid (PFSA) ionomers [16].

Fuel cells are also capable of cold starts at temperatures as low as -30°C , with research ongoing to mitigate cell degradation on cold starts [14, 18, 19].

1.3.2 Advantages

Fuel cells and batteries work in similar applications and markets. Batteries however are energy storage devices and require more or larger batteries to increase the maximum energy of the device [20]. Conversely, to increase the fuel cells energy storage a larger fuel tank is required [20]. In addition a fuel cell system will continue to produce electricity as fuel is supplied, with no slow recharging neces-

sary. Instead fuel cell systems are refuelled in much the same way as typical fossil fuel powered vehicles [20]. Fuel cells offer benefits in applications such as heavy duty vehicles, where long range and fast refueling is essential [21]. Like batteries, hydrogen fuel cells have zero emissions at point of use [22]. PEM fuel cells also offer much higher efficiencies than ICE engines with only water and heat as waste products [20, 22]. Furthermore fuel cells operate at low temperature, with high power densities and are easily scaled due to their modular nature, they also have quick start up times [4, 20].

1.3.3 Disadvantages

Cost, durability and lack of hydrogen supply inhibit PEM fuel cells from widespread commercial adoption [4]. The platinum required for the catalyst contributes as much as 40% of the total cost of the stack for high volume production. Materials costs are difficult to reduce and as such alternative areas of the fuel cell may have to be targeted to reduce stack cost [4]. In 2008 Crabtree et al. found that hydrogen fuel cells currently cost roughly 100 times more per kW than gasoline engines, $\$3000\text{ kW}^{-1}$ compared to $\$30\text{ kW}^{-1}$ respectively [9]. However these price points are converging. Ajanovic et al. carried out a review in 2021 and found that fuel cells cost between €100 and €120 per 100 km whereas internal combustion engines cost between €35 to €40 per 100 km of driving (includes capital, maintenance and fuel costs) [23]. Forecasts by Gray et al. found that heavy duty PEM systems could achieve cost parity with diesel engines by 2040 given the right development, electricity and fuel costs [24]. Cost and performance need optimisation

to effectively challenge internal combustion engine vehicles, this presents materials challenges for bipolar plates, GDLs, catalysts and membranes [9].

Hydrogen infrastructure is seen as a major inhibitor to the adoption of hydrogen fuel cells. Globally only 385 hydrogen stations exist for transportation with 78.4% of these open to the public [25]. Research is being carried out as to best assess the requirements of hydrogen infrastructure but full deployment has not yet been achieved [21, 25].

1.3.4 Structure

System

PEM fuel cell systems can be considered as 4 subsystems; reactant supply, power electronic subsystems, thermal and water management [20]. The reactant subsystem is responsible for the delivery of the reactants, this includes the compressor (or blower), hydrogen tank and the necessary equipment to control the stoichiometry, pressures and flow rates of the air and hydrogen. Compressors or blowers are required for the cathode air stream, while a series of controllable valves are needed for the hydrogen tank [20]. Improper control of the gas streams can lead to fuel starvation, loss of power and efficiency. Fuel starvation also leads to degradation of the membrane electrode assembly MEA [20]. Thermal management of fuel cell stacks are vital as almost half of the energy generated by the fuel cell is heat. Heat affects the electrochemical rate of reaction, membrane humidity and the behaviour of water in the system [20]. If the fuel cell becomes too hot the structural integrity

of the membrane can be compromised, even prior to this the membrane can dehydrate increasing the ohmic resistance of the cell and decreasing efficiency [20]. Therefore it is imperative that system heat is controlled. High power systems, in excess of 1.5 kW, require liquid cooling as air cooling does not achieve a sufficient rate of cooling. In addition water management is crucial to PEM fuel cell systems. Membranes require sufficient water to conduct protons but excessive water results in mass transport losses as gas diffusion to the catalyst is inhibited [20]. If too much water is removed from the MEA then the resistance of the membrane increases and membrane stability is reduced. Water management is aided by the use of humidifiers [20]. Humidifiers are used to humidify the inlet gas streams [20]. PEM fuel cells produce a direct current (DC), the voltage and current of which will vary depending on the operation and design of the system and cell [20]. Power management consists of voltage regulators, DC/DC converters and chopper circuits. Inverters may also be utilised depending on the application of the system [20]. Fuel cells are often employed with batteries to maintain a continuous fixed system voltage.

PEM Fuel Cell

Multiple cells are stacked together and compressed using end plates to form a stack as depicted in figure 1.2 [20]. Each cell is made up of a polymer membrane as an electrolyte positioned between two electrodes, the anode and cathode as shown in figure 1.3. This makes up the membrane electrode assembly (MEA) [20]. The MEA itself is compressed between two microporous layers and GDLs, these in turn are compressed between bipolar plates, making up a single cell [20].

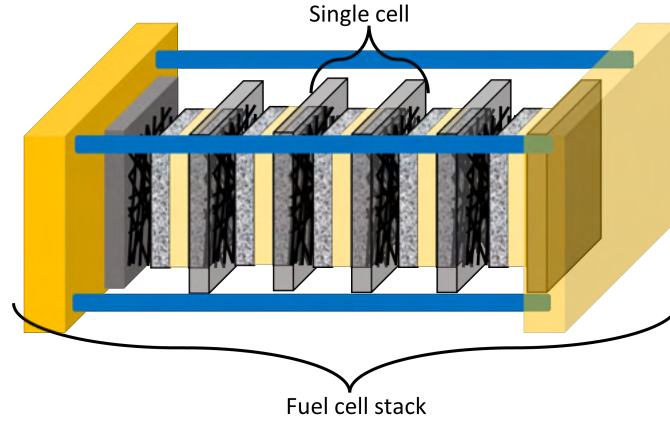


Figure 1.2: Structure of a PEM fuel cell stack (not drawn to scale).

For a PEM fuel cell, each cell has a maximum theoretical thermodynamic open circuit potential (OCV) of 1.226 V. This potential cannot be achieved due to non-standard conditions, hydrogen crossover, current leakage, electrolyte poisoning and catalyst poisoning [14, 26]. PEM fuel cells also exhibit large activation overpotentials for the cathode reaction; which is about 200-300 mV [14, 20]. Ohmic and mass transport overpotentials also contribute to the losses inside the fuel cell [14]. Within the catalyst layers of the MEA the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) take place. Proton transport is facilitated within the MEA by ionomer, which is used in electrodes and the polymer membrane [27]. The HOR and ORR can be seen by equations 1.1 and 1.2 respectively [16, 27]. Hydrogen is supplied to the anode where the HOR occurs upon the catalyst; the electrons are conducted away via the catalyst support to the MPL where the electrons conduct to the next cell via the GDL and bipolar plate [28]. The hydrogen ion, a proton, is conducted via the membrane to the cathode. At the cathode the ORR occurs forming water [16, 27]. The complete reaction can be

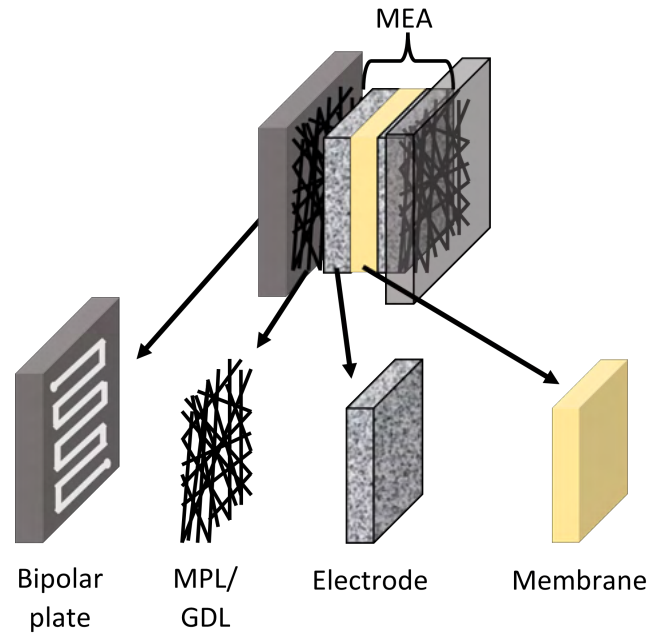


Figure 1.3: Components of a single PEM fuel cell (not drawn to scale).

seen in equation 1.3.

Anodic half reaction:



Cathodic half reaction:



Complete reaction:



1.3.5 Components

Membrane

Polymer membranes (usually Nafion®) facilitate proton conduction via a proton hopping process (Grotthuss mechanism) [4, 29]. This mechanism requires hydration of the membrane, however this has to be balanced with flooding [4, 9]. Polymer electrolyte membranes utilise a $C - F$ backbone with sulphonic acid side chains [9]. The membranes serve further function by providing electrical isolation between the two electrodes, preventing a short circuit and separation of reactant gases [4]. Optimal hydration is determined by the rate of water generation, electro-osmotic drag, gas crossover (back diffusion) and water permeation across the membrane [4].

Key material issues faced by membranes include: acid loading (which provide further proton conduction pathways), polymer crosslinking (associated with thermal and mechanical stability) and increased surface area to enable effective ionic conductivity between the electrodes [9].

Catalyst Layers

The catalyst layer facilitates the oxygen reduction and hydrogen oxidation reactions at the cathode and anode respectively [4, 14, 28]. At the cathode of PEM fuel cells the catalyst promotes the reaction of the protons, electrons and oxygen to produce water in an oxygen reduction reaction (ORR). This is the rate limiting step for PEM fuel cells [9]. Due to the slower reaction in the cathode,

catalyst loadings are typically higher than in the anode [30]. Oxidation of hydrogen occurs at the anode (HOR) [4, 14]. Reactions occur at the triple phase boundaries, where the electrolyte, catalyst and fuel or oxidant meet [4]. At these triple phase boundaries the electrochemical reaction between the gases, electrons and protons can take place, in reality some of the gases will permeate through the polymer ionomer creating a larger area than the initial triple phase boundary [28]. The gases diffuse through the porous electrode to reach the catalyst surface, these pores also allow for the removal of water [28]. Protons are conducted through ionomer in the catalyst layers and membrane [20, 28]. Catalyst layers are typically in the region of 5 to 15 μm . Short proton pathways and minimised gas permeation distances can increase potential [28, 29].

Most of the catalysts used for low temperature fuel cells are noble metals: platinum, iridium, ruthenium, palladium, gold and silver [14]. The electrochemical reactions occur on the surface of these catalysts; as such it is imperative that high surface area catalysts are developed [14]. For this reason PEM fuel cells employ dispersed nanoparticles upon carbon supports as catalysts [9, 14]. Carbon is electrically conductive and can be produced through many veins with high surface area [14]. Typically Vulcan XC72R is used as support material [28]. Platinum based materials are typically used as a catalyst for both the anode and cathode, they can be crystallised on the support to form many crystals, as small as 2 nm in particle size [4, 14, 28]. By this method the catalytic surface area can be quadrupled or more for a given mass as compared to platinum black [14]. This is essential for minimising capital costs of the fuel cell and is the basis for much research [14]. Other metals, when alloyed with platinum group metals, can increase catalytic

activity, they include: nickel, iron, cobalt, chromium, vanadium, molybdenum, tin, tungsten and others [14]. Alloying platinum with nickel yields an increase in catalytic activity by a factor of 10, this is achieved due to the alteration of the platinum electron shell by the nickel [9]. Platinum catalyst material is typically applied with an area density of $0.3\text{-}0.4\text{ mgcm}^{-2}$, this catalyst is mixed with an ionomer to provide proton conduction pathways [28, 29]. The catalyst active area can be maximised by including ionomer in the the catalyst ink, 28% by weight of ionomer in the catalyst ink was found to produce the highest performance [28]. However the optimum ionomer loading will depend upon the application.

Electrodes are deposited on the membrane to produce catalyst coated membranes (CCMs) or deposited on the gas diffusion layers (GDLs) to form gas diffusion electrodes (GDEs) [14]. Maximising platinum surface area, while maintaining durability, and testing exotic alloys are the current research trends of the catalyst field. To improve catalysts for PEM fuel cells it is essential to increase platinum utilization, this will allow for decreased costs through reduced material requirements [28].

Micro-Porous and Gas Diffusion Layers

Gas diffusion layers (GDLs) are porous carbonaceous electrically conductive materials [31]. In PEM fuel cells, GDLs are responsible for:

- Diffusion of the fuel and oxidant (hydrogen and oxygen/air) from the flow field on the bipolar plate to the anode and cathode respectively

- Necessary for the Hydrogen oxidation reaction (HOR) at the anode and oxygen reduction reaction (ORR) at the cathode
- Water management
 - Prevent flooding of the cell by extracting water
- Providing electron conduction pathway
 - Conduct electrons between the bipolar plate and electrodes

From [4, 29, 31].

GDLs are hydrophobic and are typically impregnated with (polytetrafluoroethylene) PTFE, of 5 to 30% weight percent, to prevent the blockage of pores with water [14, 31]. The thickness varies between 100 - 400 μm with a porosity in the range of 70 and 80%, the pore size it typically between 20 and 50 μm [29]. Microporous layers (MPL) are added to improve the water removal from the cathode electrode, increase the electrical contact conductivity and reduce the penetration of the catalyst ink for GDEs [29, 31]. MPLs have been reported to improve performance and increase durability [31]. MPLs have smaller pore sizes than GDLs with values between 0.1 and 0.5 μm [29]. Water can accumulate in the gaps between the MPL and catalyst layer, cracks also lead to water accumulation. Cracks provide pathways for water to the GDL where it can migrate toward the bipolar plate [29].

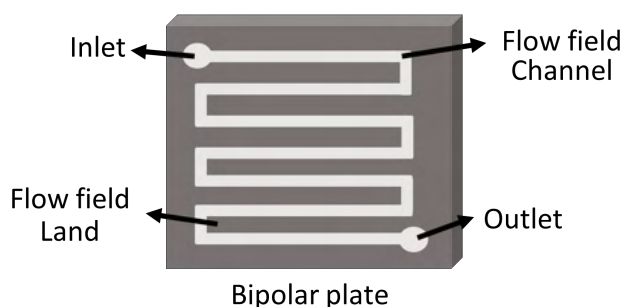


Figure 1.4: Example of a single serpentine BPP (not drawn to scale).

Bipolar Plate

The bipolar plate is responsible for structural support, heat management (through cooling channels) and electron conduction in fuel cells. The BPP has a stamped or machined flow field for distributing reactant gases to the cell, it also acts in water management and fuel supply [29, 32]. Bipolar plates should have a low bulk electrical resistance and low electrical contact resistance with the carbonaceous GDL to limit ohmic losses. High thermal conductivity is also required to enable thermal management of the stack [29]. It is imperative that the plate is impermeable to the reactant gases, as to prevent mixing of the fuel and oxidant [29]. Within the fuel cell, plates are exposed to harsh electrochemical conditions. Increased temperatures and transient potentials can be damaging to bipolar plates. Therefore it is essential that bipolar plates are resistance to electrochemical corrosion [29]. Lastly, it is essential that bipolar plates are economic to produce on a mass scale. Excellent manufacturability of materials and automated production processes are required for economical bipolar plates [29, 32]. Performance requirements are quantified in the DoE targets listed in table 1.1.

Table 1.1: DoE targets for bipolar plates [4].

Characteristic	Units	2015 Status	2020 Targets
Cost	$\$/kW^{-1}$	7	3
Plate mass	kg/kW^{-1}	<0.4	0.4
Plate H_2 permeation coefficient	Std $cm^3(s^{-1}cm^{-2}Pa^{-1})$, 3 atm, 100% RH 80°C	0	$< 1.3 * 10^{-14}$
Anode corrosion	$\mu A/cm^{-2}$	No active peak	<1 and no active peak
Cathode corrosion	$\mu A/cm^{-2}$	<0.1	<1
Electrical conductivity	S/cm^{-1}	>100	>100
Interfacial contact resistance	Ωcm^2	0.006	<0.01
Flexural strength	MPa	>34 (carbon plate)	>25
Forming elongation	%	20-40	40

that can be achieved, this restricts the systems applications.

1.3.6 Applications

PEM fuel cells offer power generation solutions to a vast range of industries. PEM systems are modular and offer a wide window of power supply, from micro to mega watts systems, allowing for a far reaching market diversity [14, 20, 33]. Fast start up times increases the versatility of these systems [4, 20].

As of November 2002, Song et al. reported that PEM fuel cells have 3 main applications: transportation, stationary and portable power units [9, 13]. There has been a global (US, Japan and the EU) uptake in the research of fuel cell buses, trains and personal vehicles [13]. With buses being close to full scale validation by meeting the ultimate 25,000 hour targets set by the U.S. Department of Energy [4]. Use of hydrogen fuel cells in the transportation sector enable the reduction of environmental pollution and reduce crude oil dependency [4, 9, 13]. PEM fuel cell vehicles are publicly available now with vehicles from Toyota, Honda and Hyundai [34–37].

Power generators are another sector which could see rapid changes with the mass commercialisation of PEM fuel cells. High power output systems have been implemented in hospitals, hotels and office buildings [20]. Fuel can be stored onsite allowing for back up power in situations when grid power is not available, such as emergencies. Data-centres could also benefit from PEM power generation where continuous power is critical [38]. Ballard’s ClearGen 2 stationary power system, as of July 2023, utilises hydrogen in modular PEM fuel cells to deliver up to 1.5 MW per module and can be easily scaled depending on customer requirements [39].

In addition PEM portable power generators are capable of offering offer clean, quiet power solutions for events, construction and in emergency rescue situations [15, 40]. Rural and micro-grid power has also been proposed by fuel cell manufacturers where the large operating window of PEM systems are beneficial [15].

The versatility of PEM fuel cells combined with the fast refuelling time means that these systems can provide solutions in some niche applications [20, 21]. Wang et al. highlights the aerospace industry as a suitable avenue including the space industry. Fuel cells have also been integrated into hybrid power systems; comprised of photovoltaic cells, hydrogen fuel cells and batteries aboard UAVs [41]. Gadalla et al. showed that the flight time of UAVs can be increased from 470 minutes to 970 minutes [41]. Bahari et al. and Herwerth et al. both successfully investigated using PEM fuel cells to increase the range of UAVs [42, 43]. Herwerth et al. used PEM systems to provide power throughout the entire flight path of the UAV with a battery used for additional power at take off and climbing [43]. Toghyani et al. also identified PEM fuel cells to be a viable power source for UAVs and worked to decrease the mass and volume of the system, two critically important parameters for flight [44].

1.4 Bipolar Plates Materials, Designs and Challenges

The expected requirements of commercially viable bipolar plates are listed in table 1.1. From these targets it can be seen that mechanical properties, gas impermeability, corrosion resistance, cost, interfacial and bulk electrical conductivity are the crucial factors for bipolar plates [13, 45]. Mass and thermal conductivity are also important for the gravimetric power density and thermal management of the system but are not outlined in these targets [45].

Traditionally BPPs have been made from high density graphite [46]. Graphite provides excellent corrosion resistance and has a very low interfacial contact resistance with the carbon paper used as a GDL. Graphite however is costly to process and machine [46]. In addition, it is brittle and thick plates are required to provide the necessary mechanical requirements of the stack [46]. The mechanical properties of graphitic carbon result in high costs when machining the BPP flow fields. Graphitic BPPs are vulnerable to fracturing during manufacture [13]. The price of the bulk material is relatively low but production challenges inhibit mass production [14].

Non-porous graphite plates are prepared via meticulous heat raising processes, reaching temperatures as high as 3000°C [47]. This process is called graphitization and is used to create a more homogeneous and crystalline carbon structure using carbon powder/graphite powder starting materials. This process is time consuming and creates a structure with a porosity of around 20 - 30%. Pores can lead

to reactant gas mixing and leakage of reactants, therefore graphitic BPPs require further processing to reduce the porosity [13].

Graphitic BPPs can be produced by machining, injection moulding and gelcasting (Aqueous Tape Casting) methods, the advantages and disadvantages of which are listed in table 1.2 [13].

A graphitisation processes can be added after the plate is formed to enhance the performance of the plate, however this increase the cost of the plate [13]. Carbon composites are a carbon based material developed with the intention of solving the mechanical and manufacturing issues related to graphite. Composites are composed of graphite and a thermoplastic, namely polyethylene or polypropylene. Making the material less brittle, allowing for plates to be formed more easily [14]. However with a large percentage of polymer in the construction, the area specific resistance (ASR - synonymous with ICR) increases dramatically, with values of $1 \Omega cm^2$ being reported. DoE 2020 targets require an ASR of $10 m\Omega cm^2$ (a factor of 10 lower) [14]. It was reported that these carbon composite plates could match the performance of graphite equivalent BPPs but with favourable production [48].

Similar work has also been carried out on expanded graphite, whereby a raw expanded graphite plate is impregnated with a low viscosity thermosetting resin to improve the mechanical properties and to prevent gas permeation [49]. This method has the benefit of gas channels being formed by stamping and not a machining process. A plate with a density of $1 gcm^{-2}$ was produced [49]. Yan et al. reported the contact resistance between carbon paper (gas diffusion layer) and pure graphite, composite and expanded graphite bipolar plates was 13.94, 21.74,

Table 1.2: Table of bipolar plate fabrication techniques.

Method	Advantages	Disadvantages
Machining	Well established	Not possible to make plates thinner than 1.5 mm (due to low strength and brittle nature of graphite) Poor dimensional accuracy and surface quality Increased cost of plate
Injection Moulding	One step plate and flow field forming Additives can be used to improve material properties	Thick section cracking Long binder removal time (up to 7 days) Size limitations Defects can also be formed during the process
Gelcasting	Superior mechanical and electrical properties relative to injection moulding No cracks or shape distortion reported from this process Can form complex shapes	None reported

and $31.85 \text{ m}\Omega\text{cm}^2$ at a pressure of 140 Ncm^{-2} . All of which fail to meet the DoE target. Through plane resistance of the plate was not reported [49].

1.4.1 Metallic Materials

The difficulties faced by composite and graphitic plates are not present with metallic materials. Metals exhibit high mechanical strength, excellent shock and vibration durability (non-brittle), no gas permeability and superior manufacturability [32, 50]. These properties make metallic materials excellent candidates for fuel cell BPPs. To this end metallic materials have been utilised, including: stainless steel, titanium and aluminium [4, 46, 51]. Metallic materials are relatively inexpensive with exceptional thermal and electrical properties, they are also recyclable [29, 32]. High thermal conductivity of BPPs is essential for high power stacks as heat rejection becomes crucial to the performance of the stack [52, 53]. In addition, by utilising metallic BPPs, the thickness can be minimised, with industry and academia forming plates of 0.1 mm, while maintaining sufficient mechanical properties [50, 54, 55]. Thin plates allow for the volumetric energy density of a system to be maximised. This is imperative for transport applications and any market which suffers from packaging constraints [14].

Metallic materials however do suffer from electrochemical corrosion in the chemically aggressive fuel cell conditions [29]. In the PEM fuel cell environment metallic materials corrode, form passive layers and leach ions leading to performance degradation [32]. The passivation of metallic materials increases the contact resistance between the plate and the GDL, thereby reducing both efficiency and

performance. Furthermore ions can leach from the metal by corrosion processes and permeate to the catalyst and membrane, poisoning the materials and degrading performance. Ehteshami et al. reported that metal ions reduce the ionic conductivity of the membrane [29, 32, 56].

Metallic materials allow for stamping processes to be utilised, which is a well understood, cheap and quick process; allowing for the fabrication costs of BPPs to be minimised [14]. Metallic bipolar plates can be produced by stamping, hydroforming and rubber pad forming processes.

Stamping and Hydroforming

Stamping processes rely on the plastic deformation of a material, the material is given its form by using a mould and die while a force is applied. The material deforms and matches the moulds shape [13, 57]. Stamping is a low cost and high throughput process, by stamping the production of thin plates is possible (0.051 mm). Stamped plates are uniform with high strength properties. This technique is already heavily utilised by industry, including automotive and aerospace [13].

Tolerance issues can arise from these production methods. Uneven plates in fuel cells could result in asymmetric loading in the stack, this could cause an increase in ICR and damage to the CCM. Wrinkling or cracking of the metal can also occur in the micro-channels as the metal is deformed to meet the shape of the mould. Mould design can be optimised to reduce these defects [13].

Hydroforming processes use a liquid to apply force to the blank plate. This

process is advantageous because one mould is required, superior surface quality and higher tolerances can be achieved. However the production rate is slower [57]. A tight tolerance is essential for stack construction as multiple plates are stacked together.

Rubber Pad Forming

Rubber pad forming, also referred to as flexible moulding, is a relatively new stamping process, it consists of a rigid die and a rubber plate, this process improves the formability of the micro-scale flow channels. The rubber pad and rigid die do not need to be assembled, increasing the rate of production. Thereby reducing costs. Furthermore this process solves the issues of cracks, wrinkles and surface corrugations often seen on stamping and hydroforming processes [13]. The weakness of this process is that the rubber pad has to be replaced regularly. Punch velocity, punch pressure, rubber thickness, rubber hardness and draft angle can be adjusted to suit the desired product [13].

Most bipolar plates in recent years have been made from metallic materials, this has led to extensive research into the coating of metals to prevent corrosion while simultaneously decrease the interfacial electrical conductivity [50].

1.4.2 Industry Requirements

The DoE targets, seen in table 1.1, are used as a bench mark for bipolar plates. Some manufacturers have released fuel cells which display excellent performance

and longevity. As of 2020 Toyota Motor Corporation had made two iterations of fuel cell vehicles. The first of which utilised a gold coated SS316L BPP, this was optimised on the basis of cost and mass for the second generation vehicle, resulting in carbon coated titanium BPP [35, 58]. Titanium was chosen due to its lower mass which improves the volumetric power density and also the cold start capability of the stack [58]. Optimisation of the compression of the stack and changing the stack case material to aluminium resulted in a 42% mass reduction between Toyota's first generation steel BPP stack and second generation titanium BPP stack [58]. Konno et al. discussed how the superior corrosion resistance of titanium over stainless steel meant that the nano-material carbon coating was used to reduce the contact resistance without the need to increase the corrosion resistance of the plates [35, 58]. The first generation stack utilised a gold 100 nm coating upon a stainless steel substrate, this represented a large investment in the BPP due to the thick noble metal coating [58]. In the second generation stack this was replaced by a 50 nm amorphous carbon coating, removing the cost of the noble metal.

Honda has produced a fuel cell electric vehicle which employed stainless steel BPPs with a wave flow channel. Stainless steel was chosen over graphite plates because the thickness could be reduced by 50% and the five-fold increase in thermal conductivity meant the start up time of the cell was reduced. The stainless steel was passivated for use in the stack [34, 36, 59].

1.5 Thesis Structure

The US DoE states the focus of research and development for BPPs are: decreasing volume and weight, developing and evaluating new coatings and materials to decrease corrosion and cost, identifying degradation mechanisms and developing strategies for mitigating degradation to improve durability [22]. Bipolar plates represent a key area in which both economic and performance gains can be made. Stainless steel has been a well established bipolar plate material for some time but coatings are either insufficient to achieve the necessary performance or require expensive coatings [60, 61]. This work will try to create a low cost simple coating for stainless steel bipolar plates.

For niche or high performance sectors stainless steel will never match the volumetric power densities of lighter materials such as aluminium or titanium. Aluminium has the potential to reduce the mass of the stack, resulting in a high volumetric power density. This could allow for the adoption of PEM fuel cells into a wider range of aerospace industries as volumetric power density is critical.

A low cost polymer coating has been developed and characterised. Corrosion and contact resistance testing of the coating has been carried out. Later work investigated different aluminium substrates and coatings produced by Teer coatings. High purity aluminium was coated with a range of coatings and assessed for corrosion resistance and contact resistance. 3 of the coatings were then tested on an aluminium alloy, namely Al6082, due to the widespread adoption of this alloy in the automotive and aerospace industry. Coatings were then applied to the Al6082 cathode single cell plate of for *in situ* AST. This allowed for the performance of

the substrate and coating to be assessed in more relevant conditions.

Chapter Two

Literature Review

2.1 Introduction to Bipolar Plate Materials Corrosion

2.1.1 Corrosion Phenomenon and Processes

Electrochemistry Background

Electrochemical corrosion is an electrochemical process in which an electronic and ionic charge transfer occurs. Therefore the process requires electrically conductive electrodes and an electrolyte which facilitates the ionic charge transfer. In terms of the bipolar plate arrangement the metallic plate serves as the electrode and liquid water on the surface permits the ionic conductivity through the dissolved ions [2].

The metal ions in the bipolar plate are organised in a crystal lattice with electrons existing as a cloud around the metal ions. The electrons are bound to the material but are free to move around the volume. The free flowing electrons are what give the metal its electrical conductivity [2].

In a fuel cell a liquid electrolyte can form on the surface of the bipolar plate.

This is an aqueous solution containing positive (cations) and negative (anions) ions. It is these ions that conduct the ionic charge. Metal ions form an aqueous phase at the surface, metal ions can move from the aqueous to metal phase and back again [2]. This can be seen in the following chemical equation, where aluminium is used as an example:



In equilibrium the rate of forward and reverse reactions will be equal, this is the exchange current density. Corrosion is the process in which this equilibrium is weighted to the forward reaction:



This results in an electrical current flow, it is called the anodic current, which by convention is positive. The cathodic current is the result of a reduction reaction, which by convention is a negative current. An electric field is generated at the interface of the metal and aqueous solution [2]. This field is a result of the charge generated by the electron transfer between the metal and an oxidant [2].

Electrical double layer

An electrical double layer is generated between the metal and solution interface which is in the order of 10 nm [2]. A potential difference is generated through: the

adsorption of species onto the metal surface and the charge transfer in the metal and solution interface. Chloride ions for example can create dipoles between the metal and solution [2]. The properties of this electrical double layer control the corrosion processes. The electrical properties to double layers are akin to that of a capacitor and resistor in parallel, they are referred to as the electrical double layer capacitor and the transfer resistance respectively [2].

Multiple models have been proposed to explain the form of the double layer; these include: Helmholtz, Guoy Chapman, Stern and Bockris-Devanathan-Muller [2]. The layer is compromised of three layers, the most important of which for corrosion is the first; the Stern layer is a few tenths of a nanometre. Orientated water molecules and small specifically adsorbed anions such as chlorides make up this layer.

Electrochemical reactions require the anions to reach the metals surface. The metallic cations need to be able to leave the metals surface and enter the solution. An ions: charge, size and level of hydration defines its ability to reach the metals surface [2]. Small anions such as chloride ions readily reach the surface of the metal. Whereas sulphate ions will be solvated, making them very large, therefore less likely to reach the metals surface [2]. Solvation is where a solute, this case the sulphate ion, is surrounded by solvent, in this case water. The dipole present upon water causes it to form a hydration shell around the sulphate ion [2].

Reactions on the metals surface can be accelerated when the equilibrium between the metallic and aqueous phases are displaced toward the aqueous phase of the metal. This displacement can occur under the effect of an external current

or in aggressive solutions. When the equilibrium is shifted toward the aqueous phase, a net metal dissolution occurs [2].

Corrosion Potential

The corrosion potential, also known as open circuit potential, is the difference in electrical potential between the metal and solution at equilibrium [2]. This equilibrium is of the oxidative anodic and reductive cathodic reactions, chemical equations 2.2 and 2.6 respectively. The corrosion potential can be obtained experimentally from linear sweep voltammograms (LSVs). Aeration, temperature, stirring and measured area must all be considered when measuring the corrosion potential [2]. Considerations and methods of which are discussed in the experimental methodology section of this work.

Aluminium is very susceptible to localised corrosion, therefore the measured area is very important. Small areas will test a fewer number of surface inclusions and defects. An area of 25 mm^2 area would incorporate several hundred thousand inclusions whereas an area of 0.1 mm^2 in diameter would only incorporate around 120. By testing larger areas a more noble corrosion potential is observed [2].

2.1.2 Electrochemical Corrosion

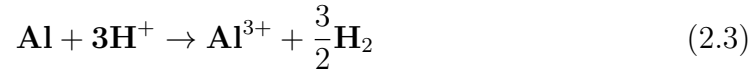
Corrosion of metals is the result of two reactions; oxidation of the metal and a reduction reaction facilitated by the solution. The oxidation of the metal can be a dissolution or passivation reaction.

Oxidation and reduction reactions occur simultaneously at the metals surface but at different and very particular locations. The location of oxidation reactions is known as the anode, the current generated at these sites is called the anodic current. Reduction takes place at cathodes and generates a cathodic current. Many anodic and cathodic reactions can occur simultaneously on the metal surface [2].

The anodic and cathodic reactions bear a relationship with potential and reaction rate which can be measured through the current. These parameters form curves called polarisation curves which can be produced experimentally. Intensiokinetic curves are made by varying the current and measuring the voltage; by varying the voltage and measuring the current potentiokinetic curves can be made, these are both linear sweep voltammetry techniques [2].

In fuel cell operating conditions bipolar plates are subject to acidic conditions, with a pH of around 3 [62]. In acidic or neutral conditions protons react with aluminium in an oxidation reaction to produce hydrogen. Protons are present due to the dissociation of water and due to the hydrogen oxidation reaction HOR at the anode in the fuel cell. To balance the oxidation reactions there are two possible reduction reactions. The first is the reduction of protons to form hydrogen, this reaction can be dangerous in sealed environments due to a build up of hydrogen [2]. As 27 g of aluminium corrodes it will form 33.6 L of hydrogen [2]. The second of which involves dissolved oxygen in the solution reacting with the protons and electrons generated, to produce water. The aforementioned reactions are shown below:

Oxidation of aluminium in an acidic or neutral environment:



Dissociation of water:



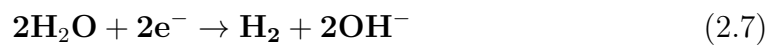
Proton reduction:



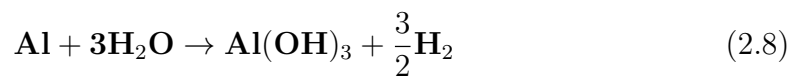
Oxygen reduction:



The oxygen reduction reaction (2.6) shows the importance of dissolved oxygen in the solution to facilitate this reaction. A reduction of the oxygen concentration can change the surface chemistry. In neutral and deaerated environments the reduction of water can occur [2]. The generated hydroxide ions promote the oxidation of the anode material:



However the oxygen concentration for metals such as aluminium has been seen to be independent to the rate of corrosion. This is due to the passive oxide film that occurs on the surface of aluminium. The corrosion of aluminium is the process of oxidation of aluminium and the reduction of water, this results in the formation of aluminium hydroxide ($Al(OH)_3$) [2]. This hydroxide is insoluble in water and precipitates as a white gel, it is typically found in corrosion pits. The reaction is shown below:



Stainless steels and titanium have been used extensively in PEM fuel cells but both like aluminium suffer from corrosion in the PEM fuel cell environment [63–66]. As these metals corrode, metallic ions can leach from the substrate, for stainless steel this includes: Fe^{3+} , Cr^{3+} and Ni^{2+} , these ions can poison the ionomer present in the MEA resulting in reduced performance [61, 63]. In addition oxide layers can grow on metallic substrates which significantly increase the interfacial contact resistance between the plate and GDL [61].

2.1.3 Pourbaix Diagram

Pourbaix diagrams show the role of potential and pH on the thermodynamically stable phases of a material. They are constructed using thermodynamic principles [2]. Reactions that are only influenced by potential are shown by horizontal lines. Reactions that are only influenced by pH are shown by vertical lines. Diagonal

lines show reactions that are governed by both pH and potential [2]. The diagrams show the range of pH and potential where the metal corrodes, possible corrosion products and areas where the metal is immune to corrosion. Dotted lines show the stability of water. Pourbaix diagrams display 3 distinct areas: corrosion, passivation and immunity. Areas of corrosion on the Pourbaix diagram show the set of conditions in which metal attack is thermodynamically possible, with the formation of soluble species [2]. In passivation areas corrosion is thermodynamically plausible. However, oxide layers form and are stable, isolating the base metal from the solution, drastically reducing the rate of corrosion [2]. In areas of immunity the metal is stable and corrosion is thermodynamically impossible [2].

Pourbaix diagrams of aluminium, like the one shown in 2.1, show how aluminium is attacked at both extremes of pH (acid and alkaline conditions). Pourbaix diagrams provide information on stable species, the environment in which they are stable and the direction of the possible equilibrium reactions. They do not however provide information on corrosion rate and the mechanism of corrosion [2]. The diagram ignores localized corrosion phenomena which dominate the corrosion of passive metals such as aluminium. This is because thermodynamic data is used without consideration of kinetic data. The diagrams are also constructed from theory in which: ideal liquids are considered (chemically pure water, at 25°C) and only high purity metals are considered [2]. This makes Pourbaix diagrams a guide for aluminium and does not necessarily reflect the true nature of the metal under these conditions.

Figure 2.1 shows that aluminium stability will occur below $-1.6 V_{NHE}$ in acidic pHs of 1 - 4. This is well below the water stability range displayed by the

dotted lines, it is therefore impossible for aluminium to achieve cathodic protection without the likelihood of cathodic corrosion due to the accumulation of $2OH^-$ from water decomposition. Under these conditions the formation of aluminium hydrides is also possible along with the evolution of hydrogen [2].

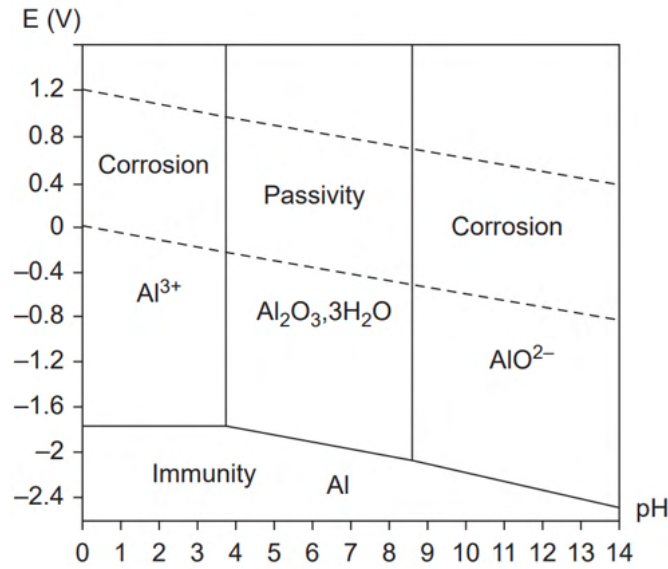


Figure 2.1: Pourbaix diagram of aluminium, from Vargel et al. with permission [2].

Experimental constructions of Pourbaix diagrams of alloyed aluminium (AA5086) have shown that the true picture is far more complex than displayed in figure 2.1 [2, 67]. Gimenez et al. showed that above potentials of -700 mV_{SCE} general attack is expected for all acidic pHs [67].

Passivisation

Aluminium by nature is a passive metal, covered in an oxide layer [2]. The open circuit potential in most aqueous solutions is in the order of -500 mV_{NHE} [2]. This electronegative potential suggests that aluminium would suffer severely in oxidising environments such as air and water. However it displays passive behaviour due to a continuous and uniform oxide layer. The layer has a composition similar to Al_2O_3 [2]. The reaction occurs very quickly and is spontaneous; as soon as aluminium is exposed to oxidising media as follows:



The electrochemical behaviour of aluminium, like all metals, is very dependant on the pH of the aqueous solution [2]. Changes to the pH can affect the stability of the oxide film and the dissolution rate. As the stability of the oxide film is reduced the passivity of the material is also reduced, this leads to increases in the rate of dissolution. The oxide films stability is highest between pH 5 and 8. As the pH shifts to either acidic or alkaline extremes the stability is reduced, this highlights the amphoteric nature of the aluminium oxide layer.

The pH is not the only critical consideration when evaluating the corrosion resistance of aluminium in a given solution. The anions and their salts associated with the given acid is also a decisive parameter.

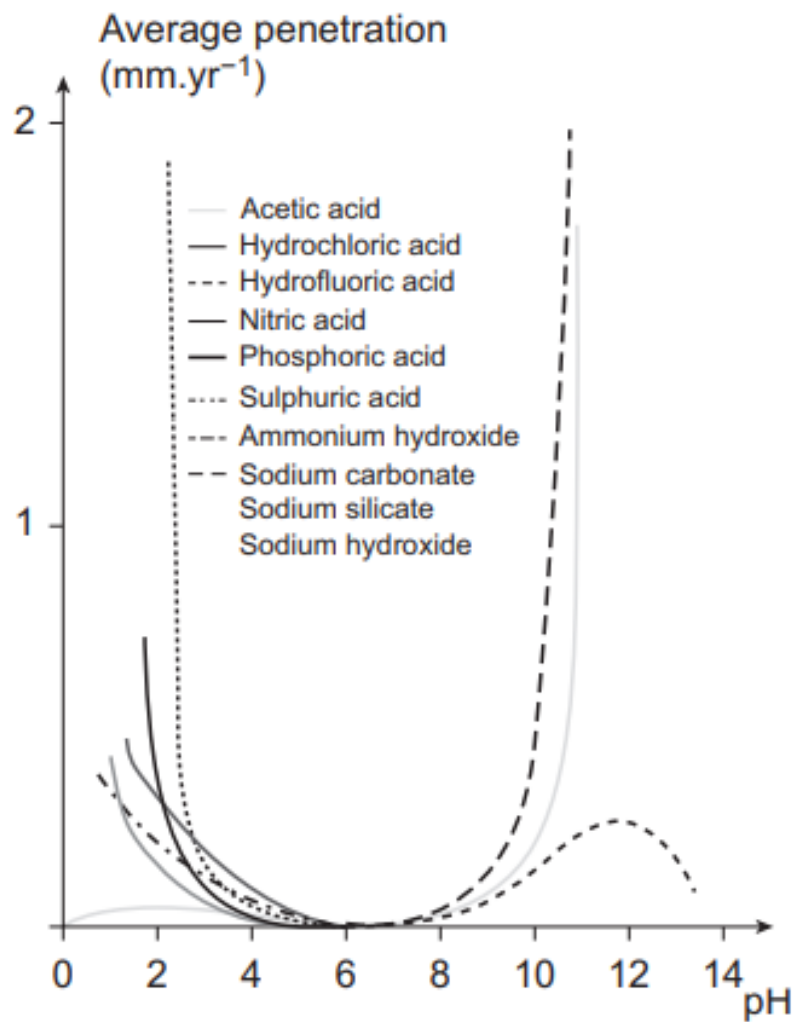


Figure 2.2: AA1100-H14 aluminium dissolution rate dependence upon pH and acid, base type from [2].

Uniform Corrosion

Uniform corrosion or general corrosion occurs when the rate of corrosion is ubiquitous across the surface of the material [2]. The reaction is considered to be with the hydrogen ions, in acidic media, which results in the oxidation of the base metal while also forming hydrogen [3]. Uniform corrosion is a result of the location of each reaction, the metal oxidation and hydrogen ion reduction, constantly changing [2, 3]. The locations of metal oxidation are referred to as anodic sites while locations of reduction are the cathodic sites, the anodic regions will be the locations in which dissolution or passivation occur [3]. As the base substrate is an electrical conductor each reaction does not need to occur at the same location, in limiting cases each reaction typically occur within a few atomic diameters of one another [3]. These sites constantly change with time which results in uniform corrosion, if these sites do not change then uniform corrosion will not occur [3].

For aluminium uniform corrosion typically occurs in very acidic or very alkaline media in which the passive film is highly soluble [2]. The more extreme the pH the faster the dissolution rate, close to neutral or neutral pH results in very low rates of general corrosion, around $1\text{ }\mu\text{m}$ per century [2].

For materials where the corrosion product is a non-porous, well adhered, poor electrical conductor, the rate of corrosion will decrease by as much as several orders of magnitude [3]. Standard polarisation curves of an active-passive alloy material can be observed in section 2.1.4, stainless steel is such a material [3]. If the conditions are right (temperature, potential, pH and low aggressive cation concentrations) then passive films can form, which protect the underlying material

from further corrosion or greatly reduce the rate of corrosion [3].

Intergranular Corrosion

Grain boundary interfaces can be comprised of different compositions when compared to the bulk material, due to the grain boundary providing nucleation sites for the precipitation of alloying elements [3]. The precipitation at grain boundaries can be continuous around the grain or discontinuous. The precipitation itself is the cause of this form of corrosion as the precipitation can have a different electrode potential as compared to the bulk material [3]. This can result in the precipitate behaving as an anodic or cathodic site for corrosion reactions. When the precipitate is an anodic site the precipitate corrodes which can result in dissolution at the grain boundary [3]. When the precipitate behaves as a cathodic site the grain itself can be corroded.

Precipitates form from the alloying elements of the substrate, these elements could potentially be the ones that typically protect the material from corrosion by forming stable passive layers. At grain boundaries alloying elements cannot provide the same corrosion resistance [3]. Stainless steel can suffer from this form of corrosion as the chromium, which produces the stable passive film, can precipitate at the boundary forming chromium carbide or iron containing chromium carbide [3]. These precipitates can consist of 60 to 70 *wt.%* chromium, thus depleting the local area of chromium. It is possible that the chromium content in these areas become so low that it can no longer support the passive film. At these locations corrosive attack will occur on the grain [3]. Proper heat treatment of substrate

materials can prevent the formation of chromium carbide and should be carried out for potential alloy bipolar plate materials [3].

Intergranular attack is dependant upon the environment, composition and thermal treatment of the material [3]. For aluminium the susceptibility of intergranular corrosion is highly related to the galvanic effects of the precipitate at grain boundaries and bulk material [3]. The non-conductive oxide layer on aluminium limits its ability to perform as a cathode for corrosion [3]. As such the relative electrode potentials of the precipitate and local grain are the dominating factors in the mechanism of corrosion at intergranular sites for aluminium alloys [3]. This form of corrosion will occur when the substrate is in corrosive environments, has a high density of precipitate at grain boundaries and a potential difference of about 100 mV between the precipitate and bulk material [2]. Cathodic sites can form at grain boundaries when the formation of Al_3Fe and Al_2Cu occurs, whereas anodic sites occur where $MgZn_2$, Al_3Mg_2 and Mg_2Si form [2]. Like with stainless steel, heat treatment and quenching can influence an alloys susceptibility to intergranular corrosion. The heat treatment applied should be considered along with the mechanical effects of each treatment [2].

The rate of corrosion during intergranular corrosion can be several orders of magnitudes higher than that of homogeneous corrosion as a result of the large cathode-to-anode area [3].

Exfoliation corrosion

Exfoliation corrosion is the process in which corrosion spreads following the direction the substrate was rolled or extruded [2]. Planes of material become separated by corrosion product, causing the metal to swell, this can cause the metal to peel and form flakes of metal [2]. The corrosion mechanism is the same as galvanic corrosion where precipitates cause excessive localised corrosion. The products of which cause the delamination of the layers [2]. Exfoliation can occur whenever a corrosive environment, a highly fibrous microstructure and an anodic pathway is present in the material [2]. Just as with intergranular corrosion this form of corrosion can be mitigated with a suitable heat cycle and quenching or isolation of the substrate from the corrosion environment [2].

Filiform

At some sites, pitting immediately penetrates the sheet (pitting corrosion). At other sites, following film penetration, corrosion tunnels form under the passive film [2, 3]. This type of corrosion is typically observed in painted: steel, aluminium and magnesium surfaces [2]. Filiform corrosion requires a passive layer under which the substrate is corroded, the reaction continues to borrow creating path ways from the initial break in surface film [2, 3].

To prevent this form of corrosion in bipolar plates defects in coatings need to be minimised or removed.

Galvanic corrosion

Galvanic corrosion occurs when two conductors are in electrical and ionic contact (through an electrolyte) [2, 3]. The two materials form a galvanic couple in which the corrosion potentials and corrosion currents significantly differ from each materials uncoupled state [3]. The more electronegative material of the two will be the location anodic reactions, while the more noble and electropositive material will be the site of cathodic reactions [2, 3]. Typically a difference in electrode potential needs to be at least 100 mV for galvanic corrosion to occur [2]. Galvanic corrosion occurs very localised at the point of electrical contact with the more noble material [2].

PEM fuel cell bipolar plates are in contact with carbon GDLs. Carbon poses a significant risk of galvanic corrosion, especially with aluminium, due to the relative electrode potentials, $0.23 V_{SHE}$ and $-1.68 V_{SHE}$ respectively [2, 68, 69]. Vargel et al. states that in humid environments graphite and aluminium (including all of its alloys) will form a galvanic couple causing galvanic corrosion [2].

To prevent galvanic corrosion only materials with similar electrode potentials should be in direct contact; in reality this is not feasible and significantly limits material selection [2]. Electrical or electrolytic isolation of the two materials is another option, as this will not facilitate galvanic corrosion. Electrical contact with GDLs is essential to the function of bipolar plates, meaning electrical isolation is not possible. In addition it is not possible to exclude electrolytes, as the formation of water and the acidic nature of PEM fuel cells means liquid electrolytes are always present. Therefore a coating of more noble electrode potential, closer to

that of carbon, is required as to prevent the GDL forming a galvanic couple with the bipolar plate.

Crevice corrosion

Crevice corrosion is a localised corrosion that occurs in areas with limited diffusion [2]. The limited diffusion of gases and bulk solution to crevice areas, combined with the reactions occurring in the crevice, result in the composition and pH of the solution changing rapidly compared to the bulk solution [2]. Inside the crevice, metal ion concentration increases while the oxygen concentration decreases, with the rate dependant on the surface of the metal [3]. The increase in metal cations can lead to an influx of aggressive anions, if they are present in the bulk solution [2]. The geometry of the crevice changes the rate of diffusion to the area, the more limited the diffusion the more severe the corrosion will be [3]. Once the oxygen concentration in the crevice hits a critical point, cathodic reactions will occur outside the crevice where oxygen diffusion is faster, while in the pit anodic reactions occur [3]. Anodic reactions occurring in the crevice will lower the pH combined with limited oxygen concentrations, passive films will break down [3].

In the fuel cell environment the GDL will create crevices in addition to a galvanic pair [62]. In these regions it is possible that the rate of corrosion will be many times greater than for channels due to the limited oxygen diffusion, stagnant solution and galvanic couple that could form. G. Hinds et al. suggested that *ex situ* test conditions fail to accurately replicate the PEM fuel cell environment as polarisation of the bipolar plate occurs as a result of the galvanic couple and

crevices created by the GDL [62].

Pitting corrosion

Pitting corrosion is a corrosion mechanism that is typically seen among passive metals, aluminium is one such metal [70]. Localised corrosion occurs in areas of breakdown of the oxide film. Reboul et al. proposed a ten step mechanism for the pitting corrosion of aluminium:

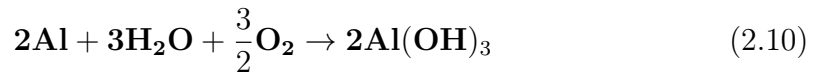
1. Cl^- adsorption occurs in micro-flaws in the oxide film. The small ion size, charge and electric field on the aluminium encourage Cl^- adsorption [2, 70].
2. The slow rate of oxygen reduction on cathodic areas of the aluminium result in charging of the double layer (μFcm^{-2}).
3. Breakdown of the oxide film at micro-flaws.
4. Fast oxidation of the bare aluminium - producing soluble chloride complexes.
5. Dissolution of chloride complexes and repassivation of the pit.

The first 5 steps results in as many as 10^6 cm^{-2} pits with a diameter between 0.1 - $1\mu\text{m}$.

6. The slow cathodic reaction limits the propagation to a few pits, the chloride build up is high enough to form a stable chloride/oxychloride layer at the bottom of these pits. For this to be sustained the chloride/oxychloride layer must be replenished faster than it dissolves. This implies a large enough cathodic area for each active pit.

7. Hydrolysis of soluble chlorides/oxychlorides. Formation of $H_3O^+_{(l)}$ causes acidification of the pit - this ensures the conditions to maintain pit activity.
8. Al^{3+} diffusion occurs from within the pit to the bulk solution.
9. Auto-corrosion caused by the aggressive conditions in the pit ($AlCl_3$ and low pH) causes the evolution of hydrogen. These bubbles limit the build up of Cl^- ions and the acidification of the solution.
10. Repassivation of the pit occurs when the conditions for the stability of the chloride layer are met

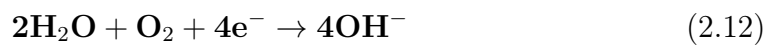
From Raboul et al. [70]:



This shows the corrosion of aluminium. It is the sum of two electrochemical half-reactions. The anode reaction:



And the cathode reaction:



These are similar to the equations referenced from [2] in section 2.1.2. However Raboul et al. considers the reaction of dissolved oxygen. After formation of

the pit, diffusion of oxygen to the internal surface of the aluminium can become limited, this would then favour the hydrogen evolution shown in equation 2.8 as discussed by Vargel et al..

Pitting potential is the potential above which aluminium undergoes pitting corrosion [2]. The value of which can be obtained experimentally from LSV tests. The pitting potential is heavily dependant upon chloride content and temperature [2]. As the temperature and chloride content increases the value for the pitting potential decreases [2]. From experimental data the pitting potential is very close to or equal to the OCP value for the aluminium in solution. However some researchers have suggested that the pitting potential for aluminium is not useful in determining its corrosion susceptibility [2].

2.1.4 Corrosion of Materials in Simulated Fuel Cell Conditions

Fuel cell conditions

Cathodic *ex situ* corrosion tests are typically carried out with a pH between 0.7 - 5, with a potential of 0.6 V and temperatures between 70 - 80°C. Some researchers also use the addition of 2 ppm of HF as to mimic the possible breakdown of the membrane which will release fluorine containing substances [57, 62, 71, 72]. The mechanisms and rate of electrochemical corrosion will be influenced by all of these parameters [2, 3].

G. Hinds et al. however suggests that these *ex situ* conditions do not accurately replicate the fuel cell condition as there is low ionic conductivity between the bipolar plate and the nearest electrode [62]. This is due to the discontinuous liquid electrolyte between the two components. Furthermore investigations into the waste water produced by PEM fuel cells reveals a liquid with a pH in the range of 3 - 5.

Fuel cell conditions could be more aggressive as crevice corrosion and galvanic coupling may take place [62]. G. Hinds et al. measured the pH *in situ* under a range of operating conditions, it was found that the pH for the cathode was between 3.4 - 4 while in the anode values of 5 - 7 were observed [62]. This lower pH was associated with the oxidising conditions of the cathode which results in more hydrolysis which lowers the local pH [62]. Under fully humidified conditions the potential of the anode was very stable at 0.0 V, the cathode bipolar plate was also stable between 0.6 - 0.7 V, while the cell potential was swept between 0.2 - 0.9 V [62]. Potential spikes however occurred at the cathode plate during start up/shut down simulations, transient potentials of 0.9 V were observed [62].

Aluminium corrosion

Aluminium is often heralded for its corrosion resistance. Aluminiums corrosion resistance to atmospheric conditions arises from the spontaneous formation of aluminium oxide [2]. This oxide layer is continuous with an amorphous structure that forms at the surface of the metal [2]. As can be seen from figure 2.1 the oxide layer of aluminium is stable between pH 4 - 8.5, higher and lower pH values however

result in passive film breakdown [2]. At sufficiently low potentials, the aluminium substrate is immune to corrosion and passivation. At low pH values, between 0 and 4 and potentials greater than around -1.7 V, aluminium dissolution becomes thermodynamically favourable. By increasing the pH from this region aluminium will passivate spontaneously, this is the state of aluminium in atmospheric conditions. The formation of the oxide layer in this region prevents the corrosion of the underlying material despite it being thermodynamically possible [2]. Increasing the pH to over 8.5 will result in corrosion of the underlying substrate and instability of the oxide layer [2].

The main challenges for aluminium bipolar plates are: the non-conductive oxide film and the acidic pH of the fuel cell [62]. From theory it would suggest that aluminium will corrode in the fuel cell environment and would not be suitable as a material without proper corrosion mitigation.

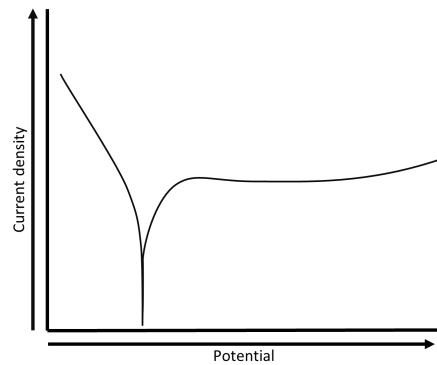


Figure 2.3: Standard polarisation curve of Al in an acidic solution, recreated from [3].

The polarisation of pure aluminium is near impossible due to the rapid spontaneous formation of an oxide layer [3]. In aqueous acidic conditions the oxide

layer become hydrated forming a complex structure, this influences the behaviour observed in polarisation curves [3]. Aluminium does not display the same passive and transpassive behaviour as stainless steel [2, 3]. There is no peak between the active and passive region due to the oxide layer already forming [2]. Furthermore the oxide layer is non-conductive which means that oxygen evolution does not occur at higher potentials, instead the oxide film grows thicker [2].

Stainless Steel Corrosion

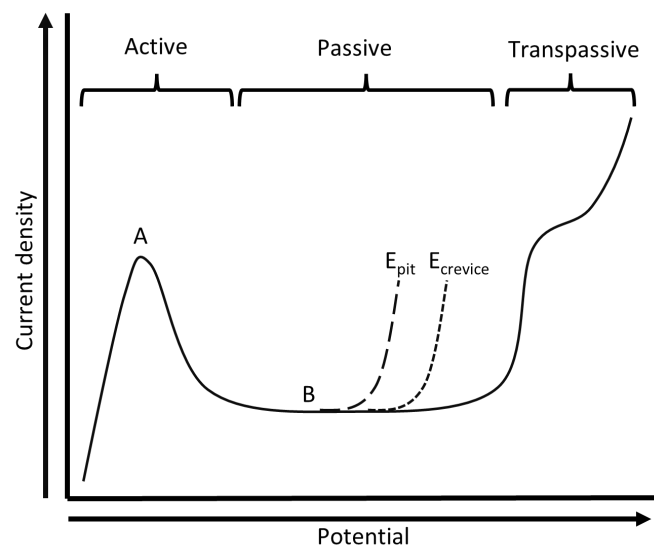


Figure 2.4: Standard polarisation curve of SS, recreated from [3].

A standard polarisation curve of stainless steel in an acidic aerated condition can be seen in figure 2.4. Three distinct areas exist on the polarisation curves of active-passive metals, these are: active, passive and transpassive regions. The peak location in the active region labelled A is the point of passive film formation, this results in the lower currents observed in the passive region [3]. The passive

region is so named due to the low currents observed, in this region the oxide film is thermodynamically stable [3]. As the potential is swept further the polarisation curve moves into the transpassive region where the surface oxide is no longer stable, in this region film breakdown occurs [3].

The transpassive region of the LSV will grow as the chloride concentration increases, this results in a smaller passive region on the LSV [3]. To prevent corrosion aggressive ions such as Cl^- and to a lesser extent F^- concentrations should be minimised. If the conditions are met for pitting or crevice corrosion then an increase in current will be observed before the typical transpassive region [3]. This is due to corrosion taking place at lower potentials as a result of the localised corrosive conditions [3].

2.2 Metallic Bipolar Plate Substrates

Metallic materials offer superior manufacturing capabilities, possibility for ultra thin plates, superior mechanical properties, gas impermeability and high thermal conductivity as compared to carbon based bipolar plates. Metallic bipolar plates have become the norm for fuel cells with graphitic carbon plates still used in some applications [13, 73]. Aluminium, aluminium alloys, titanium, stainless steel, high carbon steels, copper alloys and nickel alloys have all been investigated. Currently SS is the leading contender for metallic plates due to its tendency to passivate in the fuel cell environment and low cost relative to titanium [74]. Yuxi Song et al. also suggests that the low cost and abundance of stainless steel also explains the

materials proliferation [13].

2.2.1 Stainless Steel

Stainless steels have been investigated for use as a metallic bipolar plate. Stainless steels offer good strength, chemical stability, very low gas permeability and are applicable for mass production [50, 75]. Stainless steel also offers low material and processing costs [50]. Stainless steel has been readily used in industry so is well understood. Stainless steel however does suffer from corrosion in the fuel cell environment but the rate of corrosion is slow and the cell performance remains stable for many hours [50]. It was reported that in the acidic pH 2-3 and 80°C temperatures in the fuel cell that stainless steels are prone to corrosion [76]. This results in an increase in electrical resistance, leading to a reduction in power output of the cell [76]. Nevertheless research has shown that stainless steel is a viable material for PEM fuel cell bipolar plates. Coatings however must be applied to prevent corrosion, a solution that has seen some commercial success [50, 58]. The first generation Mirai for example used stainless steel as a BPP substrate material, a gold coating was applied to achieve the necessary performance and degradation results [58].

Grades

The grade of stainless steel being used can greatly affect the corrosion resistance of the material. One of the advantages of stainless steel is the passivating nature,

passive films prevent further corrosion of the base substrate [77]. The corrosion resistance of stainless steel arises from the existence of a thin, 1 - 3 nm, passive chromium oxide rich film [77]. The composition of the SS, namely the Cr, Mo, Ni and N content is what influences the chemical resistance of the material [77]. R.F. Silva et al. carried out research on a range of stainless steel grades. Higher contact resistances were attributed to the thickness the non-conductive passive oxide films formed on the surface [78]. Typically the oxide layers formed, namely Chromium oxide, is a beneficial layer as this layer effectively prevents the corrosion of the underlying metal [78]. Silva showed that Cr and Fe content are directly proportional to contact resistance however comparison after corrosion testing SS304 showed a much larger increase in contact resistance than when compared to 904L. The better performance of 904L after corrosion could be related to the higher Cr content, although 904L also incorporates 4.9% Mo and 1.2% Mn content (by wt.%) and higher Ni content. Both Mo and Ni elements can contribute to the passivation layer (form oxide layers), but it is expected these would increase the contact resistance of the substrate. When testing different substrate materials it was found that the trace elements can be of an equal or greater influence on the bulk properties of the substrate than the major elements [78]. It is clear that the composition of SS has a large influence on the performance.

Heli Wang et al. suggested that the selection criteria for candidate SS were mainly the Cr, Mo and N content, this was in consideration of the pitting resistance of the substrate, in addition higher alloying element contents led to a reduction in ICR value [79]. It was also found that among researchers contradictory results could be found, this was attributed to the differences in pre-treatment of

the materials that would affect the surface passivation layer. H. Wang found that the SS substrates performed in the order $349\text{TM} > 904\text{L} > 317\text{L} > 316\text{L}$, where 316L showed the highest corrosion current and potentials with the highest ICRs. However only the 349TM was tested by means of static corrosion, this means the ICR after corrosion cannot be compared among the samples. This work suggests that 349TM would be the best SS substrate for bipolar plates. However this work does fail to examine the cost of the bulk material.

Current Research

Stainless steel bipolar plates are well established in the industry as shown by the production of the first generation Toyota Mirai [58]. However expensive and slow production of the plates, due to the coating materials required, hindered mass production and therefore commercial success of the system [58]. This is highlighted by the transition to titanium plates for the second generation Mirai, in-part chosen due to the superior corrosion performance of titanium over stainless steel [58]. This also resulted in thinner coatings and a material change which, meant no expensive noble metals were required. This transition from stainless steel to titanium displays the need to find cheaper coatings and coating methods for the commercial success of stainless steel BPPs.

Linfa Peng has presented a review investigating increasing throughput of different bipolar plate production methods, with considerations of dimensional stability through the stack [65]. The key points are: flow fields designs need to be optimised for a metallic stamped plate and not machined channels like those

that have been used in graphitic plates, various stamping processes offer solutions for production scale bipolar plates, grain size should be considered when targeting dimensional accuracy of production, laser welding present the most cost effective solution to the welding of bipolar plates and finally coatings should be carbon based or metal nitrides as these can achieve the requirements of the DoE targets but need to be validated *in situ* [65].

2.2.2 Aluminium

Property	Unit	Value	Note
Atomic number		13	
Density, ρ	kg.m^{-3}	2,698 ^a	
Melting point	$^{\circ}\text{C}$	660.45	$<1,013 \times 10^{-3}$ bar
Boiling point	$^{\circ}\text{C}$	2,056	$<1,013 \times 10^{-3}$ bar
Vapour pressure	Pa	3.7×10^{-3}	At 927 $^{\circ}\text{C}$
Mass internal energy, υ	J.kg^{-1}	3.98×10^5	
Mass thermal capacity, C_p	$\text{J.kg}^{-1}.\text{K}^{-1}$	897	At 25 $^{\circ}\text{C}$
Thermal conductivity, λ	$\text{W.m}^{-1}.\text{K}^{-1}$	237	At 27 $^{\circ}\text{C}$
Linear expansion coefficient, α_l	10^{-6}K^{-1}	23.1	At 25 $^{\circ}\text{C}$
Electrical resistivity, ρ	$10^{-9} \Omega.\text{m}$	26.548	At 25 $^{\circ}\text{C}$
Magnetic susceptibility, K		0.6×10^{-3}	At 25 $^{\circ}\text{C}$
Longitudinal elastic modulus, E	MPa	69,000	
Poisson's ratio, ν		0.33	

^aThis is the generally accepted value for the density of metal between 99.65% and 99.99% pure. At 700 $^{\circ}\text{C}$, the density of molten metal of 99.996% purity is $2,357 \text{ kg.m}^{-3}$.

Figure 2.5: Properties of pure aluminium from [2].

Aluminium is the second most utilised metal in industrial use [80]. Aluminium is the lightest of all common metals with a density of 2700 kgm^{-3} , which is almost one third that of steel. Literature suggests that structures made from aluminium can be up to 50% lighter when made from aluminium as compared to steel [2, 80]. It has a range of advantageous properties that include: high conductivity

for both heat and electricity, excellent corrosion resistance (in most conditions) and it can be readily cast or fabricated into a broad range of products [80]. Aluminium is also readily recycled, an important property for a cyclic economy, with remelting of scrap metal only requiring 5% of the total energy required to extract the same amount of primary metal from the ore [80]. Aluminium has a relatively long life-cycle because of its durability [80]. Aluminium has been increasingly utilised in the transport sector due to the materials low density relative to commonly used steel and iron [2, 80, 81]. This is because the mass of the vehicle can be reduced, which allows vehicles to achieve an increased fuel economy [2, 80]. For the same reasons aluminium is the primary material used for aerospace applications. Carbon fibre based materials have also become prominent in the industry, although fail to compete with aluminium in regards to tolerance to damage, isotropic mechanical properties, recyclability, electrical and thermal conductivity and cost [2]. Reducing the mass of fuel cell stacks can lead to higher gravimetric power densities, in addition lower cold start temperatures can be achieved due to the reduced thermal mass [58].

The primary advantage of aluminium over stainless steel is the reduction in mass that can be achieved. When the Toyota Mirai switched to titanium bipolar plates from stainless steel, along with other changes to the system, the stack mass was reduced by 42% [58]. This led to increased cold start capabilities, which would be further improved by utilising aluminium bipolar plates due to the further reduction in mass that can be achieved [58]. Aluminium does suffer from corrosion and as such will require coating.

2.2.3 Current research

There is currently limited literature available for aluminium bipolar plates. Current literature however highlights the low density of aluminium and focuses on mitigation of the corrosion through surface treatments and coating [13, 50, 82, 83].

2.2.4 Disadvantages of Metallic Bipolar Plates

Metallic plates however are prone to corrosion in the fuel cell environment. Leached ions may also poison the membrane and catalyst, reducing the cells performance. It has been reported that these ions reduce the ionic conductivity of the membrane [13, 56]. This prevents metals from being used uncoated in PEM fuel cells but literature has shown promise in preventing corrosion through coating [13]. Most bipolar plates in recent years have been made from metallic materials, this has led to extensive research into the coating of the materials to prevent corrosion while simultaneously decreasing the interfacial electrical conductivity [50].

2.3 Coatings for Metallic Bipolar Plates

2.3.1 Methods

Typical surface modification methods include, electroplating, electrophoretic deposition, physical or chemical vapour deposition and surface treatments [50, 65, 84]. The purpose of coating stainless steel is to decrease the contact resistance

between GDLs and bipolar plates [65]. Coatings should also isolate the substrate from liquid electrolytes and be corrosion resistant. Literature states the coefficient of expansion of substrate and coating materials should be similar [73].

Electroplating

Electroplating is the process in which metal ions migrate to an electrode and undergo a reduction reaction causing the metal cations to deposit on the electrode, forming a coating. This process requires an external direct current to be applied to the electrodes [85]. This forms a high quality surface with a continuous thickness which can be accurately controlled [85]. Morphology and composition can also be modified by adjusting the coating parameters. Electroplating is a low-cost coating solution [85, 86].

It is a mature technology that has been readily accepted and utilised by industry, around 37% of all metal finishing is performed using electroplating [85]. PGM, chromium, zinc, tin, copper and nickel are some of the most commonly deposited metals [85]. The cost of materials however and the environmental concerns of some materials hinders the use of electroplating to some degree [85].

Electropolymerisation can also occur in an electroplating process. Monomers are polymerised at the working electrode surface to form a polymer coating upon the surface [85]. The subsequent polymer coating can be well-adhered with fewer cracking issues than other coating methods [85]. These polymer coatings have been used for electrochemical sensors, coloured deposits and as anticorrosion coatings. Polymer coatings however do pose concern as the precursors risk environmental

toxicity and potential degradation over time [85].

Electrophoretic Deposition

Electrophoretic deposition often referred to as EPD is an electrochemical process that deposits a powder coat on surfaces. Coatings are then typically densified by a thermal sintering or curing process to get a strong, well adhered layer [87]. Coating particles are suspended in a liquid, forming a suspension or colloid. These particles migrate to the electrode, or in this case a bipolar plate, by applying a potential. This migration along the electric field is referred to as electrophoresis [87].

EPD can be carried out on any fine powder that is smaller than $30\ \mu m$ or forms a colloidal suspension, this includes but is not limited to metals, polymers, carbides, oxides, and nitrides [87]. Intricate designs can be coated due to the diffusion of particles and liquid to all areas of the part and the electric field present across the surface of the part [87]. This allows porous materials to be coated, which is advantageous for some bipolar plate designs [87, 88]. Complex structures and layers can be made using EPD.

Advantages of EPD include, high throughput, high degree of automation in the process, homogeneity of the coating with a high density when compared to dipped or sprayed coatings [86, 87]. This has led to the use of EPD for coatings in the automotive, electronic and appliances sector [86, 87].

Physical Vapour Deposition

Physical vapour deposition is an advanced and commercialised coating technique that has been readily used by industry to produce hard corrosion and wear resistant coatings [89]. Tools such as drill pieces are often coated using PVD to produce hard wearing items, which increase the lifetime of the tool [89]. Well adhered homogeneous layers with controlled morphology and structures can be produced using a diverse range of materials. The thickness of coatings can easily be controlled [89, 90]. This makes PVD a useful method for coating BPP.

Physical vapour techniques energise solid materials, referred to as target, in a manner to eject material as ions, small particles or molecules [89, 91]. This is carried out under a vacuum with a pressure below 0.1 mbar. Heating, laser sources or arc discharges can be used to heat the target to achieve evaporation of the solid target. Each of these methods require the target to reach a critical temperature as to eject material, the kinetic energy of the evaporated atoms is dependant upon the temperature to which the target was heated [91]. The method of heating can change the consistency of the ejected material. Atoms, molecules and clusters of different sizes can be ejected [91]. Laser sources have also been reported to release ions [91].

Sputtering is another method of PVD. Targets are bombarded with ions, these ions require an energy of 30 eV or higher and will result in the ejection of surface particles and secondary electrons [91]. The ion energy is responsible for the energy of the ejected material. Chemical reactions can take place between the ions and the target material, this will influence the ejected materials composition and

consistency. Reactions will also affect the sputtering efficiency which is a measure of the number of ejected particles per impinging ion [91]. Magnetron sputtering is a form of sputtering, it works by a magnetron being placed near the target. While under vacuum an inert gas is introduced into the chamber, this gas is then accelerated toward the target by means of a very high potential difference between the substrate and the target [89]. The inert gas, often argon, strikes the target causing the release of ions which form a plasma in the chamber [89]. The potential applied to the substrate and the energy of the ions are controlled to influence the coated layer. Reversing the polarity of this process causes the substrate, intended to be coated, to be stripped or cleaned. This prepares the surface for coating. Bombarding the substrate can be used to remove oxide layers, which has been shown to increase interfacial contact resistance [89, 90]. Some coating techniques will bombard the coated layer with argon ions during coating, or intermittently, to adjust the structure of the coated layer; this is called ion plating [89].

Inert gases such as argon are typically used, under the high energy conditions found within PVD chambers the target and coating do not react with the argon [89]. Nitrogen and other gases can be added to the chamber in different ratios with argon. Nitrogen will ionise and react with the target or ejected material, allowing nitrogen to be incorporated into coating layers. This can be used to create nitride layers such as AlSiN and TiN, whereby changing the ratio of nitrogen to argon the nitrogen content of the coating can be adjusted [89].

Defects occur in all PVD surface modification techniques. These defects can create undesirable properties in surfaces, this could lead to: increased corrosion and decreased adherence at defect sites. There are many different types of defects

that can occur during PVD processes; vast research has been carried out to reduce such defects [92, 93]. Pin-hole defects extend through the whole coating and would allow solution to propagate to the surface of the substrate, pin holes can be over come with thicker coatings but this will require more time to coat, more material and more energy to produce [93]. Pin holes can lead to shadowing effects, however shadowing is not exclusively caused by pin holes [93, 94]. Shadowing effects result from large surface structures or recessed areas that prevent coating of the hidden area. This is due to PVD being a 'line of sight' coating method. The rate of deposition and structure are dependant upon the direction, count and energy of the impinged ions [92, 94]. The surface morphology of the substrate, including pits or voids, can vary the count and energy of impinging ions which will alter the coating in these areas. Furthermore defects in the substrate surface can act as crack initiation locations, which could degrade the coating performance as aggressive ions could reach the substrate [92].

Substrate surfaces also have to be properly prepared as foreign particles could produce shadowing effects, inclusions in the coating and changes to local growth conditions, which would lead to inhomogeneous layers [94]. Flake and open void defects are caused by foreign particles present on the surface before coating begins. Open void defects occur when the foreign particle is removed during or after coating [94].

PVD provides a method of producing dense layers with a range of coating materials but is a relatively slow and expensive process [90]. The performance of layers would need to be considered against the cost of the materials and method.

2.3.2 Materials

Noble Metals

Gold and platinum are two of the typically utilised noble metals found as BPP coatings. The materials however are expensive, meaning they are typically only used in systems where performance is more important than the economics of the stack, such as the aerospace industry [13]. Alternatively these materials can be used with ultra-low loading (tens of nano-metres) to reduce the material costs of the coating.

Literature has shown that noble metals coated onto SS316L BPPs show satisfactory ICR and corrosion resistance. Song et al. concluded that noble metals will become a hotly researched topic in the transport sector as these materials meet the demands of the high power densities required by this sector. The first generation Toyota Mirai for example utilised a gold coating but the expense of the vehicle coupled with the availability of hydrogen limited the adoption of this vehicle [58].

PGM coated bipolar plates can match or even out perform the *in situ* performance of graphite plates. Wang et al. showed this was possible with a gold coating upon titanium substrate [95]. Details on the coating are not provided due to the involvement of industry and strict intellectual property around the coating. Yoon et al. tested several different coating materials: Au, Ti, Zr, ZrN, ZrNb and a bilayer of ZrN/Au [96]. All coatings were produced by PVD and coated on 3 different grades of stainless steel: 304, 310 and 316. The results show that 10

nm gold coatings were required to provide the necessary corrosion resistance for bipolar plates but just 2 nm of gold was found to significantly decrease interfacial electrical resistance [96].

PGM coatings are inherently expensive due to the method of application and the cost of the materials involved. Nevertheless the high performance of the coatings makes the process and materials an interesting avenue for researchers. The cost of materials can be overcome to some degree by the use of ultra-thin layers but work will still be needed to ensure long term durability [96].

Metal Nitrides

Literature has shown progress in the development of metallic bipolar plates by coating plates with transition metal nitrides [45, 53, 97, 98]. Metal nitrides, most notably chromium nitride (CrN) and titanium nitride (TiN), have been investigated due to the effective corrosion protection and electrical properties of the materials [33, 45, 98–100]. This is a result of the materials high chemical inertness, superior interfacial conductivity, and excellent adhesion [101]. Group 4 metal nitrides, namely titanium nitride, are typically used for coatings on cutting tools due to superior hardness and the chemical and thermal stability of the material [101]. Titanium remains metallic in the nitride matrix due to the electron structure in the metals d orbital, this metallic structure results in titanium nitride showing good conductivity [102]. Furthermore, the materials resistance to oxidation results in TiN maintaining good electrical conductivity in aggressive conditions like that of the fuel cell environment [102].

Deposition of titanium nitride in industry is typically achieved via PVD, although other methods involving CVD or plasma nitriding are also popular [101]. These methods are typically expensive, requiring vacuum chambers and very pure targets. Vacuums are difficult to scale and will thus limit production rates, in turn increasing costs. S. Pugal Mani coated 316L with TiN, TiAlN and a composite layer of TiN/TiAlN via a cathodic arc evaporation system [97]. The TiN sample displayed the highest corrosion potential and the lowest corrosion current, which suggest better durability than both the other coated samples and the bare substrate. The TiN also showed the lowest ICR before corrosion and the second lowest after corrosion with a value of around $1\text{ m}\Omega\text{cm}^2$. S Pugal Mani, shows that a TiN coating can be an adequate coating for metallic substrates, however the use of cathodic arc evaporation would increase the cost of production, due to the need for batch production [97].

Some sources suggest that coatings must have a similar coefficient of thermal expansion as the base metal, as the coating may crack or wrinkle as the temperature of the cell fluctuates between nominal conditions and the shut-down state [13]. Stein et al. noticed that PVD coated TiN coatings have shown excellent corrosion and contact resistance properties [103]. However it was reported that coating defects are responsible for the degradation of TiN coatings and that these defects led to local corrosion phenomena such as pitting and crevice corrosion [103]. The differing thermal expansions between TiN coatings and substrates were determined to lead to more defects, which results in degradation of coatings. Stein et al. selected 416 stainless steel due to the similar coefficient of thermal expansion of the alloy with TiN. By matching the coefficient of expansion between

coating and substrate the number of defects in the coating can be reduced but sample preparation by polishing is also advantageous in preventing coating defects [103].

Chromium nitride is another well researched material [104, 105]. Haye et al. produced 50 nm CrN layers upon 316L using a magnetron sputtering process. The optimised coating achieved both contact and corrosion resistance targets. However the potential for the corrosion test was $0.728 V_{NHE}$, which is lower than some other sources [104]. The sulphuric acid concentration however was 0.6 M, which would result in a pH lower than what would be expected in fuel cell conditions [104]. Haye et al. proved that the material costs of metal nitride coatings can be minimised by depositing ultra-thin layers. It was also determined that surface preparation is key to achieving superior corrosion currents, interfacial contact resistance and well-adheared layers [104]. Forouzanmehr et al. tested bare 410 stainless steel against both CrN and TiN coatings on the same substrate [105]. The coating was deposited by cathodic arc evaporation. In these tests the CrN coating out performed the TiN coating in both the rate of corrosion and contact resistance values [105]. Stein et al. reported a lowest ICR value of $18 m\Omega cm^2$ for the TiN coating whereas Haye et al. achieved $8 m\Omega cm^2$, despite being at a lower compaction force [103, 104]. This is similar to the results of Forouzanmehr, who achieved ICR values of 9.26 and $11.23 m\Omega cm^2$ for CrN and TiN coatings respectively and from the literature reviewed by Liu et al. [105].

In addition multilayer coatings whereby a layer, typically Ti or Cr, is deposited then covered with TiN or CrN have been studied. This was to improve the corrosion resistance of samples by reducing the number of imperfections in the

coating [45]. This displayed improved corrosion resistance for all variations tested. Graded layers of TiN were also tested, these layers increased the concentration of nitrogen in the PVD chamber throughout coating to increase the nitrogen content of the layer. This resulted in a TiN coating with superior corrosion resistance and contact resistance [45]. Literature suggests that dual layer or graded layers should be utilised for PVD coatings [45, 100].

Metal Carbides

Metal carbide layers are typically prepared by electroplating or PVD processes and utilise transition metals such as Ti and Cr [45]. Changing the current density and reactant concentrations can allow for the optimisation of electroplated layers [45]. Haghghat et al. investigated electroplated Cr on 316L stainless steel which was then either plasma nitrided or reacted in a solid carburizing process to form CrN and CrC layers respectively [106]. The corrosion potentials increased for both coatings and the corrosion current exhibited during simulated fuel cell conditions decreased [106]. Although only the nitrided layer achieved the DoE target for this test. No details were shared regarding the contact resistance of the layers. Characterisation of the layers displayed large cracks and voids in the electroplated layer. The nitriding and solid carburizing processes did reduce these defects but could still be observed in cross sections of the coating [106]. Liu et al. reported a lowest ICR of $16.54 \text{ m}\Omega\text{cm}^2$ for an electroplated CrC layer, which does not meet DoE targets [45]. More success was observed for PVD coated layers where NbC, MoC and TiC achieved ICR values of 8.5, 6.5, $8.3 \text{ m}\Omega\text{cm}^2$ respectively [45]. This suggests from current literature that PVD coated layers are superior to

electroplated layers for corrosion resistance and interfacial contact resistance.

Havigh et al. utilised a multilayer coating, of TiC on aluminium, as literature suggested that multilayer coatings produce a more chemically resistant layer than single layers [100]. Titanium was utilised to both increase the corrosion resistance and reduce the contact resistance. The amorphous carbon coating was chosen for the same reasons. The coated samples improved the corrosion resistance but no information was provided on the contact resistance. However the coating failed to protect the aluminium alloy from corrosion, with pits occurring on the surface [100]. More work is required to protect more active substrates such as aluminium.

Shi et al. investigated TiC layers on Ti substrates and utilised a double glow plasma surface modification technique with a graphite target to apply the coating [107]. The coating successfully reduced the the corrosion current by a factor of 10 in simulated fuel cell conditions. The ICR was also reduced from 98.1 $m\Omega cm^2$ for the bare titanium substrate to 7.5 $m\Omega cm^2$ for the coated material, this however did increase to values that exceed the DoE targets after static corrosion testing [107]. Both Shi et al. and Havigh et al. chose titanium and aluminium due to the reduction in mass that can be achieved relative to stainless steel.

Wang et al. had similar success using PVD processes to apply transition metal carbides, although upon stainless steel [108]. Firstly samples were polished down with a grit of 1500 SiC abrasive paper, then coated with varying thicknesses of MbC, one sample also included a 100 nm Cr layer between substrate and the MbC layer [108]. Coatings were applied with a magnetron sputtering device, the

316L stainless steel substrate was also sputtered prior to coating to remove any oxide layer [108]. All MbC coatings improved corrosion resistance with the thickest (1052 nm) coating exhibiting the lowest corrosion current, this was further reduced by the addition of the Cr interlayer [108]. ICR was quoted at a high compaction force of 210 Ncm^{-2} which will reduce the contact resistance values, however the thickest coating displayed the lowest contact resistance of the MbC layers with a value of $7.9 \text{ m}\Omega\text{cm}^2$. The ICR was further reduced, to $6.5 \text{ m}\Omega\text{cm}^2$, by the addition of the Cr interlayer [108]. The Cr transition layer is responsible for enhanced adhesion of the MbC layer upon the substrate. The Cr layer serves as a "seed layer" which aids the crystallization of the coating [108].

Carbon

Carbon coatings have been investigated on stainless steel, titanium and aluminium bipolar plates and have seen varying degrees of success [72, 109–111]. Kai feng et al. achieved ICR values between 8.3 and $5.2 \text{ m}\Omega\text{cm}^2$ for compaction forces of 120 and 210 Ncm^{-2} respectively by applying an amorphous carbon coating on SS316 samples, therefore achieving the 2020 DoE ICR targets [109]. Kai feng showed, by AFM and Raman spectroscopy, that the amorphous coating produced by close field unbalanced magnetron sputter ion plating produced a dense and compact coating. The coating had a small crystallite size and a large number of disordered bands. It was thought the dense and continuous coating could effectively block electrolyte migration to the surface of the substrate [109]. The amorphous carbon coatings reduced corrosion current density to $0.06 \mu\text{Acm}^{-2}$ compared to $21 \mu\text{Acm}^{-2}$ for bare 316L substrate.

Show et al. also produced amorphous carbon coatings but on titanium substrates, it was found that the growth temperature of the carbon coating was paramount to the electrical performance of the layer [110]. Carbon coatings grown at room temperature increased the contact resistance of the sample from $5.3 \text{ m}\Omega\text{cm}^2$ to $440 \text{ m}\Omega\text{cm}^2$ but if the growth temperature was raised to 600°C then the contact resistance is reduced to $2.5 \text{ m}\Omega\text{cm}^2$ [110]. It was shown that by growing the carbon at room temperature there was no principle peak at the D band. The G band was much flatter and wider [109, 110]. This change in structure is responsible for the lower conductivity.

Zhuguo et al. produced TiN and CrN layers with a surface carbon layer using close field unbalanced magnetron sputter ion plating (CFUMSIP), the samples were cleaned via ultrasonication in a solution of acetone and distilled water and dried before the physical vapour deposition (PVD) technique [112]. The conditions used for the coating were the same as those used by Feng et al. on SS [109]. Zhuguo noted that the 0.8μ carbon layer appeared to be more dense than the TiN and CrN coatings produced, although some abnormal growth occurred for the carbon coating [112]. Potentiodynamic polarization tests showed reduced current densities in anodic conditions from $268.8 \mu\text{Acm}^{-2}$ for the bare alloy (AA-5052) to $4.6 \mu\text{Acm}^{-2}$ for the carbon coated sample [112]. Although the corrosion current was also reduced in the cathodic conditions, by more than one order of magnitude, it was still large at $46.7 \mu\text{Acm}^{-2}$. Zhuguo suggested this could be too high for a cathode BPP conditions. The potentiostatic tests displayed an end of test corrosion current of $100 \mu\text{Acm}^{-2}$, which is 10 times higher than DoE targets, meaning that CFUMSIP carbon coatings either need further refinement or are not

capable of achieving corrosion protection alone. The ICR of the carbon coating was $6.39 \text{ m}\Omega\text{cm}^2$ at a force of 150 Ncm^{-2} , thus achieving the 2020 DoE target.

Growth of perfect carbon coatings is typically inhibited by several types of growth defects and variable substrate morphology [113]. Vetter et al. described different methods for deposition of PVD deposited a-C coatings with the intention of minimizing defect density with homogeneous surface coverage and structure. Vetter et al. tested a DC magnetron sputtering set-up, in this setup the temperature of the substrate was measured by a pyrometer with tests conducted with and without shielding (which had the same plasma potential as the substrate) [113].

Vetter et al. compared two differing pre-treatments: Pretreatment A, Electron enhanced plasma: bias 200 V, pressure 1 Pa (Ar), current 2.5 A, time 15 min; pre-treatment B glow discharge: bias 760 V, pressure 3.1 Pa (Ar), current 0.4 A, time 10 min [113]. Pre-treatment A resulted in a starting substrate temperature in the range of 300°C and was referred to as a strong ion cleaning process, whereas B resulted in a starting temperature of approximately 150°C . Between test condition 1 and 2 a shield was introduced between the substrate and the target material, with this change Vetter et al. noted a reduction of defect density from 6000 flake defects per mm^2 to 800 flakes per mm^2 [113]. Shielding of the substrate reduced the number of impinging particles, preventing large particles depositing on the surface of the substrate. From tests 2 to 3 a more gentle ion cleaning process was used, which also resulted in a lower starting temperature. In addition a lower power was used for the coating process (1/1 compared to 5/2.7 kW cleaning/coating power respectively) [113]. These changes resulted in no big flake defect being observed, however a very high number of cone defects in the

order of 0.5 - 1 μm were observed. Flake defects are generated when particles are present at the start of the coating process or deposits on the substrate during the coating process. Flakes were observed to modify the morphology and growth behaviour of the coating [113]. It is suggested that the different growth conditions at the site of the flake give rise to changes in the local coating properties.

Vetter et al. used Raman spectroscopy to characterise the coatings and found that higher sputtering powers and higher temperatures result in the carbon coatings become more graphitic i.e. higher order is obtained by increasing energy input [113]. By using the 'soft' ion cleaning and lower sputtering power a sp² dominated hard a-C coating can be formed [113].

Vetter determined that the cleanliness of the chamber, the ion cleaning step (which is responsible for the starting temperature of coating), the sputtering power (this also relates to growth rate and substrate temperature) and shielding of the surface are the key concerns for defect generation [113]. Aharonov et al. and Panjan et al. also noted that higher temperatures increased defect density [93, 94]. Vetter et al. proposed that high sputtering power can lead to micro arcing which can lead to flakes being deposited. By varying the coating conditions Vetter et al. reduced the defect density by a factor of 10 between conditions 1 and 2 and by even more between conditions 1 and 3. The optimum condition included a shield and lower energy ion cleaning.

Yi et al. reviewed literature in depth in 2019 and found amorphous carbon coatings with contact resistances as low as 2 $m\Omega cm^2$ while the corrosion resistance largely depended upon the substrate material [114]. Yi et al. also investigated

literature around metallic (Ti, Cr, Fe, Mn, V, Co, Ni, Cu, Al) and nitrogen doped amorphous carbon coatings. Doping was primarily used to reduce the internal stress of carbon based PVD coatings but it was found that the durability and electrical conductivity of the layers could also be increased [114].

Literature suggests that the conditions used for the growth of carbon coatings need to be controlled to ensure minimal defects in the carbon layers. Some conditions however may require optimisation, for example the conductivity of carbon coatings are dependant upon the temperature of coating but higher temperatures also result in a higher defect density. Multilayers or doped layers may provide an avenue for low temperature carbon coating while maintaining adequate interfacial conductivity [92, 115].

Polymer Coatings

Vast research has been committed to conductive polymers due to the excellent chemical stability, relatively high conductivity and redox functions of the materials [116, 117]. Polymers also offer low costs in terms of deposition processes and materials. Polyaniline and Polypyrrole are two such conductive polymers.

Electroplated polyaniline coatings are formed by the electropolymerisation of aniline monomers into polyaniline. Polyaniline can form an effective barrier to the permeation of aggressive ions to the surface. Polyaniline forms a cross linked amorphous structure. This minimises the number of paths to the surface and increases the mean free path, leading to improved corrosion resistance. However, as reported by Sharma et al., thicker directly applied electrochemically synthesised

coatings change the microstructure of the coating. Thicker coatings appeared to have a more porous structure, which is in agreement with other literature [74, 118]. Shine Joseph et al. also reported increased thickness in polyaniline coatings led to increased pin hole defects [119]. However this trend may not follow with painted coatings, Rafael Bandeira et al. suggested that the corrosive media is closer to the surface for thin coatings and that thinner coatings are less effective in blocking the solution from reaching the metal surface, it was found that samples in the middle of the range of thicknesses had the most positive corrosion potentials and the lowest corrosion currents [117]. On the other hand thicker coatings have worse adhesion to the substrate surface, which could lead to exposed metal from stamping of the bipolar plate or during construction of stacks [74]. Furthermore thicker polyaniline coatings have been reported to have high contact resistances, this would be detrimental to the performance of the stack [74, 118].

Shine Joseph et al. compared an electroplated polypyrrole coating and a painted polyaniline coating. The thicker painted coatings exhibited improved corrosion resistance over the thinner painted layers, this is in contrast to the results of electropolymerised polyaniline coatings [120]. Kun Zhang et al. electroplated polyaniline layers upon stainless steel and found that thinner layers provided preferential corrosion and contact resistance properties [74]. This suggests that the application method can determine whether thicker or thinner coatings are more effective. Alternatively it could be a result of the number of defects in each coating, this was not quantified by either author.

Polyaniline can also be chemically synthesised, it can then be treated to obtain polyaniline in the conductive green emeraldine salt state. Shine Joseph

et al. had some success painting polyaniline onto the surface of the substrate by dissolving the polyaniline in xylene and painting the solution onto the substrate [119–121]. The coating was dried overnight and heated to remove air bubbles. Rafael Bandeira et al. chemically synthesised polyaniline and formed an ink by dispersing the polyaniline in N-methyl-2-pyrrolidone (NMP), the substrate was coated via a casting method by depositing a volume of ink onto the substrate and drying at 60°C for 12 hours [117].

More research has been committed to electrochemical synthesis of polyaniline. The electrochemical synthesis of polyaniline has been carried out in acidic electrolytes with varying concentrations of aniline. A static or cyclic voltage is then applied to the substrate, polymerising the aniline by anodic oxidation [122]. This process directly synthesizes a polyaniline layer by polymerising aniline on the electrodes surface, typically metallic substrates. Static oxidation is typically carried out at potentials between $0.7 - 1.2 V_{SCE}$, whereas cyclic voltammetry is carried out between -0.2 to $0.7 - 1.2 V_{SCE}$, sweep rates are typically between 10 and 100 s^{-1} [122]. Synthesis via cyclic voltammetry leads to a more homogeneous product, which was confirmed by SEM. Temperature also affects the coating, reaction rate is directly proportional with temperature in the range of 0°C to 60°C [122]. Therefore coating thickness can be controlled by both the number of CVs and the coating temperature.

Polyaniline effectively increased the corrosion potential of metallic substrates and reduced the corrosion current, under simulated fuel cell conditions [123].

Li Jiang et al. reported that the conductivity of polymer coatings can be improved by doping with acid groups, namely sulphuric (SO_4^{2-}) and camphorsulfonic acid (CSA) [124]. The larger CSA group created a less rough surface with no microcracks, CSA improved the corrosion properties over doped polypyrrole. Interestingly the CSA doped coating displayed an increased corrosion potential but the polypyrrole/doped polypyrrole coating displayed a reduced corrosion current. Y. Ren et al. suggested doping with larger molecular acid groups would provide a more effective coating, results showed the larger dopant molecule increased corrosion resistance, creating a more uniform and defect free surface before and after corrosion [125]. The larger dopant molecule also resulted in positive effects on contact resistance. It is clear that doping of polymer layers can lead to improved corrosion and contact resistance, this is supported by many researchers [74, 120, 124].

M.A. Deyab doped polymer coatings with carbon nanotubes (CNTs) to study the effect on corrosion resistance and contact resistance, the highest CNT loading was 0.8%. The results showed conductivity increased and corrosion currents and potentials were reduced relative to uncoated and exclusively polyaniline coated samples [121]. Another benefit was increased adhesion of coating.

Some researchers investigated bilayered coatings, these coatings aim to combine the benefits of multiple materials to create better coatings [116, 120, 125–127]. Both Y.J. Ren et al. and T.J. Pan et al. produced composite layers with a polypyrrole base layer and a polyaniline top layer. However Y.J. Ren used doped polymer layers with the base polypyrrole layer galvanostatically electrodeposited and the top polyaniline layer being deposited by cyclic voltammetry. Whereas T.J. Pan

used cyclic voltammetry to create a base PPY layer and galvanostatically electrodeposited a polyaniline layer over the PPY layer [116, 125]. The results however are difficult to compare due to the differing corrosion conditions, notably the temperature 25 vs 80°C , and the different substrates used, copper vs 304SS. However both composite coatings increased the corrosion potential. Neither reported interfacial contact resistance measurements. Comparing the doped bilayer of Y.J. Ren to the doped galvanostatically synthesised polypyrrole layers of Li Jiang with both coatings on 304SS. The bilayer of Y. J. Ren increased the corrosion potential by 376 mV whereas Li Jiang's CSA doped coating and polypyrrole/doped polypyrrole (doped with small SO_4^{2-} ions) coating increased the corrosion potential by 434 mV and 625 mV respectively [124, 125]. Both authors reported largely different corrosion potentials for the bare substrate, Ren reported corrosion potentials of -262 mV_{SCE} while Jiang reported -405 mV_{SCE} , therefore it is hard to make direct comparisons. However from both sets of work it is clear that bilayers increase the corrosion potential. In Jiang's work a single doped polypyrrole layer produced a corrosion potential of -28 mV_{SCE} , while the bilayered coating increased potentials by 268 mV for the same substrate.

Polymer coatings typically exhibit unacceptable interfacial contact resistance values (ICR). S. Joseph et al. compared polyaniline and polypyrrole coated aluminium samples and reported ICR values of 0.35 Ωcm^2 and 1.75 Ωcm^2 respectively, while many authors investigating polymer coatings do not report on the ICR [128–130]. These values exceed DOE targets. Surbhi et al. reported ICR values of nearly 1 Ωcm^2 for a CV electropolymerised 10 cycle polyaniline coating, with thicker coatings displaying even higher contact resistances [118]. Polymer

coatings inherently have high ICR values, this must be addressed in PEM fuel cells as high ICRs will dramatically reduce the efficiencies of PEM fuel cells [118]. The high contact resistances associated with polymer coatings can be somewhat lessened by doping of the polymer. By doping with CSA, Jiang achieved a contact resistance value of $5.5 \text{ m}\Omega\text{cm}^2$, satisfying the DOE target of $10 \text{ m}\Omega\text{cm}^2$. K. Zhang et al. and Surbhi et al. investigated TiN and gold nano-particles respectively in an attempt to reduce contact resistance values of polymer coatings. K. Zhang found that TiN successfully reduced contact resistance values of polymer coatings [74, 118]. Therefore future polymer coatings should include both organic and metallic dopants to reduce contact resistance values.

Chapter Three

Experimental

This chapter will cover the materials, experimental techniques and analysis that have been used in this work. From table 1.1, the DoE targets identify: cost, plate mass, plate hydrogen permeation coefficient, anode and cathode corrosion resistance, electrical conductivity, interfacial contact resistance, flexural strength and forming elongation as the primary BPP factors. According to literature materials like stainless steel and aluminium have low hydrogen permeability [131, 132]. However this property is not the subject of this research. This work will investigate the corrosion and contact resistance properties of different BPP coatings and substrates. Low cost coatings were utilised on SS samples to address the cost targets of BPP. Aluminium was considered as a low cost lightweight alternative to titanium as BPP material. Conductivity tests have not been a subject in this work since the bulk conductivity of aluminium and stainless steel is measured in millions of Siemens per metre, which exceeds DoE targets [2, 133].

Metals suffer from electrochemical corrosion and high interfacial contact resistance. Accelerated *ex situ* electrochemical corrosion testing is used to investigate corrosion resistance. The interfacial contact resistance was measured for bare, coated and corroded samples.

3.1 Substrate Materials

Aluminium and stainless steel substrates were chosen for this work. Aluminium with a purity of 99.0% and Al6082, a typical automotive grade of aluminium, were selected. The compositions of which can be seen in table 3.1. Selected stainless steel (SS316L) with the following composition: 18% Cr, 10% Ni, 3% Mo and Fe balance was selected.

Single cell tested bipolar plates were produced from Al6082 billets by CNC. Coatings were applied by a PVD coating process described later in this chapter. Graphitic bipolar plates were used as a reference sample.

Table 3.1: Table of the chemical composition of the aluminium metals used in this work, in at.%.

Substrate	Fe	Al	Cu	Zn	Si	Mn	Mg
99.0%	<0.7	99.0	<0.1	<0.1	<0.5	<0.1	-
Al6082	-	97.4	-	-	1	0.7	0.9

3.2 Coating Processes and Materials

3.2.1 Polyaniline Titanium Nitride Coating

An electroplating three-electrode cell was designed using TinkerCAD software and 3D printed with a MakerBot Replicator 2 FDM printer. Two platinum mesh

counter electrodes positioned on either side of the working electrode were used to get a homogenous coating on both sides of the sample simultaneously. The SS316L sample (30x50mm) was used as a working electrode and placed in the central port of the electroplating cell.

A saturated silver/silver chloride electrode was fixed to the edge of the cell as a reference electrode. By using one reference electrode the potential could only be measured on one side of the sample. This could have led to inconsistent potentials either side of the sample. The solution was agitated prior to coating to ensure a well dispersed coating suspension. The sample area was equal on each side of the substrate, both of which should limit inhomogeneous potential distribution.

Before coating the stainless steel, samples were first wiped with ethanol to remove grime from the surface. Samples were then immersed in 50% sulphuric acid solution for 10 minutes to remove the passivation layer on the SS surface. After which, the samples were removed and immersed in deionized water, rinsed and dried under a nitrogen gas stream.

The electroplating solution was prepared as follows: 0.1 M sulphuric acid, 0.1 M aniline monomer (Sigma Aldrich). TiN nanoparticles (SkySpring Nanomaterials Inc.; >97% purity and 20 nm particle size) were added for the composite coatings, the loading was fixed at 0.5 gL^{-1} . The solution was sonicated for 10 minutes and then cooled to a temperature of 5°C in an ice bath, then agitated, before being used in the plating cell.

Applied potentials were implemented via an IVIUMSTAT.XRi potentiostat. The electropolymerisation of aniline and co-deposition of TiN was achieved by

cyclic voltammetry (CV) as per literature. The potential was swept from -0.18 to +1.00 $V_{Ag/AgCl}$ at a scan rate of 50 mVs^{-1} for 5 cycles (potential step of 5 mV) [74, 118]. Static potentials were used to create a TiN surface layer (for the bilayer coatings). Potentiostatic deposition of TiN has been shown in literature, albeit at higher voltages (0.90 V). This work was carried out at a lower voltage of 0.5 V, EDX tests displayed adequate deposition at this voltage [134]. After plating, samples were removed from the cell, rinsed with DI water and then dried under a nitrogen gas stream.

3.2.2 Physical Vapour Deposition Coating

Physical vapour deposition (PVD) coatings were carried out by Teer Coatings Ltd using a proprietary close field unbalanced magnetron sputter ion plating (CFUBM-SIP) system. Ti, Cr, Au and graphite target materials of 99.99% purity were used for coating. The argon and nitrogen sputtering gasses were both of 99.99% purity. Nitride layers were produced by the introduction of nitrogen into the reaction chamber, all other coatings were produced using argon. Turbo molecular and rotary pumps were used to reach pressures below 3.0 mPa. Substrates were ion cleaned prior to coating by sputtering with Ar ions to remove passive surface layers. This was done by applying a -500 V bias voltage to the substrate while supplying argon to the vacuum chamber. Layers were deposited initially using single targets followed by multiple targets to create a transition and surface layer.

3.3 *Ex situ* Accelerated Stress Test

3.3.1 Equipment

A three electrode setup was used for electrochemical testing. 99.999% purity graphitic carbon counter electrodes were used as a counter electrode and purchased from Sigma - Aldrich. A mercury/mercury sulphate (MSE) reference electrode was used for the work with SS substrates whereas a saturated silver/silver chloride electrode was used for the remaining work. The MSE was damaged before the completion of the later chapters and as such was replaced with another available electrode. The graphitic counter electrode and saturated silver/silver chloride electrode can be seen in figure 3.1 and were used in an electrochemical cell. The saturated potassium chloride (KCl) solution was replaced between tests. Fresh saturated KCl solution was prepared by adding excess KCl to 100 ml of DI water, until KCl sediment was seen to build up in the beaker. The electrode potential was measured, using a multi-meter, against a normal hydrogen electrode and another saturated silver/silver chloride electrode in a 1 mM sulfuric acid solution. The electrode was calibrated periodically against two different reference electrodes to ensure that a faulty electrode could be detected before starting experiments and to account for any potential drift.

A double walled glass corrosion cell, seen in figure 3.2, was used for *ex situ* accelerated stress tests. The external cavity of the cell was connected to a recirculating water bath to control the temperature of the system. Two of the three ports on the top of the cell were used to mount the counter and reference



Figure 3.1: Graphite rod counter (left) and saturated silver/silver chloride reference electrodes (right) used for *ex situ* corrosion testing.

electrodes. A glass pipette was mounted in the remaining port and used to deliver gasses to the system. The working electrode was held in place at the end of the cell with a mechanical screw fit compression piston. The compression force resulted in a seal between the substrate and o-ring at the orifice.

3.3.2 Procedure

Corrosion tests were carried out with an exposed area of 1 cm^2 . A 1 mM sulphuric acid solution was used as an electrolyte to target a solution pH of 3. The cell temperature was maintained at either 55°C or 80°C to simulate the PEFC environment. The cell will cause crevice corrosion around the seal/substrate interface, this is an undesired result of using this cell and will be detected when the current



Figure 3.2: Electrochemical cell used for *ex situ* corrosion testing.

is measured. The crevice is of the same area between samples and as such allows for comparisons to be made between samples. Sulfuric acid solutions were tested using a HANNA instruments Microprocessor pH Meter (pH 211) device. The device was calibrated using pH 4 and 7 solutions before measurement and the probe was cleaned between each solution using DI water. Solution pH was measured at pH 2.83 in the lab environment (temperature etc.). Electrodes and samples were added to the cell with the water bath running and flowing around the water jacket. The cell was then connected to an IVIUM compactstat. Finally the solution was added to the cell.

Potentiodynamic test was carried out after bubbling solutions with nitrogen for 20 minutes, this was then blown over the surface of the electrolyte for the duration of the test. The open ports atop the cell meant that oxygen had the potential to back diffuse into the solution, this could lead to difficulty when comparing this work to the work of others. All tests in this work are comparable however due to the identical setup used between tests. Potentiodynamic test were carried out using linear sweep voltammetry; sweeping the potential from -0.5 to 1 V_{NHE} at a sweep rate of 10 mVs^{-1} for 11 cycles for SS samples. These potentials were selected as literature showed that the active peak of stainless steel is between -0.18 and 0.2 V_{NHE} depending on the set-up [74, 118]. The passive behaviour of SS can be seen up to 1 V_{NHE} with analysis past the passive region not used in this work. Sweeping 300 mV below the lower values seen for the active peaks of stainless steel allowed for all active peaks of samples to be observed with coating expected to increase the corrosion potential as per similar works on polymer coated stainless steel [74]. These parameters were initially trialed for aluminium

substrates but it was found that the active peak of aluminium was much lower and as such the potential window was shifted. For aluminium sweeping the potential between -1.5 to 0.5 V_{NHE} resulted in the active peak being observed for the bare substrates and as such was used for subsequent tests. The 11th cycle was used for analysis for both substrates, repeated sweeps were carried out as this increased the repeatability of the measurement. This experiment was then repeated after the potentiostatic corrosion test.

Potentiostatic tests were carried out between the two potentiodynamic tests. After the first potentiodynamic test the solution was bubbled with air for 20 minutes. Amperometric detection program in the Iviumsoft software was used to hold a constant potential of 0.9 V_{NHE} for up to 24 hours, for the accelerated stress test. This potential was selected to ensure this work was comparable to the results seen in literature where, similar potentials were used (between 0.844 and 1 V_{NHE}).

3.4 Characterization

3.4.1 Scanning Electron Microscopy

A Joel JSM6060LV device and Hitachi desktop SEM were used for electron microscopy, SEM images were collected using an accelerating voltage of 30 kV and 15 kV respectively. Carbon tape was used to mount the samples with additional tape across the surface of the sample to improve electrical conductivity. SEM was carried out to investigate the condition of the samples surface before and after

corrosion testing.

Further analysis of the collected SEM images was carried out using ImageJ analysis. The software was used to quantify the degree of pitting of samples. Values for pitting area were found by thresholding the features of the image and using the analyse particle function. Background subtraction was carried out to increase contrast between surface corrosion and pitted areas.

Energy Dispersive X-ray

Energy dispersive X-ray (EDX) measurements were carried out using a Joel JSM6060LV scanning electron microscope (SEM) equipped with EDX and Oxford Instruments Inca software. A 15 kV accelerating voltage was used to measure the concentration of different elements on the surface.

3.4.2 Interfacial Contact Resistance

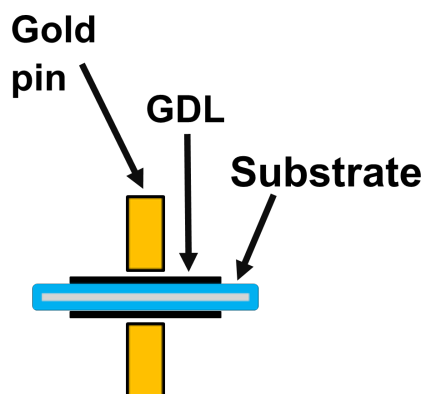


Figure 3.3: The set-up used to carry out GDL pre-cycling and ICR measurements.

ICR measurements were taken between the samples and two gas diffusion layers (Toray 60) following the method described in [74, 118]. An Instron 5848 microtester was used to control the compression force on the samples. GDL samples and gold pins were configured as per figure 3.3. Pre-cycling is conducted as GDLs have irregular compressible behaviour, which can alter the measured ICR values [135]. GDL carbon paper was pre-cycled in this set-up by compressing to 300 Ncm^{-2} between two gold plated copper pins with a surface area of 1 cm^2 and then cycled between 250 N and 300 N for 2 hours at a rate of 50 Ns^{-1} . El-Kharouf et al. found that compressing GDLs to 300 Ncm^{-2} 3 times ensured that the irregular compression behaviour was removed [135]. This work carried out further compression to ensure that the GDL did not affect ICR measurements. Samples were placed between two pre-cycled GDLs, then loaded onto the microtester between the two gold plated pins. The sample was then compressed from 20 to 300 N in 20 N intervals, with each value being held for 30 seconds as to allow the resistance value to stabilise. The resistance is measured by a precision Milli/Micro-Ohmmeter. The ohmmeter was connected using crocodile clips to the gold plated pins. The ICR value was then calculated following the work of Zhang et al. [74, 118]. The ICR was measured for the samples before and after corrosion tests to assess the stability of the coating.

From figure 3.3 the below resistances have been broken down:

- Bulk resistance of the substrate, both pins and GDLs denoted Ω_{BR}
- Interfacial resistance between the clips and pins denoted Ω_{CP}
- Interfacial resistance between pins and GDL denoted Ω_{PG}

- Interfacial resistance between GDL and substrate denoted Ω_{2ICR}

The total system resistance is equal to:

$$\Omega_{\text{Total}} = \Omega_{\text{BR}} + \Omega_{\text{CP}} + \Omega_{\text{PG}} + \Omega_{2\text{ICR}} \quad (3.1)$$

By measuring the total system resistance without the substrate and one GDL, a value for Ω_{CP} and Ω_{PG} can be measured. In addition the Ω_{BR} term can be ignored as the pin and GDL bulk resistances will be accounted for when the experiment is carried out. The bulk resistance of the substrate is many times smaller than the interfacial resistance, therefore this term can be removed from the calculation.

The resistance measured when the test is run without the substrate and one GDL is:

$$\Omega_{\text{system}} = \Omega_{\text{BR}} + \Omega_{\text{CP}} + \Omega_{\text{PG}} \quad (3.2)$$

Therefore:

$$\Omega_{\text{Total}} - \Omega_{\text{system}} = \Omega_{2\text{ICR}} \quad (3.3)$$

Comparing equations 3.1 and 3.2, the difference between the two equations is Ω_{2ICR} . Therefore it was possible to calculate the ICR by subtracting Ω_{system} from Ω_{Total} , dividing the value by two will give a value for the ICR. For corroded

samples the final ICR is not divided by two as the two interfaces between the sample and GDL will not be the same. Instead a representative ICR of the non-corroded side should be subtracted from the Ω_{2ICR} term.

3.4.3 X-ray Diffraction

XRD patterns were obtained using a BRUKER D2 PHASER 2nd generation diffractometer with a Co-K α radiation source ($\lambda = 0.179$ nm). 2θ angles of 10 to 140° were measured with a step size of 0.02°; each step was held for 0.2 seconds. Diffraction patterns were processed with DIFFRAC.EVA 5.1 software using the PDF - 2 database. Some patterns were also cross referenced with literature. Samples were analysed by converting data to Cu source radiation.

3.4.4 Raman

Raman spectroscopy relies on the non-elastic scattering of monochromatic radiation [136, 137]. The vast majority of photons are detected at the same frequency as the source, these photons could be elastically scattered, by Rayleigh scattering, but provide no information regarding the sample. Alternatively the photons could be inelastically scattered [137]. Inelastically scattered photons are described as Stokes and anti-Stokes Raman scattering [136, 138]. Stokes Raman scattering results in a decrease in photon energy and frequency whereas anti-Stokes Raman scattering results in an increase in photon energy and frequency [136–138]. Stokes Raman scattering occurs preferentially to anti-Stokes Raman scattering and is

used for Raman analysis [136]. The change in frequency of the photon is a result of changes in rotational, vibrational and or electronic energy levels of the sample [136, 139]. This leads to generating the finger print spectra characteristic for analysed material [136, 138].

Raman spectroscopy was carried out using a Renishaw inVia device at 20x magnification with a 532 *nm* laser, set to 5% power and a scan time of 30 minutes. The spectrum range was 100 and 3200 cm^{-1} .

Origin 2018 software was used for baseline subtraction followed by the Lorentzian multiple bands finder to achieve bands deconvolution. Initial band locations of 1350 cm^{-1} and 1550 cm^{-1} were used for the D and G bands respectively. This analysis follows the work of Lewandoska et al. [140].

3.4.5 Fourier Transform Infrared Spectroscopy

In Fourier transform infrared spectroscopy (FTIR), infrared (IR) radiation is directed toward a sample, if the sample is IR active some of the photons at specific frequencies will be absorbed [138, 141, 142]. The absorbed incident photons change the rotational, vibrational and or electronic energy level of the sample, the absorbed photons are specific to particular bonds and surrounding structure of the molecule [139, 141]. The transmitted photons are detected and the signal undergoes a fourier transform to deconvolute the peaks. The deconvoluted signal is plotted against the intensity to give a % absorbance or transmittance. The signal provides a fingerprint specific to each molecule which can be used to identify the

sample [142].

FTIR spectroscopy measurements were carried out to confirm the electropolymerisation of aniline using a Bruker Lumos device. The ATR crystal was wiped clean before every measurement and background scans were carried out using 64 scans on a gold reference plate. For sample measurements, 1000 scans were taken on samples specifically made for the FTIR test. The tested samples were 25 cycle pure polyaniline (25 cycle PANI) and polyaniline titanium nitride (25 cycle PANI TiN) coated SS316L. These were made because the polyaniline coatings deposited with 5 CV cycles for the test samples were too thin and could not be detected using the FTIR device.

3.4.6 Inductively Coupled Plasma - Optical Emission Spectrometry

Inductively coupled plasma - optical emission spectrometry (ICP-OES) is an analytical technique in which solutions are dispersed into an argon plasma which is specifically generated by the inductive effects of high frequency magnetic fields [143, 144]. The sample solution is quickly energised, in this excited state atoms and ions will eject photons to return to a lower energy state [144]. These photons can then be multiplied through photomultiplier tubes, the wavelength of the ejected photons is very specific to each individual element and as such can be used to detect the presence of elements [144]. In addition, the count of these photons is proportional to the concentration of the element, this is calibrated with control solutions of elements before sample measurement, this allows the concentration of

the element to be measured [144].

ICP-OES was carried out on corrosion solutions collected after the potentiostatic corrosion and two potentiodynamic tests outlined in section 3. This was to measure the ions in solution, which in a fuel cell could poison membranes and catalyst materials, degrading performance [145]. Makkus et al. suggested a cation contamination target value of less than $8 * 10^{-7} \text{ molcm}^{-2}$ during 5000 h [146]. Shabani et al found that 10 ppm of cations such as Fe^{2+} , Al^{3+} , Cr^{3+} , and Ni^{2+} in the membrane could result in a performance drop of up to 90% [147]. At the date of writing no literature could found that proposed the mechanism for cation ion migration to the CCM nor could literature be found regarding the concentration gradient that would be expected to form. However sources suggest balance of plant and bipolar plate corrosion as a source for cation contamination [147].

3.5 *In situ* Testing

3.5.1 Single Cell Testing

In situ testing was carried out using an 850e Multi Range Fuel Cell Test System and 885 Fuel Cell Potentiostat. All MEAs were commercial Johnson Matthey 15 μm membrane, with 0.4 mgcm^{-2} Pt loaded anode and cathode. Control cathode and anode bipolar plates were constructed from POCO graphite with Toray 60 paper as the GDL; Al6082 aluminium was used for the coated cathode BPPs. This grade of aluminium was selected as it has seen extensive use in the automobile

sector and was readily available [148, 149]. The cell was assembled with bolts incrementally torqued to 3.5 Nm in a cross method. The cell temperature was set to either 55°C or 80°C with a gauge anode and cathode pressure of 1.5 bar and 1.3 bar respectively. Relative humidity for the cell was maintained at 100% for each temperature. MEAs were conditioned before testing by holding a potential of 0.6 V for 6 hours. This was to ensure all MEAs were suitably hydrated. After preconditioning, baseline measurements of the OCV, polarisation curves and EIS measurements were carried out on the MEAs as a control.

Once the MEAs had been hydrated the cell was disassembled and the cathode plate was replaced with the coated metallic bipolar plate. The bolts were replaced and tightened to the same force of 3.5 Nm . The MEA was then held at 0.6 V for 3 hours before testing. The test protocol measured polarisation curves from OCV down to 0.25 V at a step of 0.05 V with each potential held for 3 minutes. This was then repeated from 0.25 V to OCV. Two EIS measurements were also carried out at 0.4 A and 0.6 V to gain insights into the behaviour of the system at low current densities and at typical operating conditions respectively [20]. Frequency response was measured between 0.1 Hz and 10 kHz.

OCV was held for 10 minutes before each polarisation curve and EIS measurement. An initial polarisation and EIS tests was carried out, with subsequent tests carried out every 12 hours after a duty cycle used for accelerated stress testing. The accelerated stress protocol (AST) was carried out for 12 hours, the potential was stepped between 0.6 V for 10 seconds and 0.9 V for 15 seconds for the duration of the test. This protocol was the same for tests carried out at 55°C and 80°C.

Once testing had been completed the MEAs were then hydrated for 3 hours using graphitic carbon plates before polarisation and EIS tests were carried out again. This was to isolate the MEA degradation from the bipolar plate degradation.

Chapter Four

Titanium Nitride Polyaniline

Bilayer Coating for Metallic Bipolar Plates Used in Polymer Electrolyte Fuel Cells

4.1 Introduction

Two materials, polyaniline (PANI) and titanium nitride (TiN), have each respectively shown promise in improving the corrosion resistance and contact resistance of bipolar plates (BPP). Polyaniline was shown to provide a barrier for the bipolar plate and to effectively lower the corrosion currents observed in *ex situ* corrosion tests. However the interfacial contact resistance (ICR) between polyaniline coatings and GDL is high and results in high electrical losses. On the other hand, TiN is reported to achieve good conductivity and in some cases improved corrosion resistance.

The two materials have also been investigated together in a composite coat-

ing and showed promising results but the contact resistance of the coating was still too high for use in a commercial fuel cell. In this study, the application of an additional layer of TiN over the TiN-polyaniline composite coating (a bilayer coating) is investigated. Composite bilayered PANI TiN coatings were deposited upon SS316L substrates, these samples were tested by means of simulated corrosion and contact resistance.

4.2 Results and Discussion

4.2.1 Coating Characterisation

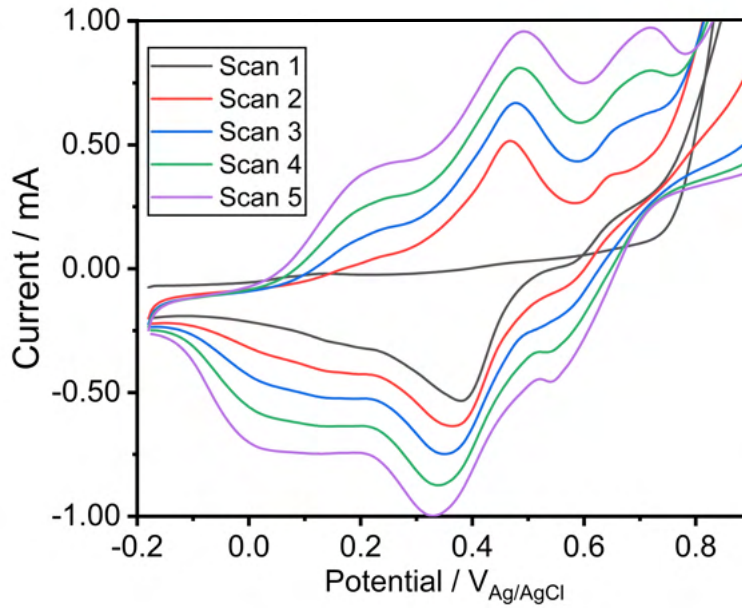


Figure 4.1: Cyclic voltammogram of a 0.1 M polyaniline and 0.1 gL^{-1} solution at room temperature (approximately $25^{\circ}C$).

Polyaniline was coated onto the SS316L substrates via a 5 cycle CV. Thin 5 cycle coatings have been shown to minimise the ICR and porosity of polyaniline coatings [117]. The reduced porosity enhances the corrosion resistance of polyaniline coatings. Literature highlighted that thicker coatings cause a more porous structure [74]. Preliminary work showed that by controlling the temperature and initiating electroplating experiments at 5°C , coatings with a lower ICR can be achieved. In addition the temperature of the lab was inconsistent ranging from 15 to 30°C (measured by a glass thermometer in ambient conditions). This led to inconsistent coatings in preliminary work, cooling the solution allowed for more consistent layers to be produced. CV carried out at 5°C however did not show the traditional peaks observed in the electropolymerisation of aniline. Figure 4.1 shows the CV cycles produced in a solution of 0.1 gL^{-1} TiN and 0.1 M aniline at 25°C . The peaks observed here are due to the higher rate of reaction occurring at the elevated temperature, this shows that polymerisation of the aniline was successful in the chosen potential window and under the specified conditions. It is likely that the peaks were not observed at 5°C because the current flowing was minimal. Three redox peaks can be seen within the CV potential window (-0.18 and 1 V_{NHE}) for the forward and reverse scan. These peaks show the change in oxidation state of the polymerized aniline monomer. Formation of the desired conductive emeraldine oxidation state corresponds to the peak observed between 0.4 to 0.5 V_{NHE} . No clear peak can be seen for the electrodeposition of TiN, however during CV scans deposition of TiN and polymerization of aniline have been reported [117]. It is possible that the TiN gets trapped in the polymer structure as the aniline polymerises. Another proposed mechanism was the electrophoretic deposition of TiN across the PANI surface. Claiming nucleation sites and slowing

the polymerisation of the PANI. The surface layer of TiN was achieved by holding a static potential of 0.5 V. A list of samples can be seen in table 4.1.

Table 4.1: Table of samples produced in this chapter.

Sample Name	CV cycles	Solution	Time potential held static at 0.5 V / s
Bare SS	0	N/A	0
PANI	5	1 M Aniline	0
PANI 150	5	1 M Aniline	150
PANI TiN	5	1 M Aniline, 0 gL^{-1} TiN	0
PANI TiN 150	5	1 M Aniline, 0 gL^{-1} TiN	150
PANI TiN 300	5	1 M Aniline, 0 gL^{-1} TiN	300
PANI TiN 450	5	1 M Aniline, 0 gL^{-1} TiN	450
PANI TiN 600	5	1 M Aniline, 0 gL^{-1} TiN	600
TiN 600	5	1 M Aniline, 0 gL^{-1} TiN	600

Figure 4.2 shows the FTIR spectrum of the 25 cycle PANI and 25 cycle PANI TiN. The intensity of the peaks is indicative to the concentration of the coating. By comparing the intensity of the 25 cycle PANI and 25 cycle PANI TiN samples it can be seen that the later has a lower PANI loading, this could mean that the TiN suppresses the polymerization of the aniline onto the surface of the sample, this would support the mechanism of TiN claiming aniline nucleation sites. This could be due to electrostatic charges being formed on the surface, the dipole present on TiN could encourage the nanoparticle to deposit at these sites.

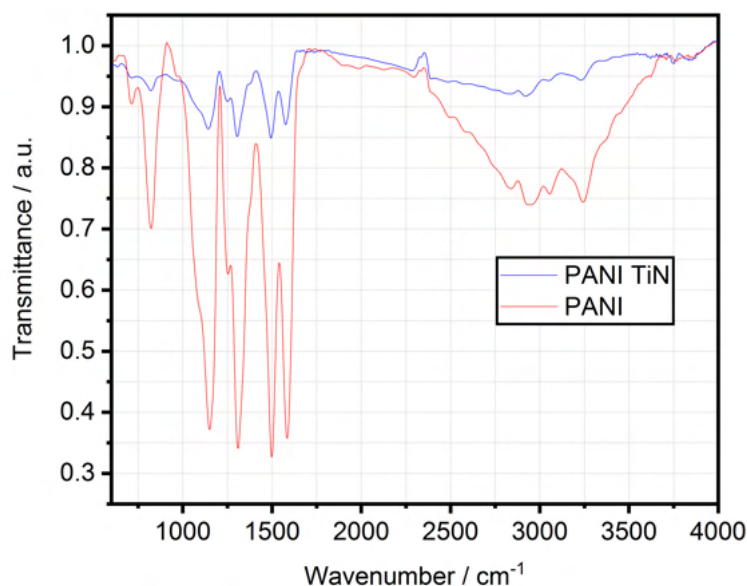


Figure 4.2: FTIR spectrums of 25 cycle: PANI and PANI TiN samples.

The peak observed at around 700 cm^{-1} is typically attributed to stretching of the Sulphur Oxygen double bond [150]. The PANI was polymerized in sulphuric acid which can cause the PANI coating to be doped with sulphate ions. The peaks at 823 cm^{-1} and 1149 cm^{-1} show the out of plane vibration and in-plane vibration of the carbon hydrogen bond, 1149 cm^{-1} also corresponds to the vibrational mode of the positively charged nitrogen hydrogen structure present in PANI [151, 152]. The shoulder at 1268 cm^{-1} and peak at 1309 cm^{-1} correspond to the vibrational modes of the carbon nitrogen bonds. The peak at 1309 cm^{-1} is a good indicator of the conductivity of the polymer as it corresponds to the π – electron delocalization, it is the extended p-orbital system that allows electrons to move from one end of the system to the other [153].

The peaks observed at 1500 cm^{-1} and 1588 cm^{-1} relate to the vibrations of the quinoid and benzoid rings present in the PANI structure. The broadband absorption that can be seen in wavenumbers higher than 2000 cm^{-1} are typical of PANI in the electrically conductive form. The bilayer was created by applying a static potential to the metal substrate. EDX measurements have shown that by holding a static potential after the CV, the TiN loading can be increased and a bilayered coating formed 4.2. Initially up to 300 seconds the TiN loading stays around 7% by weight, increasing the time held static to 450 second and 600 seconds results in the wt.% increasing to 7.11% and 8.41%, respectively. The TiN 600 sample had a lower wt.% than the PANI TiN 600 sample, this confirms that the presence of PANI increases the TiN deposition.

Table 4.2: Table of titanium loading fom EDX analysis.

Sample Name	Titanium Loading	
	Weight %	Atomic %
PANI TiN	6.87	7.63
PANI TiN 150	6.10	6.79
PANI TiN 300	5.88	6.48
PANI TiN 450	7.11	7.71
PANI TiN 600	8.41	8.94
TiN 600	7.17	7.95

4.2.2 Interfacial Contact Resistance

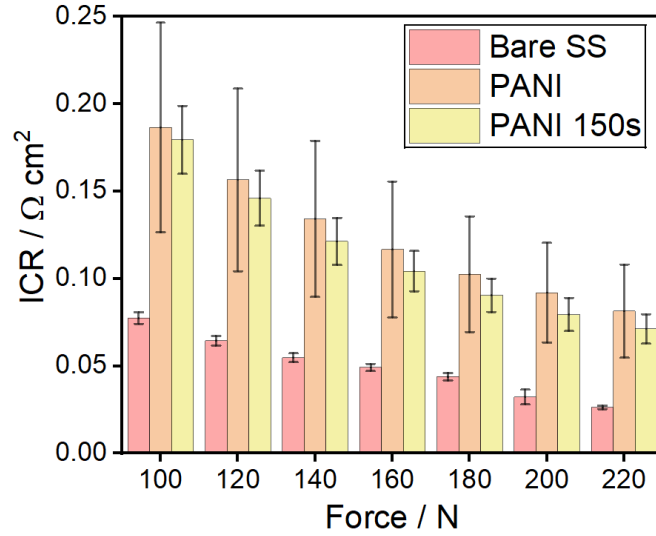


Figure 4.3: Interfacial contact resistance measurements before corrosion, displaying how PANI coating effects the ICR values, comparing the bare substrate to PANI TiN and PANI TiN 150.

The interfacial contact resistance (ICR) of the bare stainless steel, PANI and PANI 150 coated samples were measured as a function of compression force as shown in figure 4.3. Acid washed bare SS316L had an ICR of $55 \text{ m}\Omega\text{cm}^2$ at 140 Ncm^{-2} . This is similar to other reported values for SS316L [74]. Polyaniline although a conducting polymer has traditionally been problematic in BPP coatings as it greatly increases the contact resistance between the BPP and GDL. Thickness of polyaniline coatings greatly influence the ICR, with thinner coatings producing lower ICR values. As previously mentioned, the thickness of the coating can be controlled by the number of cycles, 5 cycles was found to be optimum for ICR in previous work [117]. Coatings were also carried out at 5°C to reduce the rate of polymerization and create thinner coatings, this value was found to be optimum in

preliminary optimization work. Previous work found the ICR of 5 cycle polyaniline to be $367 \text{ m}\Omega\text{cm}^2$ [117]. This work produced a polyaniline coating with an ICR of $142 \text{ m}\Omega\text{cm}^2$ (quoted values at 140 N), which is over 50% lower than previously reported values. This reduction in ICR is a result of the lower temperature forming thinner coatings.

Figure 4.3 shows the comparison of Bare SS and two polyaniline coatings, it can be seen that the Bare SS out performs the polyaniline coating even with the reduced coating thickness. The Bare SS does not have a thick passivation layer at this point due to the cleaning process employed and as such has relatively low ICR values.

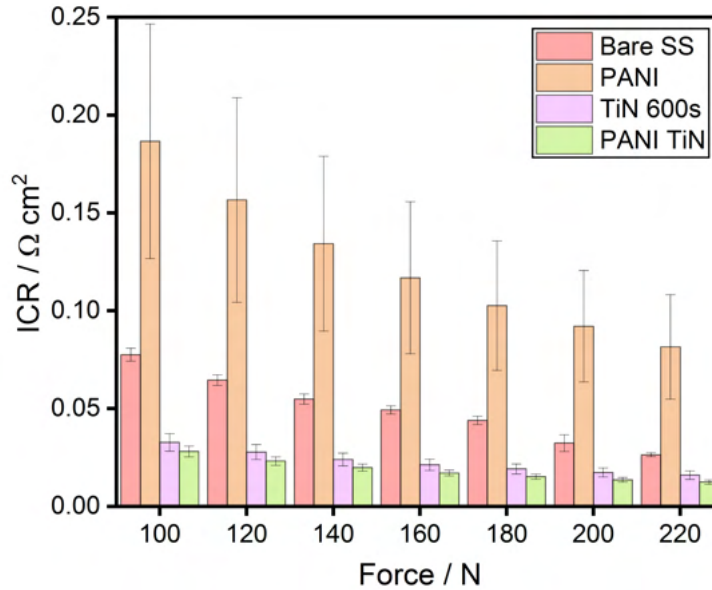


Figure 4.4: Interfacial contact resistance measurements before corrosion, displaying how TiN effects the ICR values, comparing PANI TiN and TiN 600.

The polyaniline coating was doped with TiN nanoparticles to reduce the ICR. The introduction of TiN into the polyaniline structure resulted in an ICR of $19.8 \text{ m}\Omega\text{cm}^2$ for the PANI TiN sample. This value almost satisfies the DoE target of $10 \text{ m}\Omega\text{cm}^2$ and again is an improvement upon previous literature, this is due to the thinner coating [118]. It can be seen in figure 4.4 that the addition of TiN into the polymer structure reduced the ICR relative to both the bare substrate and polymer only coating. A sample with a coating of only TiN was made, TiN 600, it was expected that this sample would have a lower ICR than the composite coating but would be greater after corrosion tests. However, it can be seen that the composite PANI TiN coating had a lower ICR even before corrosion tests. It is possible that the PANI could create an increased surface area which also increases the deposition of TiN due to more nucleation sites being available. Higher surface areas with increased TiN content would result in lower ICR values.

Figure 4.5 shows the polyaniline and TiN composite coatings, with samples PANI TiN 150, PANI TiN 300, PANI TiN 450 and PANI TiN 600 being the bilayered samples. All bilayer coatings of composite polyaniline TiN with a surface layer of TiN presented lower ICRs than bare samples and polyaniline coated samples. Static potentials were held after CV electroplating for 150, 300, 450 and 600. The ICR of the bilayers decreased as follows $150 > 300 > 450 > 600$. The PANI TiN 150 sample displayed a higher ICR than the PANI TiN sample, whereas the subsequent samples, PANI TiN 300, PANI TiN 450 and PANI TiN 600, all displayed lower ICRs. PANI TiN 600 samples achieved an ICR of $11.2 \text{ m}\Omega\text{cm}^2$. DoE targets are set at $10 \text{ m}\Omega\text{cm}^2$ at a compression of 140 Ncm^{-2} [154]. As the static potential hold time increased the ICR values decreased. A potential of 0.5

V was held to plate the surface of the samples with TiN, the longer the potential was held the more TiN electrophoretically deposited on the surface, as shown in table 4.2. The improved ICR of TiN over polyaniline results in an overall reduced ICR.

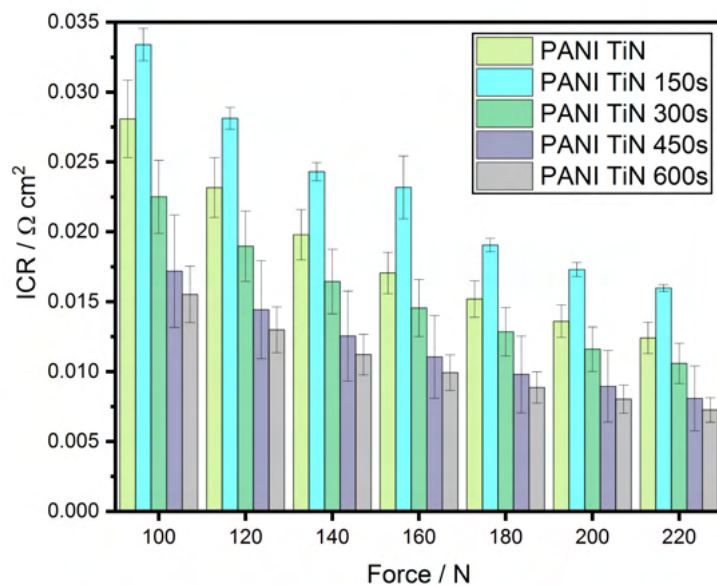


Figure 4.5: Interfacial contact resistance measurements before corrosion, displaying the trend of increased time of potential hold being inversely correlated with contact resistance.

4.2.3 Electrochemical Corrosion

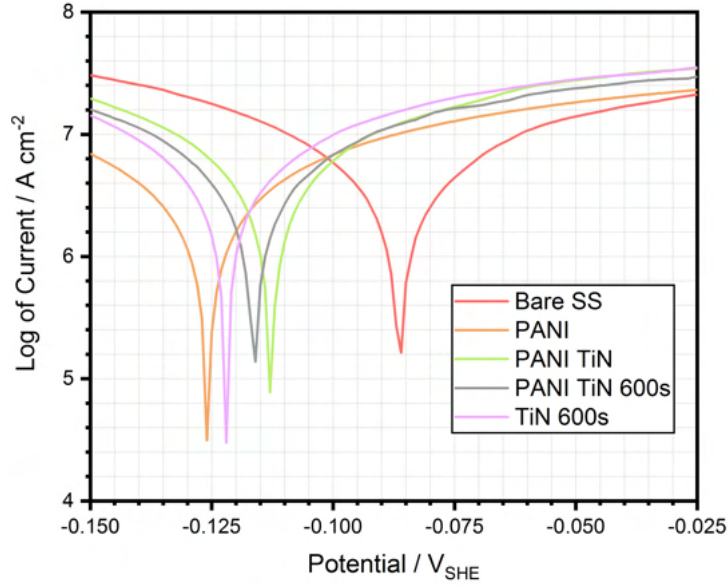


Figure 4.6: Linear sweep voltammograms (LSV) of the different samples (Conditions: pH 3 H_2SO_4 solution, $80^\circ C$ and saturated in N_2).

Figure 4.6 shows the potentiodynamic curves obtained in a 1 mM (pH 3) sulphuric acid solution at $80^\circ C$ saturated with N_2 . From the LSV analysis the highest corrosion potential measured was that of the bare SS sample, with a potential of $-0.09 V_{NHE}$. The corrosion potentials observed in this work for the PANI coating, $-0.13 V_{NHE}$, are lower than those observed for other works, $0.22 V_{NHE}$ [117]. The thickness of polyaniline coatings have been seen to change the morphology of polyaniline growth. The polyaniline coated samples in that work were thicker than those presented here. It could be possible that there is an optimal thickness for corrosion properties of the sample. The TiN doped PANI

coatings increased the corrosion potential from the PANI sample. The addition of TiN to form the composite PANI TiN coatings resulted in an increase in the corrosion potential, interestingly the bilayer saw a small decrease in the corrosion potential. It is proposed that TiN blocks pores in the PANI structure, preventing the diffusion of corrosive media to the SS surface [118].

Table 4.3: Table of potentiostatic corrosion current at $0.9 V_{NHE}$.

Sample Name	Corrosion current density / $nAcm^{-2}$
Bare SS	31.7
PANI	62.1
PANI TiN	48.1
PANI TiN 600	22.8
TiN 600	21.8

The potentiostatic corrosion current values are presented in table 4.3. The thin polyaniline coatings all achieved DoE targets with corrosion current densities in the range of $0.02 - 0.06 \mu Acm^{-2}$. This suggests that thin polyaniline coatings are an effective barrier to corrosive media, successfully preventing the corrosion of the underlying base substrate. The gold doped PANI coatings investigated in literature, [74], showed a corrosion current density of $1.4 \mu Acm^{-2}$. It would therefore be expected that TiN doped coatings would outperform the gold doped coatings in accelerated stress tests. Literature has shown that thinner PANI layers are less porous, this work aimed to minimise the thickness of the coated layer [118]. The lower porosity of the layer would better isolate the substrate from the

corrosive environment and lead to lower corrosion current values. Furthermore, in literature TiN loading has been observed to increase the density of the coating which could further enhance the corrosion resistance of the substrate [118]. As the time of potential hold increased, the bilayered coatings displayed a decrease in corrosion current density. This could be a result of the TiN filling the defects of the polyaniline structure.

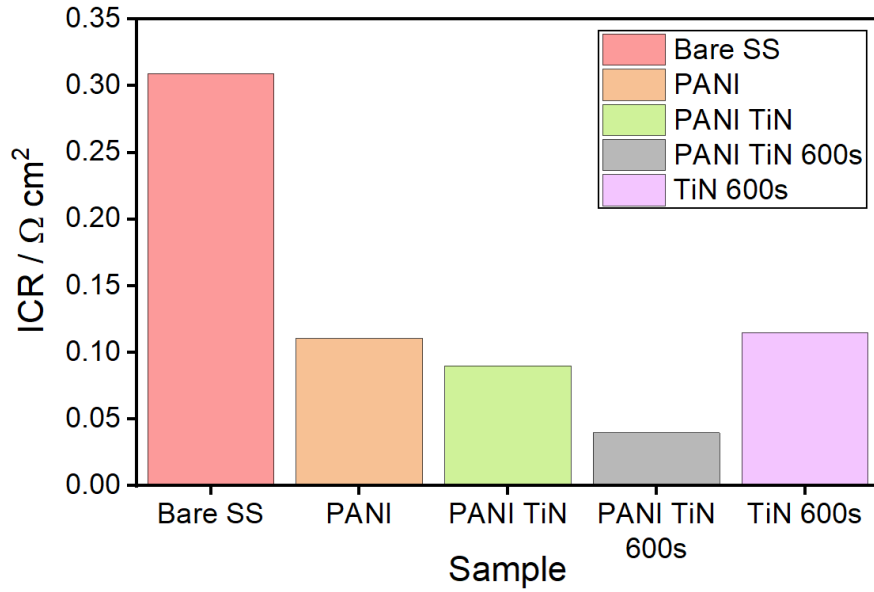


Figure 4.7: Interfacial contact resistance of samples after corrosion for 24 h at 80°C in a pH 3 solution under cathodic conditions (saturated with air, potential $0.9 V_{NHE}$).

BPPs are required to maintain low ICR values even after exposure to the corrosive environments found in the fuel cell environment. ICR tests were conducted after the corrosion test to investigate the coatings ability to maintain a low ICR after exposure. The results are shown in figure 4.7.

The bare SS sample increased in ICR to $310\text{ m}\Omega\text{cm}^2$ highlighting the need for samples to be coated. The PANI sample saw a decrease in ICR to a value of $111\text{ m}\Omega\text{cm}^2$, this has been seen in previous literature but was reported in thicker 50 cycle coatings [117]. It is possible that the PANI oxidation state was changed during the corrosion test, decreasing the contact resistance of the coating. The coating displayed adequate protection of the substrate.

For the composite coatings the contact resistance increased in both cases. PANI TiN increased from $19.8\text{ m}\Omega\text{cm}^2$ to $90.3\text{ m}\Omega\text{cm}^2$. PANI TiN 600 increased from $11.2\text{ m}\Omega\text{cm}^2$ to $39.9\text{ m}\Omega\text{cm}^2$. The TiN 600 showed a large increase in ICR from $24.0\text{ m}\Omega\text{cm}^2$ to $115\text{ m}\Omega\text{cm}^2$. The increase in ICR could be due to loss of TiN particles with the corrosion test. The PANI TiN coating with the highest TiN loading showed the lowest ICR before and after corrosion, along with the greatest resistance to corrosion.

4.2.4 Conclusion

A PANI-TiN composite bilayer was developed in a two-step electrochemical process. Deposition was confirmed by EDX and FTIR studies. The lower temperature of electroplating effectively reduced the corrosion current density of the layer relative to other works. It also had beneficial results in terms of interfacial contact resistance. The doping of the polyaniline layer did not negatively affect the corrosion properties, but improved the contact resistance of the sample. The bilayered structure further reduced the ICR bringing the value closer to the DoE target. The best coating in this work was the PANI TiN 600 sample which achieved DoE corrosion current density requirements and had an ICR of $11 \text{ m}\Omega\text{cm}^2$. This however is in excess of the DoE ICR targets. It could be possible by further optimisation that PANI TiN coatings could achieve DoE ICR targets.

However, literature along with this work has not shown success in creating a PANI coating with an ICR that achieves DoE targets [74, 117, 119–121]. This work was also unable to prevent the oxidation of the stainless steel substrate, which resulted in a further increase in the ICR. In addition aniline is: suspected of causing cancer, toxic to humans and is very toxic to aquatic life, among other hazards [155]. This presents safety concerns for users of the material. Furthermore literature has shown that metal nitrides and metal carbide coatings produced by PVD techniques are capable of achieving ICRs values of less than $1 \text{ m}\Omega\text{cm}^2$ [45]. These PVD coatings have been proven on stainless steel substrates. The 316L stainless steel used in this work is a well established material for use as a bipolar plate. However stainless steel is a dense material that will result in heavy stacks. The mass

of stacks could be reduced by using materials such as titanium or aluminium, owing to the lower density of the materials. Aluminium has a density lower than titanium and is about one third the density of stainless steel, therefore by utilising aluminium the mass of the stack can be minimised [80].

The following chapter will investigate PVD coatings on an aluminium substrate.

Chapter Five

Corrosion Resistant Plasma Vapour Deposition Coatings for Aluminium Bipolar Plates

5.1 Introduction

Metallic bipolar plates are capable of overcoming many of the downfalls faced by conventional graphite bipolar plates such as fragility and machinability. Stainless steel has emerged as the new convention for transport applications. In the previous chapter it was shown that the corrosion resistance is easily achieved when using stainless steel as a bipolar plate. Achieving contact resistance targets however is still a challenge, therefore coatings are required. Low cost coating materials and methods exist but do not appear to achieve the long term durability required to ensure that low contact resistance is maintained throughout the lifetime of the system. This has resulted in PVD coated stainless steel being adopted, these coatings achieve the $< 1\mu Acm^2$ corrosion current and $< 10 m\Omega cm^2$ contact resistance properties set out by the DoE [58, 79, 156].

For applications such as aerospace, and some automotive applications, gravimetric power density is critical; as such stacks should be as light as possible. If fuel cells are to be employed in such applications stack weight needs to be minimised. Using stainless steel for bipolar plates results in the plates accounting for around 70% of the stacks mass. With bipolar plates making up such a large proportion of the stacks mass it offers the best opportunity to reduce mass.

Aluminium has a density of around 2.7 gcm^{-3} which is 34% of that for stainless steel (stainless steel has a density of 8 gcm^{-3}) [157]. It is also more easily machined and stamped than stainless steel due to the reduced hardness of aluminium. This makes aluminium a possible candidate for metallic bipolar plates in light weight stacks [158]. However aluminium corrodes in the fuel cell environment; according to the pourbaix diagram for aluminium, the low pH (pH 3) and high transient potentials, in excess of around 0.8 V, puts aluminium in a state of corrosion [159]. Therefore aluminium too will need coating.

To this end, a range of PVD coatings, TiAu, TiC, TiN and CrC, were investigated for their electrochemical corrosion resistance and interfacial contact resistance (ICR) properties. The physical properties of the coatings were analysed using SEM, XRD and Raman before corrosion. Further analysis was carried out via SEM after corrosion.

5.2 Results and Discussion

5.2.1 Scanning Electron Microscopy and Energy Dispersive X-ray

Scanning electron microscopy (SEM) images and energy dispersive x-ray (EDX) quantification measurements were conducted before and after corrosion for the coated and uncoated samples. The loadings found through EDX analysis can be seen in table 5.1.

TiN Coating

The SEM images collected of the fresh TiN layer show a coating with large cracks across the surface. Large ridges across the surface can also be seen, with a texture occurring within these regions. It could be possible that during the ion etching step, a structure is created which the coating mimics, alternatively a charge build up could occur at the edge of the aluminium domains resulting in inhomogeneous coating [115]. Additionally differences in the thermal expansion coefficient of the coating and substrate could adversely affect the microstructure of the coating. Cracks in the coating are of concern as they provide an incomplete barrier for the underlying substrate. Cracks can provide highways for aggressive ions to reach the aluminium surface, this will lead to corrosion of the plate and eventual failure.

Table 5.1: Table of elemental concentrations as wt.% and at.% measured by EDX. Data shown for fresh uncorroded samples and samples corroded at 55°C and 80°C for 1 hour.

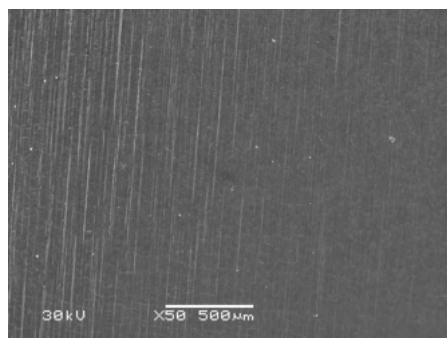
Sample	Corroded	Al	Au	Cr	Ti	N	C	O
TiN	Fresh	0.72/0.81	0.00/0.00	0.00/0.00	75.47/47.90	23.57/51.16	0.00/0.00	0.00/0.00
	55	2.86/2.66	0.00/0.00	0.07/0.03	53.60/28.09	6.17/11.06	0.00/0.00	36.97/58.01
	80	6.82/5.34	0.00/0.00	0.00/0.00	33.02/14.56	7.35/11.08	0.00/0.00	51.78/68.37
TiC	Fresh	43.66/26.98	0.00/0.00	0.00/0.00	4.64/1.61	0.00/0.00	51.28/71.21	0.00/0.00
	55	42.52/26.12	0.00/0.00	0.00/0.00	4.73/1.64	0.00/0.00	52.17/72.00	0.00/0.00
	80	38.92/25.09	0.00/0.00	0.00/0.00	5.21/1.89	0.00/0.00	37.37/54.12	16.79/18.25
CrC	Fresh	26.21/16.53	0.00/0.00	17.61/5.76	0.00/0.00	0.00/0.00	54.56/77.33	0.00/0.00
	55	25.20/15.74	0.00/0.00	17.21/5.58	0.00/0.00	0.00/0.00	55.79/78.29	0.00/0.00
	80	23.97/15.11	0.00/0.00	18.62/6.09	0.00/0.00	0.00/0.00	55.31/78.36	0.00/0.00
Thin gold	Fresh	96.06/96.29	0.60/0.08	0.00/0.00	1.02/0.48	0.00/0.00	0.00/0.00	1.41/2.39
	55	94.99/94.57	0.48/0.08	0.00/0.00	1.00/0.46	0.00/0.00	0.00/0.00	2.43/4.09
	80	68.21/57.91	0.44/0.05	0.00/0.00	0.86/0.41	0.00/0.00	0.00/0.00	27.79/39.79
Thick gold	Fresh	83.34/78.54	3.55/0.46	0.00/0.00	0.99/0.43	0.00/0.00	0.00/0.00	1.32/2.09
	55	74.20/65.05	3.19/0.38	0.00/0.00	0.90/0.45	0.00/0.00	0.00/0.00	8.74/12.93
	80	64.71/54.02	1.70/0.19	0.00/0.00	0.84/0.40	0.00/0.00	0.00/0.00	31.73/44.68

In figure 5.2a the TiN sample can be seen to have suffered severe corrosion during the accelerated stress test ($55^{\circ}C$, pH 3, $0.9 V_{NHE}$). A salt like substance could be seen on the surface of the sample and pits can be seen in the SEM images. Areas can be observed where the coating has been removed, these represent failures in the coating where corrosion solution can freely attack the susceptible aluminium. The higher magnification images in figure 5.2 show coating breakdown, the coating has fractures either due to mechanical damage as the pit has grown or chemical attack. Brahami et al. suggests that when aluminium forms pits, exfoliation corrosion occurs, connecting pits [160]. This leads to clustering of pits and exfoliation of the upper layers, this could explain the nature of the structures seen in the high magnification images.

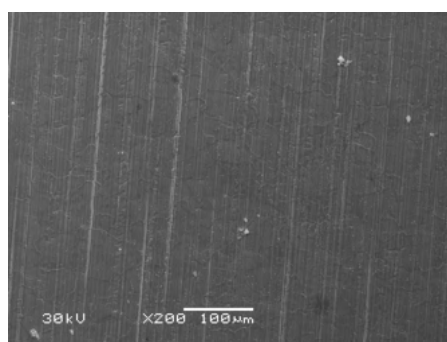
The TiN coated sample exhibited no detection of oxygen for the fresh sample, from table 5.1. Displaying adequate isolation of the aluminium from the environment. Titanium and nitrogen were the primary constituents detected, suggesting successful coating.

After the $55^{\circ}C$ accelerated stress test, the oxygen concentration increased to 36.97 wt.% with an increase also seen in the aluminium detection, from table 5.1. This is due to the removal of the TiN coating from the sample, leading to the exposed aluminium being detected. Oxygen diffusion through cracks or defects, arising from corrosion, would result in a partial or complete oxide layer on the aluminium.

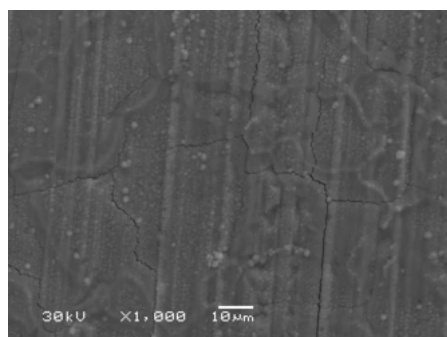
During the corrosion process some of the oxide will remain due to the local anodic and cathodic regions between the aluminium and aluminium oxide regions respectively. TiN could also form a cathodic region due to the superior corrosion



(a) x50 magnification.

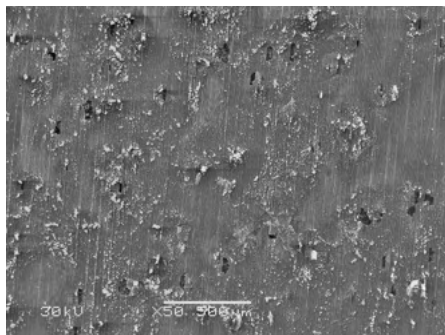


(b) x200 magnification.

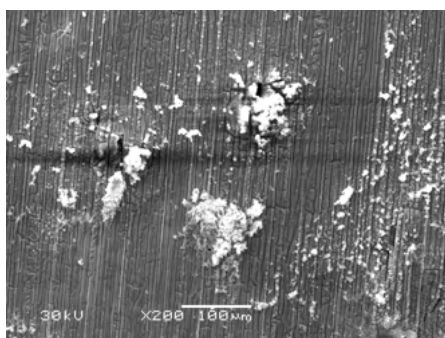


(c) x1000 magnification.

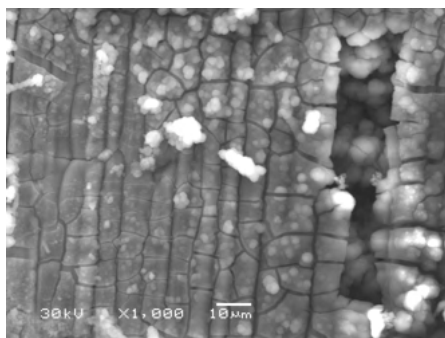
Figure 5.1: As received TiN coated 99.0% before corrosion testing at varying levels of magnification.



(a) x50 magnification.



(b) x200 magnification.



(c) x1000 magnification.

Figure 5.2: Corroded TiN samples at varying levels of magnification.

resistance of the material, this could also lead to galvanic coupling between the coating and the substrate. From the EDX maps it can also be seen that an aluminium and oxygen containing species had formed upon the surface. This will likely have formed from the aluminium ions that are generated during the anodic dissolution of the aluminium substrate occurring in pits. Further oxygen containing species can be seen around the pit mouth, this is likely $Al(OH)_3$; which is well known to form around pit openings due to the generation of Al^{3+} ions (from the anodic reaction) and OH^- ions (from the cathodic reaction) forming an ionic species.

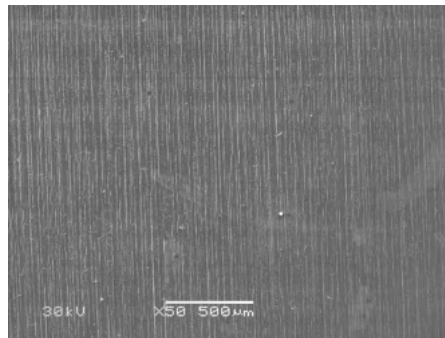
The oxidation of the substrate increased at elevated temperatures. The oxygen content of the sample increased from 0 wt.% to 51.8 wt.%, from table 5.1. Suggesting an increased rate of corrosion at $80^\circ C$ over $55^\circ C$.

TiC

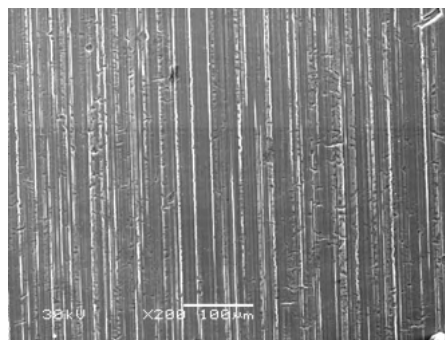
Comparing the TiC coated sample with bare aluminium sample it appears as if the underlying structure had been exaggerated from the ion etch and coating process. The lines upon the sample are attributed to the rolled nature of the aluminium substrate. After the AST test carried out at $55^\circ C$ for two hours the sample has suffered severe corrosion with a large number of pits and sulphate build up. The high magnification images show delamination of the coating, this appears to follow the machine direction (the direction in which the aluminium would have been rolled) of the rolling process. Larger pits appear to grow in both the X and Y direction, understanding of the thorough plane Z direction could not be made from SEM images. The corrosion on the TiC sample was so severe that the defect

area could not be calculated.

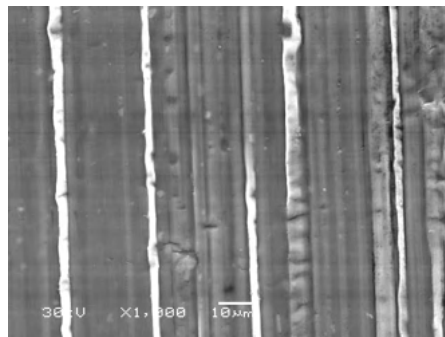
EDX analysis of the TiC sample displayed no detection of oxygen, which suggests adequate removal of the oxide layer. A high level of both aluminium and carbon was detected, with Ti only accounting for 4.64%. This suggests a relatively thick layer of carbon with a thin Ti interlayer. The high level of detection of aluminium suggests that the TiC coating was thin. EDX tests were run at 30 kV, at these accelerating voltages Lee et al. suggests that penetration would be $4\text{ }\mu\text{m}$, $8.5\text{ }\mu\text{m}$ and $7\text{ }\mu\text{m}$ in Ti, C and Al respectively [161]. The deposited coating is nanometric and as such a large degree of penetration into the aluminium substrate is expected. After corrosion at 55°C for 1 hour the EDX data remained unchanged when device uncertainties and coating tolerances are considered, this is unexpected. After corrosion for 2 hours at 55°C the oxygen concentration increased to 3%. The EDX data suggests there is little corrosion to the sample but this is in contradiction to the SEM data. When corroded at 80°C , for 1 hour, oxygen is detected at 16.79%, highlighting the increased rate of corrosion at elevated temperatures.



(a) x50 magnification.

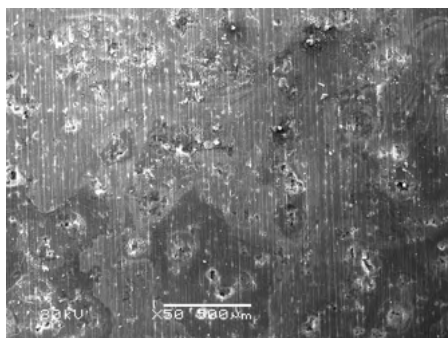


(b) x200 magnification.

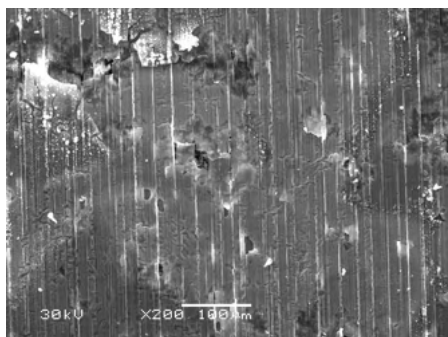


(c) x1000 magnification.

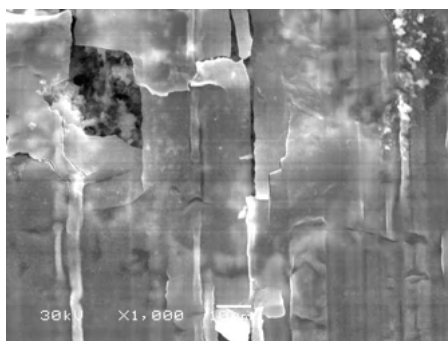
Figure 5.3: As received TiC coated 99.0% before corrosion testing at varying levels of magnification.



(a) x50 magnification.



(b) x200 magnification.



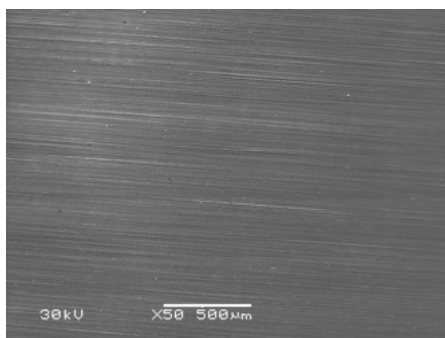
(c) x1000 magnification.

Figure 5.4: Corroded TiC coated 99.0% at varying levels of magnification.

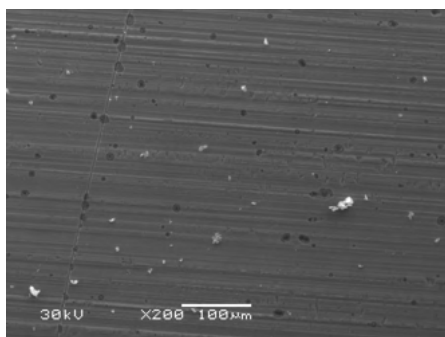
CrC

The CrC sample possess the same structure as the TiC sample, where the lines from the rolled substrate were observed. At high magnifications, imperfections can be observed on the surface. These could provide sites for pit initiation which would increase the rate of degradation. Severe localised corrosion was seen on the CrC sample, however the bulk of the material does not appear degraded by the corrosion testing when observed at low magnifications. At points of localised corrosion, a pit was observed surrounded by salt build up and an area of corrosion. At increased magnification around pits, exfoliation corrosion was observed. Similar to the TiC sample. In this process the corrosion occurs along grain boundaries where corrosion products have a higher volume than the substrate, this causes fracturing and delamination in these areas. In both the TiC and CrC samples corrosion was seen to form channels which caused fracturing at the surface. Sections of the sample display little to no corrosion, however at high magnification there appears to be many small pits. These could have terminated by pit repassivation or could be the start of stable pit growth, investigation of this would require longer corrosion testing. When compared with the TiC sample, the CrC appears to display less surface corrosion.

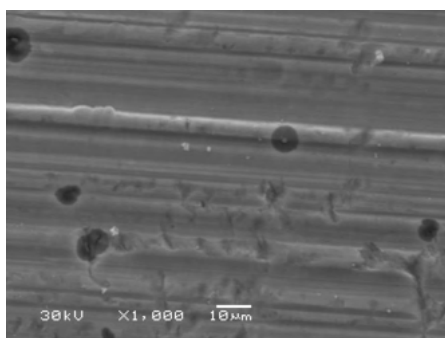
Differences in the level of corrosion across the surface meant that the calculated pit coverage percentage varied across the surface. Three areas were measured across the surface. The pit coverage percentage varied from 0.04% to 0.49%. This was the lowest value calculated for this work and aligned with observation of the samples. Pits formed on the CrC sample but did not appear to lead to delamination of the coating in the same manner as the other coatings.



(a) x50 magnification.



(b) x200 magnification.



(c) x1000 magnification.

Figure 5.5: As received CrC coated 99.0% before corrosion testing at varying levels of magnification.

The Cr content detected by EDX was 17.61 wt.% for the bare sample and was stable for the corroded sample. This was higher than that measured for the Ti interlayer of the TiC sample. The carbon content of the sample throughout the corrosion testing was also constant and found to be around 55 wt.%. No oxygen was detected for either the sample corroded at 55 or 80°C. It is likely that there was some oxide formation but it was in very low concentrations and as such was not detected. Oxygen formation could also be present within pits but could not be detected from surface EDX.

Localised corrosion occurred on the TiN sample, in these regions the coating would delaminate, exposing the aluminium substrate. However delamination did not occur on the CrC sample. The SEM and EDX data showed that the CrC sample has displayed less surface corrosion than the TiC sample. With the higher detection of Cr for the CrC sample relative to the Ti content on the TiC sample, it is possible that the thicker Cr interlayer provided a better barrier to the underlying substrate. It is possible that with an optimisation of the Ti interlayer thickness, the TiC coating could provide improved corrosion protection.

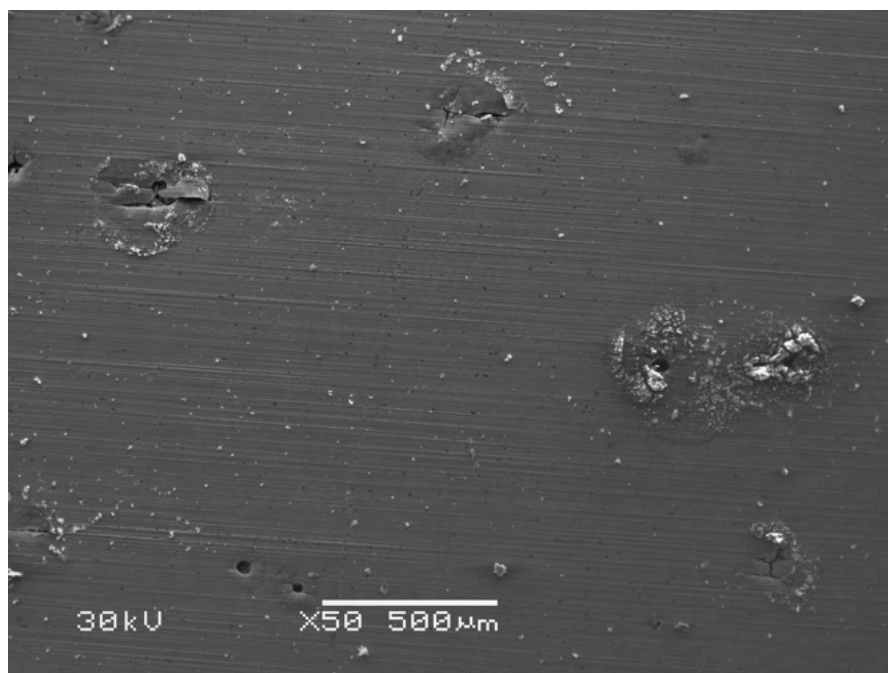


Figure 5.6: Corroded CrC sample.

Gold coatings

Neither of the two gold coatings resulted in a change on the surface morphology of the sample. Both coatings displayed lines across the surface due to the underlying aluminium substrate. The thin gold coated sample before corrosion can be seen in figure 5.7.

Both of the gold coated samples suffered from high levels of localised corrosion with large pits forming. The thin gold coating displayed fewer, but larger, pits as when compared to the thick gold coated sample. The thin gold sample also suffered from large amounts of salt build up on the surface. At higher magnifications the degradation of the thin gold coating can more easily be seen. In figure 5.8b a ring where delamination has occurred can be seen. At the edge of the rings corrosion products have accumulated. The delamination of the upper surface appears to have been caused by exfoliation corrosion. Delamination of the surface material can be more readily observed in figure 5.8c. Some regions between pits show evidence of countless micropits. Areas exist between the micropits and larger pits where no corrosion appears to have occurred. When looking at the region between two pits close to one another, an area of increased texture can be seen, these could be small amounts of salt build. Reboul et al. states that Al^{3+} ions diffuse out from pits and form $Al(OH)_2$, this can then form a sulphate salt. Which can be observed around the pits. This could explain the difference in texture close to pits compared to far from pits, as the concentration of Al^{3+} ions would decrease further from the pit. It is likely that two different corrosion processes are occurring at each of these locations. In regions close to pits, a local cathodic region is established to provide a circuit for the corrosion within the pit

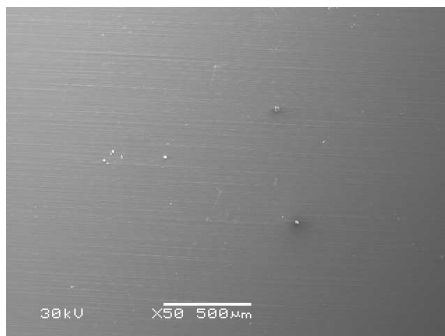
[162]. The cathodic reaction is the limiting process in aluminium pitting corrosion [162]. In the areas of micropits, corrosion appears to be more similar to general surface attack where pits either do not initiate or repassivate.

The Thick gold sample suffers from the same corrosion as the thin gold, however it exhibits smaller pits. Furthermore less salt build up can be seen on the sample which would suggest less corrosion. As can be seen from figure 5.9 it can be seen that the thick gold sample displays less exfoliation corrosion around the pits. The micropitting can also be observed further from the pits but appears less severe than the thin gold sample.

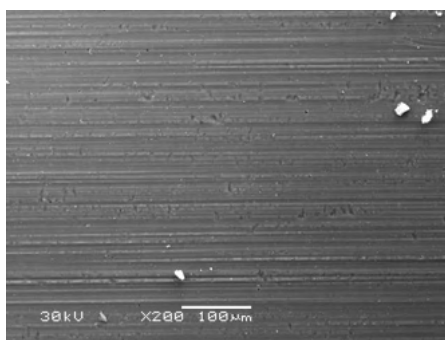
In addition, the corroded area percentage of the thin gold coating was higher than that of the thick gold coating. The thin gold coating displayed a pit area of 7.64% whereas the thick gold coating was between 2.51 and 2.96%. This suggests that the thick gold coating displays better resistance to corrosion than the thin gold samples. This could be a result of fewer defects in the layer.

Table 5.2: Defect count and corroded area (%) as measured from 50x magnification images.

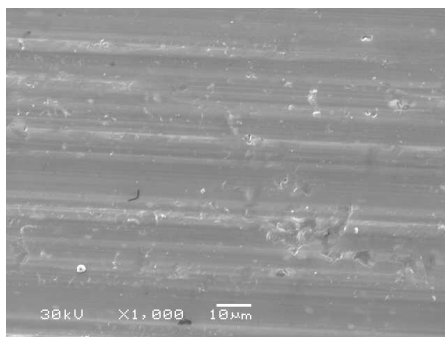
Sample	Defect area (%)
TiN	1.68
TiC	N/A
CrC	0.04, 0.28, 0.49
Thin gold	7.64
Thick gold	2.51, 2.58, 2.96



(a) x50 magnification.



(b) x200 magnification.

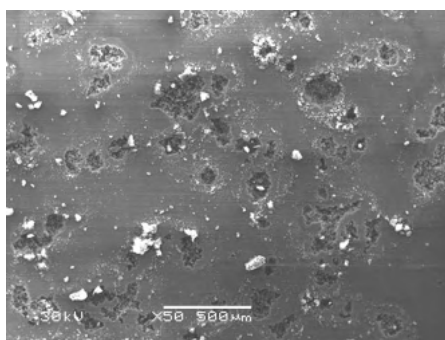


(c) x1000 magnification.

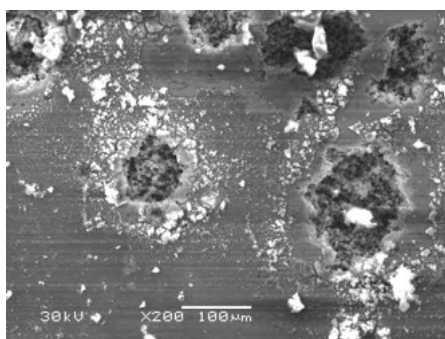
Figure 5.7: As received thin gold coated 99.0% before corrosion testing at varying levels of magnification.

Confirmation of the increased thickness of the gold layer can be made from the EDX data of both gold samples. The thin gold sample displayed an initial gold percentage of 0.6%, this increases to 3.55% for the thick gold sample. The titanium interlayers are consistent, as expected. Both coatings display a similar amount of surface oxygen, likely from an oxide. This would increase contact resistances and suggests exposure of the aluminium substrate. This could potentially be mitigated with a longer ion cleaning step; a thicker titanium interlayer may also be required to ensure the oxide does not quickly reform. Degradation of both layers can be seen from the EDX analysis. The thin gold coating loses small amounts of gold and titanium after corrosion at 55°C with only a 1% increase in the measured oxygen content. These changes are likely so minimal because the initial percentage of both gold and titanium is so modest to begin with. After corrosion at 80°C further changes in the gold and titanium concentrations can be observed. The thin gold coating displays a reduction in gold and titanium loading 0.16% for both elements. This corresponds to a percentage loss of 27% gold and 16% titanium. Critically the oxygen concentration increased to 27.79% for the 80°C test, which highlights the failure of the coating.

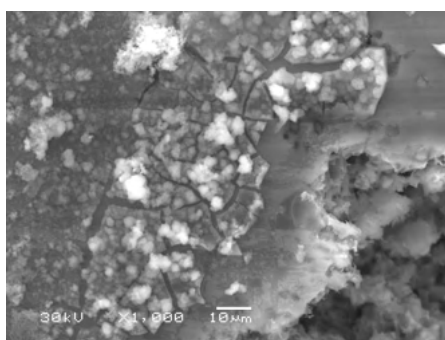
Similarly the degradation of the thick gold coating can be followed through the EDX data. After corrosion at 55°C the gold concentration and titanium concentration reduced by 0.36% and 0.09% respectively. This results in a percentage change in concentrations of 10% and 9% for the gold and titanium respectively. The oxygen concentration also increased to 8.74%, highlighting the failure of the coating. At 80°C the gold concentration reduced to 1.70% and titanium to 0.84%. Furthermore an increase of oxygen concentration to 31.73% from 1.32% indicated that the thick gold coating failed to provide a sufficient barrier for the substrate.



(a) x50 magnification.



(b) x200 magnification.



(c) x1000 magnification.

Figure 5.8: Corroded thin gold coated 99.0% at varying levels of magnification.

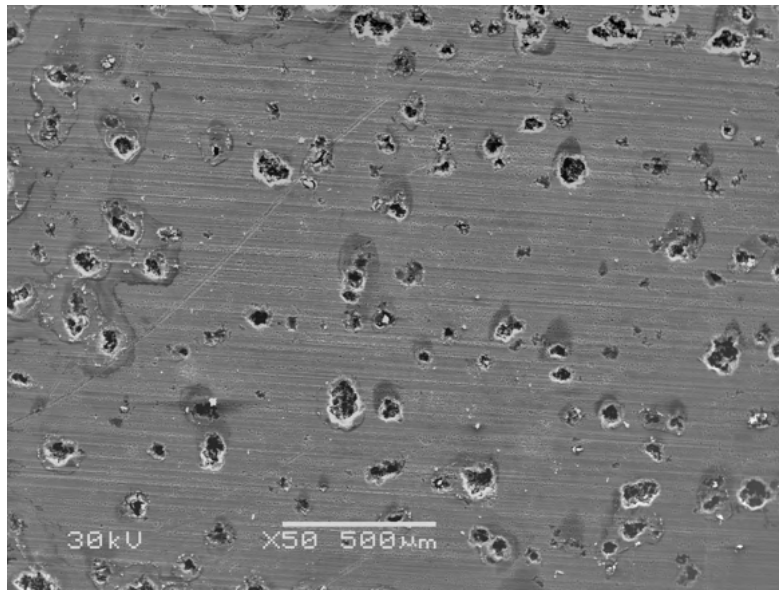


Figure 5.9: Corroded thick gold coated 99.0% sample.

SEM images taken at 50x magnification were analysed to calculate the area covered by pits as a percentage of the total area, to provide quantification of the SEM analysis. The TiN and TiC samples were both difficult to analyse due to the high degree of corrosion on the surface. Charge build up of corrosion products also caused shadows which made finding pits through ImageJ threshold adjustment inaccurate. For this reason the measurements of TiN and TiC will not be discussed. CrC, thin gold and thick gold samples displayed more localised corrosion and more distinction between uncorroded and corroded areas. This allowed pit area to easily calculated. CrC gave the lowest value for pit area with thin gold displaying the highest relative pit area. This can be seen in the SEM images as some areas of the CrC coating exhibited little to no pitting phenomena across the surface. Analysis of the pit area suggests that the the CrC sample provides the best protection against localised corrosion of the aluminium. The thick gold coating exhibited the second lowest pit area with a value of around 2.6%, this shows that the thicker

gold coating provided more corrosion protection than the thin gold coating.

5.2.2 X-ray Diffraction

Aluminium

Bare aluminium exhibited a face centred cubic (FCC) structure, which was identified through comparison to XRD diffractograms of PDF 3-065-2869 and in the work carried out by Bartsch et al. and Poole et al. [163, 164]. The peaks from left to right correspond to the crystallographic planes of (111), (200), (220) and (311), the narrow nature of the peaks also show a highly crystalline structure [165].

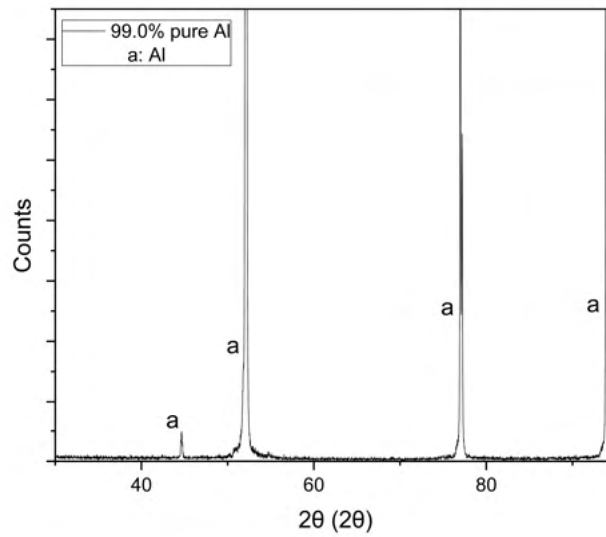


Figure 5.10: XRD diffraction pattern of as received aluminium.

TiN

The TiN coated sample displayed the characteristic peaks of TiN, Ti and Al. These were identified from PDF 03-065-05565, 01-079-6206 and 01-061-9626 respectively. There are weak signals for the hexagonal close-pack (HCP) structure of titanium [166]. The four peaks below 50° could also correspond to the tetragonal structural formation of Ti_2N , however this structure has two small peaks between 50° and 60° which were not observed suggesting little to no formation of this structure [167]. Analysis using the PDF database, crossed reference with literature suggests that the TiN formed a FCC structure [168]. There is little to no evidence of a transition layer with literature showing strong peaks around 38° for $Al_{2.5}Ti_{1.5}$, $TiAl$ and $TiAl_3$ which were not displayed in the diffraction patterns [168–170].

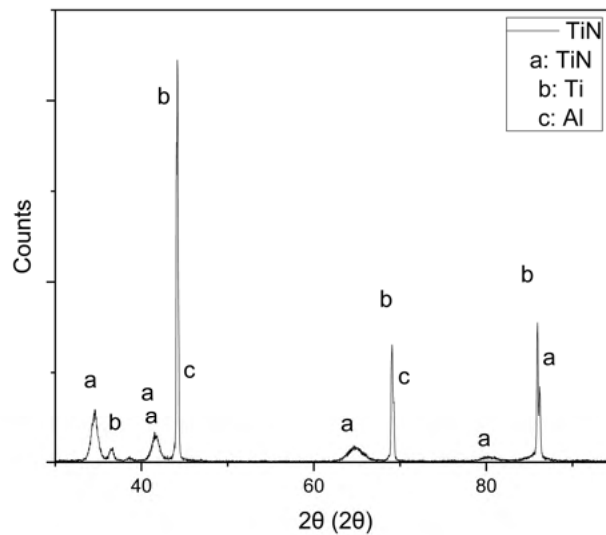


Figure 5.11: XRD diffraction pattern of TiN coated 99.0% aluminium.

TiC

The TiC coating displayed overlapping peaks for aluminium and titanium (PDF 00-002-1109 and PDF 01-079-6206 respectively) but conversely displayed small peaks that suggested the presence of a transition layer; identified by PDF 01-074-4580 and PDF 01-077-6855. Peak analysis displayed the the presence of TiAl and $Al_{0.15}Ti_{0.85}$ however the peaks for the latter are small. Suggesting a low concentration of this composition in the transition layer. The hexagonal close-pack (HCP) structure of titanium (PDF 01-079-6208) was observed [166]. TiC could not be identified from the PDF – 2 database, this suggests that no transition layer exists between the materials. Analysis of the carbon layer was carried out via Raman spectroscopy.

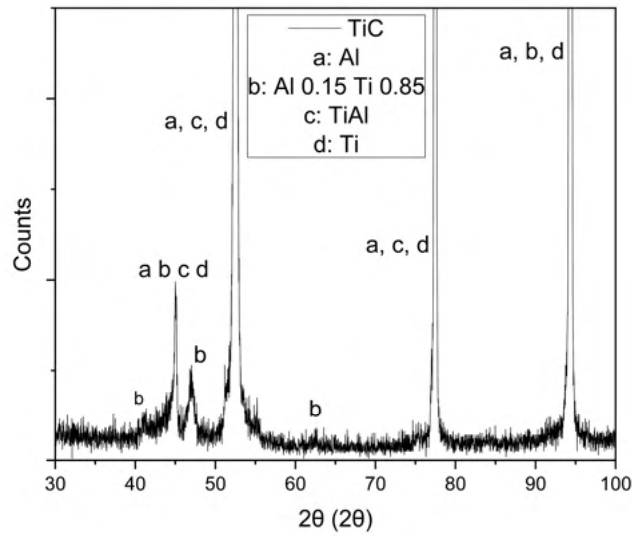


Figure 5.12: XRD diffraction pattern of TiC coated 99.0% aluminium.

CrC

Chromium can form a hexagonal close packed (HCP) structure or a body centred cubic structure (BCC) [171, 172]. Many peaks are present in diffractograms of chromium in the HCP structure, these are not present in this scan. Furthermore, the PDF database (PDF 01-081-4937) and literature identify the peaks present as a BCC structure of the chromium [172]. The aluminium again was identified as face centered cubic from the PDF database (PDF 00-001-1180) and literature [163, 164]. The Al_8Cr_5 structure has a strong peak at 42° with many smaller peaks across the scan window, the larger peak was not identified and nor were any of the smaller peaks [173]. In addition the dominating peaks of $AlCr_2$ were not present suggesting there is little to no interlayer of the two metals [174]. Utilising the PDF – 2 database a chromium carbon layer could not be identified due to peaks not

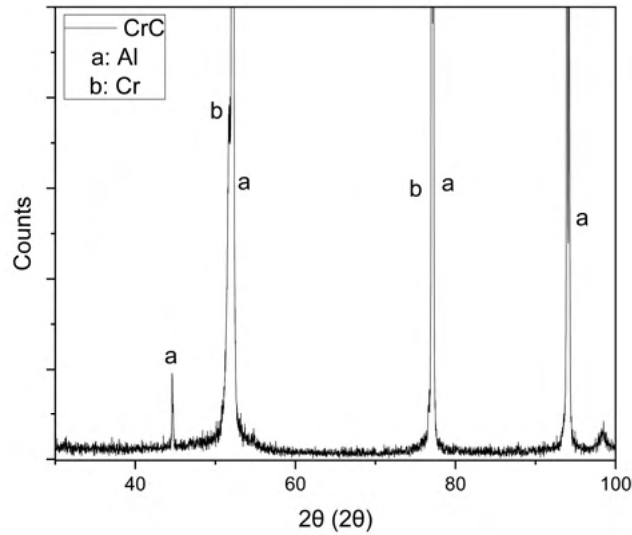
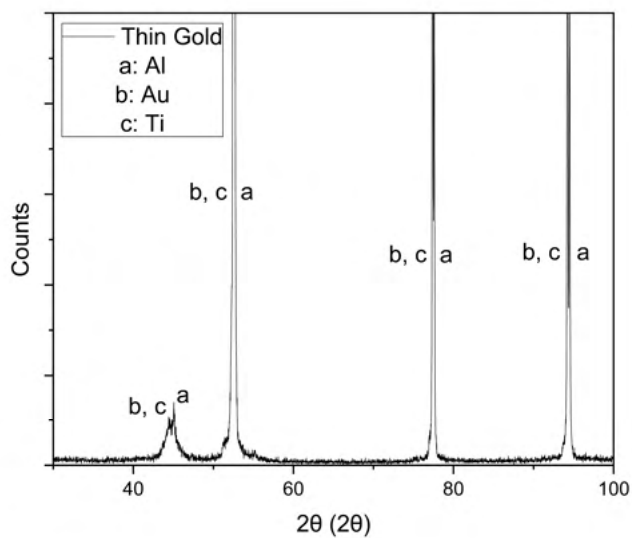


Figure 5.13: XRD diffraction pattern of CrC coated 99.0% aluminium.

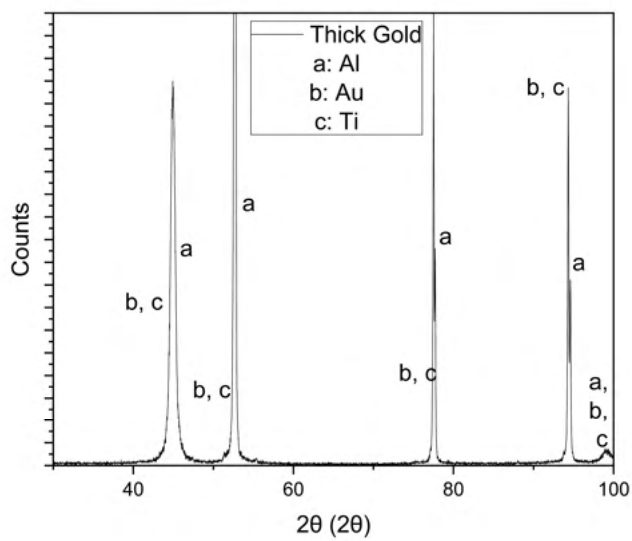
being present around 53°.

TiAu

For the thick and thin gold coatings the same peaks can be observed, except in the case of the small peak at the high angles of the thick gold scan. This is a small peak and likely only becomes apparent due to the increase in gold loading. The intensity of the first peak also increases for the thick gold coating; this is a characteristic peak of face centred cubic gold (PDF 01-071-4616) [175]. Again the FCC Al structure was observed and the HCP titanium diffractogram matched the scan well (PDF 00-002-1109, PDF 01-079-6208). Small amounts of titanium and gold were used for both coatings which would make transition layers thin and potentially hard to identify, neither TiAu and AlTi transition layers were identified from the PDF – 2 database.



(a) Thin TiAu.



(b) Thick TiAu.

Figure 5.14: XRD diffraction pattern of a) thin and b) thick TiAu coated 99.0% aluminium.

5.2.3 Raman Spectroscopy

Carbon coatings can be of a graphitic nature with a high degree of order or an amorphous structure with little order (amorphous carbon: a-C). An amorphous coated film can range from soft polymer like carbon (PLC) to hard diamond like carbon (DLC), both with very different properties [176, 177]. Raman spectroscopy can be used to investigate these materials. Two bands dominate the Raman spectra of carbon based materials; the D1 band is located near 1350 cm^{-1} with the second, the G band, being located around $1510 - 1600\text{ cm}^{-1}$ [177]. The shift in the D band position can reveal details of the structure of the carbon. Graphitic, nanocrystalline, amorphous and tetraheadral amorphous carbon exhibit G band positions of 1580 cm^{-1} , 1600 cm^{-1} , 1510 cm^{-1} and 1570 cm^{-1} respectively [177]. The D1 band is related to the defects in the material, it arises from the complex interactions between the electron band structure near the K point, which give rise to phonons in the A_{1g} symmetry [177–179]. The G band corresponds to the sp^2 bonded carbon atoms and is due to the doubly degenerate E_{2g} band at the centre of the Brillouin zone centre which leads to phonons in the E_{2g} symmetry [177–179]. The position, width and intensity of the G and D bands provide information on the allotrope of coated carbon [177]. The G band is the ordered graphitic band with the D band characteristic of carbon disorder [180]. Brubaker et al. states that additional bands exist in this region, namely D2, D3 and D4 bands (also referred to as D', A and I band respectively) [178]. These bands arise from disordered materials, as such when witnessed they are considered as amorphous and impurity bands [178].

Raman spectroscopy was used to identify the form of the carbon coating

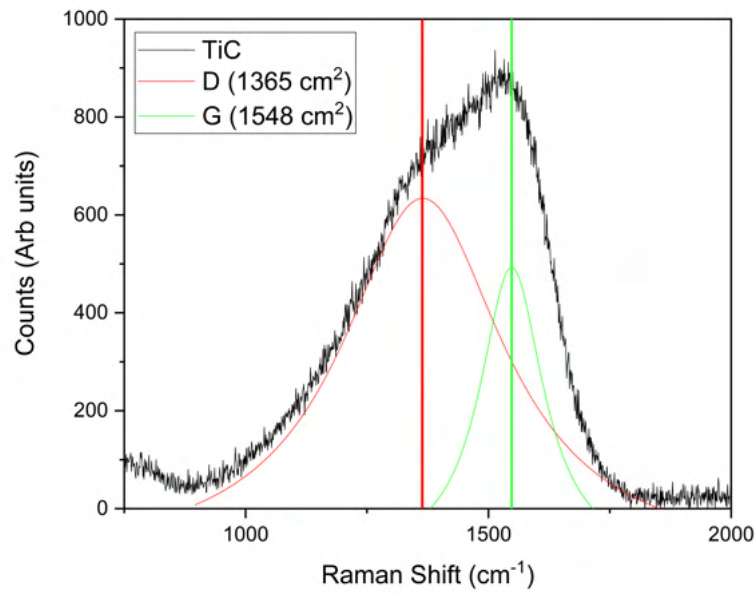
deposited on the aluminum sample [177]. Analysis of Raman spectra allows for the differentiation between, disordered, amorphous carbon (a-C) and diamond-like carbon [176]. The intensity ratio of the D and G bands decreases when moving from a nanocrystalline carbon to an amorphous carbon structures [178]. In addition Tuinstra and Koenig noted that the intensity ratio is inversely proportional to L_a (the crystallite size) which is described by:

$$L_a = \frac{I_g}{I_d} * C(\lambda) \quad (5.1)$$

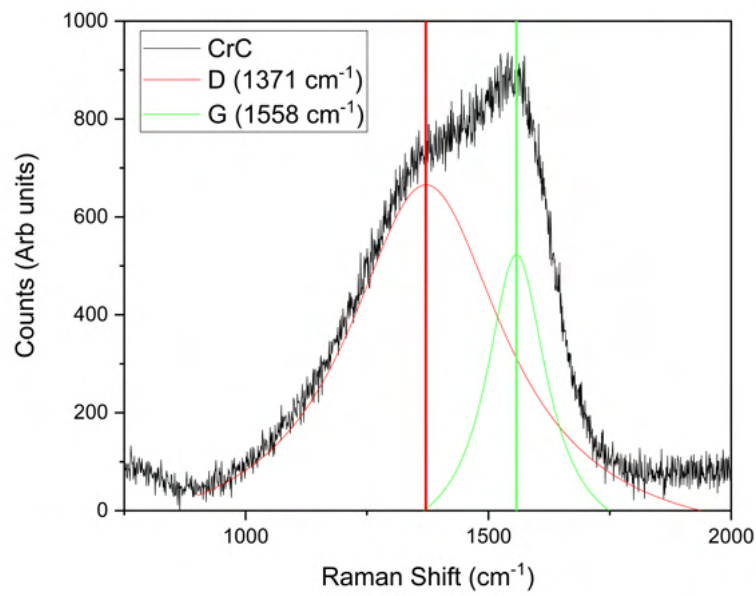
where $C(515.5 \text{ nm})$ is approximately 44. This equation holds true for the shift from graphite to nano-crystalline graphite [177, 181].

In figure 5.15 it can be seen that both carbon coatings displayed a wide, shouldered band. This band represents the overlapping of the D and G bands. The bands collected, closely match the work of Marton et al. who tailored D and G band intensities of amorphous carbon coatings by adjusting the gas mixture of the pulsed arc discharge coating method used [179].

From the Lorentzian multiple band finder used for deconvolution, the band positions can be calculated. The G band position of the TiC sample was 1548 cm^{-1} with an intensity ratio of 1.286 (I_d : 634, I_g : 493), this fit had an R^2 value of 0.98. This band position according to Ferrari et al. suggests a heavily tetrahedral amorphous carbon coating or a mixed structure of nanocrystalline graphitic carbon and amorphous carbon [177]. The intensity ratio of 1.286 suggests a mixed structure of either graphitic and nanocrystalline graphitic carbon or a mix of nanocrystalline graphitic carbon and amorphous carbon. The combination of these results indicate



(a) TiC.



(b) CrC.

Figure 5.15: Raman spectra for TiC and CrC coated 99.0% aluminium.

that a structure between nanocrystalline graphitic carbon and amorphous carbon was formed. This suggests that many small disordered nanocrystalline planes exist giving rise to the high intensity of the D band; furthermore this could be asymptomatic of an inter-defect distance of 2-3 nm [178, 179].

The G band position of the CrC sample was 1558 cm^{-1} with an intensity ratio of 1.273 (I_d : 666, I_g : 523), this fit had an R^2 value of 0.99. This suggests the same structure as the TiC sample; a nanocrystalline amorphous carbon mix. Comparing the two samples would suggest that the CrC sample is closer to a nanocrystalline structure than the TiC sample due to the higher I_d/I_g intensity ratio. However this is in contradiction of the the G band position [177, 178]. Both carbon coatings display a large amount of disorder and appear to show a structure between amorphous carbon and nanocrystalline carbon.

5.2.4 Interfacial Contact Resistance

Table 5.3: Table of interfacial contact resistance under varying compression forces.

Sample	100 Ncm^2	120 Ncm^2	140 Ncm^2	160 Ncm^2	180 Ncm^2	200 Ncm^2
99%	55.81	56.56	57.73	59.30	61.08	60.43
TiN	13.15	12.55	11.89	11.41	10.86	10.25
TiC	16.25	14.15	12.60	11.55	10.75	10.00
CrC	5.30	4.78	4.34	4.07	3.88	3.73
Thin gold	3.50	3.45	3.36	3.34	3.31	3.28
Thick gold	1.45	1.05	1.05	1.00	1.00	1.00

The interfacial contact resistance of the bare and coated samples were measured while varying the compression force. The obtained values are displayed in table 5.3, all values displayed are prior to any corrosion testing. The ICR values for post corrosion could not be reliably obtained due to the corrosion product that built up on the surface of the material. The 99% pure aluminium exhibited a contact resistance value of $57.73 \text{ m}\Omega\text{cm}^2$, this exceeds the DoE target of $10 \text{ m}\Omega\text{cm}^2$ which was taken from Wang et al. [79]. Therefore regardless of corrosion properties, aluminium will require coating to obtain an acceptable contact resistance. There are few sources which provide a value for the contact resistance of high purity aluminium. However Li et al. found the contact resistance of an aluminium alloy, AA-5052, to be $61.58 \text{ m}\Omega\text{cm}^2$ [112]. This is similar to the value measured in this work for the 99% pure sample and was similar to the values reported on bare stainless steel. Indicating no disadvantage, in terms of contact resistance, for selecting aluminium over stainless steel [74, 118]. Aluminium forms passive oxide layers under atmospheric conditions. The passive layer is a poor electrical conductor and leads to high contact resistances between the BPP and GDL [105, 118, 182]. It is critical that this oxide layer is removed prior to coating, as without doing so would result in contact resistances remaining high.

All coated materials displayed the trend of decreasing contact resistance as compression force increased, as seen in literature [182]. Furthermore all coatings proved to decrease the interfacial contact resistance of the plate. Part of the deposition process includes an argon ion cleaning stage, this removes oxide from the surface under low pressure conditions. Removal of the oxide with subsequent coating under vacuum prevents the build up of an aluminium oxide layer, thereby reducing the contact resistance of the sample. Coating materials were selected due

to the positive results observed in literature. However the titanium nitride and titanium carbon coatings both failed to meet the DoE target for interfacial contact resistance [79]. Although both did improve the value with a relative change of around 79%. These values were taken before corrosion, it is expected that contact resistance will increase throughout corrosion. This means these materials would need optimisation to meet DoE contact resistance targets.

Chromium carbon, thin and thick gold all exhibited excellent contact resistance with the GDL with values of $4.34\text{ m}\Omega\text{cm}^2$, $3.36\text{ m}\Omega\text{cm}^2$ and $1.05\text{ m}\Omega\text{cm}^2$ respectively. These materials, across the entire compression range, out performed contact resistance targets. These coatings are therefore acceptable for improving the contact resistance of aluminium bipolar plates. From 160 Ncm^{-2} to 200 Ncm^{-2} the thick gold coating does not produce a reduction in the contact resistance, this could be due to the change in contact resistance being minimal. Contact resistance decreased as follows: $99\% > \text{TiC} > \text{TiN} > \text{CrC} > \text{Thin gold} > \text{Thick gold}$, with the uncoated 99% performing the worst and the thick gold performing the best.

The TiN, TiC and gold samples were compared to investigate how the surface layer affected contact resistance while the interlayer was controlled. TiN and TiC both failed to meet contact resistance targets. These coatings differ in structure; in that TiN is metallic and crystalline throughout. Whereas TiC is a crystalline titanium layer with an amorphous carbon structure on the surface. Both however failed to meet DoE targets, this could suggest that titanium is not an appropriate material to use as an interlayer. However the gold coatings also utilised a titanium interlayer and achieved DoE targets. This shows the importance of the

surface layer. The two gold samples differ in gold loading. The increase in gold loading between the thick and thin gold coatings result in a reduction in contact resistance. The thick gold coating exhibits excellent contact resistance properties which would translate to increased cell performance.

Two different interlayer materials were used for this work, titanium and chromium. Interlayers are important for the adhesion of the coating. Which can affect the durability and contact resistance of the sample. By changing the interlayer from Ti to Cr, as in the case for the TiC and CrC samples, the contact resistance was reduced by around $10\text{ m}\Omega\text{cm}^2$. This shows that the interface between layers and behaviour of the layers need to be considered and optimised. The CrC layer highlights that expensive PGM coatings are not necessary to achieve DoE targets.

5.2.5 Electrochemical corrosion

Corrosion at 55°C

Corrosion potential is the point at which the mixed potential of anodic and cathodic reactions have no net current flow [183]. High corrosion potentials are beneficial to metallic bipolar plates because reductive reactions are more likely and oxidative reactions are less likely. This means the anodic metal dissolution reaction is less thermodynamically likely, therefore decreasing the rate of corrosion. Corrosion potential alone however cannot be used to understand corrosion behaviour as dissolution and passivation are both oxidative processes. Static corrosion tests can help build the understanding of these processes. The corrosion

current is the current flow from the anode to the cathode at the corrosion potential. High current values indicate increased levels of corrosion but should be considered with the corrosion potential.

Table 5.4: Table of corrosion current, corrosion potential and pitting potential values before and after two hours of static corrosion.
Test carried out at $55^{\circ}C$.

	LSV before $\pm$ SD			LSV after 2 hours		
Sample	E_{corr} ($V_{Ag/AgCl}$)	I_{corr} (μAcm^{-2})	E_{pit} ($V_{Ag/AgCl}$)	E_{corr} ($V_{Ag/AgCl}$)	I_{corr} (μAcm^{-2})	E_{pit} ($V_{Ag/AgCl}$)
99%	-0.68 $\pm$ 0.04	1.42 $\pm$ 0.49	-0.23 $\pm$ 0.17	-0.69	5.76	-0.04
TiN	-0.40 $\pm$ 0.02	5.39 $\pm$ 0.28	0.10 $\pm$ 0.22	-0.49	31.79	-0.05
TiC	-0.04 $\pm$ 0.09	4.88 $\pm$ 0.49	0.33 $\pm$ 0.15	-0.22	70.44	0.17
CrC	-0.16 $\pm$ 0.01	0.46 $\pm$ 0.11	0.20 $\pm$ 0.09	-0.64	5.81	0.14
Thin gold	0.34 $\pm$ 0.05	4.62 $\pm$ 0.97	N/A	-0.12	219.03	N/A
Thick gold	0.61 $\pm$ 0.08	9.65 $\pm$ 3.18	N/A	-0.15	225.25	N/A

Table 5.5: Table of corrosion current values of static corrosion testing. Test carried out at $55^{\circ}C$.

	Static corrosion (mA) $\pm$ SD					
Sample	Initial	30 min	1 hour	2 hour	4 hour	24 hour
99%	0.86 $\pm$ 0.13	0.92 $\pm$ 0.13	0.93 $\pm$ 0.18	1.15		
TiN	1.01 $\pm$ 0.32	1.24 $\pm$ 0.32	1.25 $\pm$ 0.30	1.22 $\pm$ 0.26	1.03 $\pm$ 0.04	0.73
TiC	1.01 $\pm$ 0.37	1.19 $\pm$ 0.24	1.27 $\pm$ 0.25	1.34 $\pm$ 0.22	1.46 $\pm$ 0.26	0.68
CrC	0.34 $\pm$ 0.34	0.72 $\pm$ 0.41	0.85 $\pm$ 0.43	1.15 $\pm$ 0.47	1.30 $\pm$ 0.48	0.72
Thin gold	0.67 $\pm$ 0.16	0.99 $\pm$ 0.13	1.04 $\pm$ 0.13	1.09 $\pm$ 0.13	0.95	
Thick gold	0.49 $\pm$ 0.31	0.72 $\pm$ 0.35	0.87 $\pm$ 0.20	0.96 $\pm$ 0.09	0.98 $\pm$ 0.08	0.92

Table 5.6: Table of corrosion current, corrosion potential and pitting potential values before and after one hour of static corrosion.

Followed by corrosion current values of static corrosion testing. Test carried out at $80^{\circ}C$.

	LSV before $\pm$ SD			LSV after 1 hour			Static corrosion (mA)		
Sample	E_{corr} ($V_{Ag/AgCl}$)	I_{corr} (μAcm^{-2})	E_{pit} ($V_{Ag/AgCl}$)	E_{corr} ($V_{Ag/AgCl}$)	I_{corr} (μAcm^{-2})	E_{pit} ($V_{Ag/AgCl}$)	Initial	30 min	1 hour
99%	-0.89	157.13	-0.38	-0.86	203.03	-0.43	1.17	1.33	1.39
TiN	-0.74	5.23	-0.09	-0.73	24.12	-0.13	1.35	1.73	1.78
TiC	-0.65	3.18	-0.13	-0.67	13.13	-0.25	1.38	1.64	1.73
CrC	-0.39	0.30	n/a	-0.71	1.23	0.34	0.06	0.48	0.72
Thin gold	-0.38	6.80	0.04	-0.45	103.45	-0.27	1.17	1.51	1.65
Thick gold	-0.46	12.66	-0.15	-0.48	117.83	-0.25	1.25	1.57	1.60

Table 5.4 shows the results of the linear sweep voltammetry carried out before static corrosion, after two hours of static corrosion and the results of the static corrosion test, all carried out at 55°C . Bare aluminium has a very low corrosion potential - as expected in a pH 3 sulphuric acid solution. According to the pourbaix diagram all potentials greater than -1.5 V_{NHE} in a pH 3 solution will result in the dissolution of aluminium and the formation of Al^{3+} ions. Stainless steel has a corrosion potential of -0.09 V_{NHE} under the same conditions. Stainless steel will passivate through an anodic reaction, whereas active metals such as aluminium undergo an anodic dissolution reaction. The passivation layer of stainless steel inhibits further corrosion, providing excellent corrosion resistance [107, 184].

Bare aluminium displays high corrosion currents of 1.42 mAcm^{-2} , indicating that dissolution readily occurs, from table 5.4. Although high, this value is lower than all but one of the coated samples. This could be explained by a reduction in the galvanic coupling occurring. The static corrosion results show the current increasing during the two hours of corrosion testing. This indicates the removal of a passive film, as the current stabilises, steady state corrosion occurs. The initial current value of 0.86 mAcm^{-2} is much greater than the DoE target of less than $1 \text{ }\mu\text{Acm}^{-2}$ [79]. The results of the LSV and static corrosion testing display why aluminium requires coating.

Another LSV test was carried out after 2 hours. The corrosion potential was stable, decreasing by only 17 mV but the corrosion current increased to $5.76 \text{ }\mu\text{Acm}^{-2}$. This increase in corrosion current could be caused by an increase in surface area. Localised corrosion in the form of pits occurs during the static test, these pits increase the electroactive surface area and could increase the corrosion

current. The increase in current throughout the static corrosion test is likely caused by the removal of the oxide layer. Once the oxide layer is removed, corrosion would become diffusion limited. This meant that when the second LSV was carried out, the current increased due to more reactive aluminium being exposed rather than aluminium oxide.

The Ti and Cr interlayers were intended as passivation barriers. Defects in the carbon coating should therefore have a continuous interlayer below, which will passivate and prevent the dissolution of the aluminium. Titanium is often used as a bipolar plate material in PEM electrolyzers due to the excellent corrosion resistance displayed by the material [185]. Titanium similarly displays corrosion resistance in the PEM environment, whereby the titanium forms a passive oxide layer upon exposure to the fuel cell environment [107]. Chromium has been used as a coating material as it displays excellent chemical stability. Chromium is also responsible for the chemical stability of stainless steel grades such as 310 and 316L [156, 186, 187].

The corrosion potential for the TiN increased by 173 mV as compared to bare aluminium, suggesting that the coating is aiding in corrosion resistance. A corrosion current of $5.39 \mu A cm^{-2}$ was observed however, which suggests a higher rate of reaction. However at this mixed potential the titanium is undergoing an anodic reaction, whereby passivation is occurring. This passivation will contribute to the current. On the other hand if the coating is not sealing the aluminium from the electrolyte, there is the opportunity for aluminium to be in both electrical and ionic contact with the TiN coating. This facilitates the requirements for a galvanic couple to be established. This coupling can exacerbate the degradation of

the sample.

The static corrosion results provide further evidence of increased corrosion rates, as the current flow is greater than that of bare aluminium. The current during the static test increased for the first hour and then began to decrease, mirroring the behaviour of bare aluminium substrate. This decrease in current could be down to salt formation on aluminium substrate decreasing the exposed area of aluminium. TiN coatings on stainless steel exhibited a current flow of 0.05 and 0.08 $\mu A cm^{-2}$ after 1 hour at potentials of 1 and 0.8 V_{NHE} compared with 1.25 $m A cm^{-2}$ at 0.9 V_{NHE} of aluminium samples from this work. This suggests that the aluminium substrate is contributing to the increase in corrosion current, therefore demonstrating that the coating has formed an incomplete barrier. Cracks in the TiN layer lead to pathways in which electrolyte could penetrate to the aluminium substrate. Within cracks limited diffusion occurs, preventing oxygen from reaching the substrate. Which could lead to decreases in the pH of electrolyte solution as reactions occur. This could accelerate localised corrosion. With the substrate and coating exposed to the electrolyte, a galvanic couple can occur. Further accelerating localised corrosion.

The LSV carried out after two hours displays an increase in corrosion potential, suggesting a reduced rate of the anodic dissolution reaction. However the corrosion current increased by a large amount to 31.79 $\mu A cm^{-2}$ showing that the rate of corrosion has increased. Considering the small change in corrosion potential and the large increase in corrosion current, it is expected that the sample has become more susceptible to corrosion. As the titanium nitride sample corroded it could be seen from the SEM analysis that pores occurred in the TiN layer, in-

creasing access for the corrosion solution to reach the aluminium substrate. The aluminium substrate is more unstable in the fuel cell environment than TiN and therefore would produce a higher current.

The TiC coating exhibited a large improvement in the corrosion potential, with an increase to $-0.04 V_{Ag/AgCl}$ which is higher than that of stainless steel [184]. The corrosion current of $4.88 \mu A cm^{-2}$ however is large. The large increase in corrosion potential shows that the current contribution of the anodic reaction had been reduced and cathodic reactions dominated for a larger potential window. Comparing the TiC and TiN coatings, it can be seen that the amorphous carbon coating is more effective in preventing aluminium dissolution, most likely through providing a more complete barrier. Before static corrosion had commenced the TiC coating exhibited a corrosion potential 0.47 V higher than that of TiN. This difference reduced to 0.27 V after static corrosion but TiC was still superior in this attribute. The corrosion current in the LSV test after static corrosion increased to $70.44 \mu A cm^{-2}$, this is much higher than that seen for the TiN sample. The pits in TiN and TiC samples can be observed in figures 5.2a and 5.4a respectively.

The corrosion properties of the TiC sample declined through the static testing as displayed by the reduction in corrosion potential and increase in corrosion current. The decline is attributed the loss of the TiC coating throughout the static corrosion test, which can be seen from the SEM images. Pores and localised corrosion increased the penetration of the corrosion solution. Leading to further substrate corrosion which could shift the potential to lower values. In addition, the surface area has also been increased, which could increase the corrosion current. The current measured during the static corrosion test displayed an increasing cur-

rent, this was also observed in the TiN and bare metal tests. Both TiN and TiC however displayed large current flows with TiC reaching the highest at 2 hours with a value of 1.34 mAcm^2 . Furthermore, optically TiC and TiN both displayed signs of severe fouling, indicating that neither coating is suitable for an aluminium substrate. Both coatings effectively reduced corrosion on stainless steel plates but require optimisation for use on aluminium.

The chromium carbon coating improved the corrosion potential to $-0.16 V_{Ag/AgCl}$. The corrosion current was the lowest achieved in test, albeit at lower potentials than the TiC and gold coatings, with a value of $0.46 \mu\text{Acm}^{-2}$. As compared to the TiC, it would appear that under these conditions the CrC coating is more dominated by the anodic reaction but the rate of reaction is far lower. Which would suggest that under the same conditions the CrC coating would provide better corrosion resistance. LSV results suggest that a chromium interlayer provides a better barrier to corrosion solution than the titanium interlayer. However the LSV carried out after the static corrosion displayed a large reduction in the performance of the coated plate. The corrosion potential decreased to $-0.64 V_{Ag/AgCl}$ which suggests the susceptibility of the plate to anodic dissolution increased dramatically. The corrosion current also increased to $5.81 \mu\text{Acm}^{-2}$ despite being measured at a lower potential. From these results it would suggest that the plate would be heavily degraded. This was not observed in the SEM analysis. The SEM images showed large areas of near pristine coating with few large areas of heavily localised corrosion. TiN and TiC coatings display both uniform and pitting corrosion on the surface, the CrC sample however displayed primarily localised corrosion with less removal of the coating. It is possible that the pits formed are large but hidden under the coating.

The static corrosion of the CrC coated sample, again displayed an increase of current through the test up to 4 hours. The current at the start of the test was the lowest observed in testing and remained lowest until the 1 hour mark. From 1 hour until the end of the test the sample displayed the highest current flow. Contradictory to this the SEM appears to suggest the lowest levels of corrosion observed, with few large localised corrosion locations. This would suggest that in these pits there is severe corrosion occurring. M.C. Reboul et al. and Szklarska-Smialowska suggested that Al^{3+} ions react with the water, where decomposition of the solvent then occurs. This leads to the formation of $\text{Al}(\text{OH})_3$ and 3H^+ [162, 188]. The generation of hydrogen ions decreases the pH, Szklarska-Smialowska suggested that the pH could reach as low as 1, this was in the presence of Cl ions however. In fuel cell conditions, fluorine ions are more likely due to the decomposition of the membrane, these ions would exacerbate the rate of metallic bipolar plate degradation. From the corrosion data and SEM images it would suggest that less repassivation of pits occurs and that pitting corrosion afflicts the CrC coating more so than the other coatings.

The two gold coatings displayed the highest corrosion potentials both before and after corrosion. The Thin gold coating displayed a corrosion potential value of 0.34 V_{NHE} whereas the thick gold coating was 0.61 V_{NHE} before static corrosion testing. Both coatings display a large increase over the bare substrate, with the thick coating increasing by almost 1 V. The high corrosion potentials displayed by both these materials suggest that the coatings would provide adequate corrosion resistance in the fuel cell environment. The thin gold sample possessed a corrosion current of $4.62 \mu\text{Acm}^{-2}$ which is lower than that of TiN and TiC despite being at a higher potential. The thick gold had a greater corrosion current of $9.65 \mu\text{Acm}^{-2}$,

although this current was measured at a potential 265 mV higher.

The LSV carried out after the accelerated stress test showed a loss in corrosion protection by both coatings. The thick gold coating degraded more so than the thin gold coating. The thick gold produced lower corrosion potentials and larger corrosion currents after the static corrosion test than the thin gold coating. The corrosion potentials dropped by 0.75 V and 0.46 V for the thick and thin gold coatings respectively, this is a large decrease and would suggest that more of the aluminium became exposed to the corrosion solution for both samples. The corrosion currents increased also, with the thick gold coating reaching a corrosion current of $225 \mu A cm^{-2}$ and thin reaching $219 \mu A cm^{-2}$. This shows the rate of corrosion has increased for the sample during testing and would lead to uncertainty in the stability of the coating in the PEM fuel cell environment.

During the galvanostatic corrosion testing, the gold coatings displayed the same behaviour that had been observed for the other coatings. The current increased throughout testing and then plateaued. At the two hour mark both gold layers displayed the lowest corrosion currents with the thin gold and thick gold producing 1.09 and $0.96 mA cm^2$ respectively. Compared to bare aluminium these values show improvement.

Corrosion at 80°C

At 80°C cell temperature the 99% bare aluminium sample showed a decrease in the corrosion potential by 0.21 V relative to the 55°C test. This shift to lower potentials means that more anodic dissolution is occurring at a lower potential.

Suggesting the sample is more prone to dissolution. The corrosion current increased from 1.42 to 157.13 μAcm^{-2} , suggesting a large increase in the rate of reaction and therefore the rate of corrosion at the elevated temperature. After the static corrosion the corrosion potential was largely unchanged, however the corrosion current increased to 203 μAcm^{-2} from 157.13 μAcm^{-2} . The increase could be due to a larger area being present, due to the pit formation observed in SEM. The static corrosion testing showed an increase in corrosion currents for the entire time of testing, indicating that the rate of corrosion was increased at the elevated temperature.

At the elevated temperature both the TiN and TiC samples displayed a decrease in the corrosion potential before static corrosion testing, suggesting both are more susceptible to corrosion. The TiN sample displayed a lower corrosion potential and higher corrosion current than the TiC sample. This reflects what was seen at the 55°C test. This behaviour was also observed in the LSV carried out after corrosion testing, where both increased by a large amount. Both coatings before and after static corrosion testing displayed improved corrosion properties when compared to bare aluminium sample. This is in contradiction to the 55°C test, therefore corrosion resistance of the samples is not linear with temperature. The static corrosion test values were greater than that of bare aluminium, just as they were at 55°C. Both the TiN and TiC had similar values for the static corrosion test. The TiC sample started initially higher but increased more slowly as compared to the TiN sample. This resulted in the TiC sample producing a lower static corrosion current relative to the TiN sample after 30 minutes into the static corrosion test. The TiC sample displayed better corrosion potential and current values from the LSV tests. At 80°C TiC also displayed lower current values during

the static corrosion. This suggests that the TiC coating provides better protection than the TiN coating. This could be due to the cracks seen in the TiN coating providing pathways for the electrolyte to the aluminium substrate. Both TiN and TiC however displayed corrosion current values that are in excess of DoE targets [79].

The corrosion potential value of the CrC coating decreased from the 55°C to the 80°C test by a value of 0.23 V. At 80°C this was the second highest potential measured. From 80°C to 55°C the dynamic corrosion current decreased from $0.46 \mu\text{Acm}^{-2}$ to $0.30 \mu\text{Acm}^{-2}$. Suggesting that the CrC sample performed better as a coating at 80°C than 55°C . The corrosion current increased to $1.23 \mu\text{Acm}^{-2}$ after static corrosion testing. This was the lowest seen for both 55°C and 80°C testing across all samples.

The highest value observed during static corrosion testing for the CrC sample at 80°C was 0.72 mA after 1 hour, this again was the lowest observed across both temperatures and all samples. This suggests that the CrC is more resistant to corrosion at this temperature and is the most corrosion resistance sample. SEM analysis supports this observation.

When comparing the TiC and CrC samples, CrC appears to be the superior coating due to the lower corrosion parameters observed during corrosion testing. The SEM analysis of the samples highlight that the CrC coating resulted in fewer pits. This would suggest that the chromium interlayer provided a better barrier to the corrosion solution. However from the EDX data it appears that the Cr interlayer is much thicker than the Ti layer used on the TiC sample. It is possible that the thicker layer resulted in fewer pathways for the corrosion solution to the

underlying aluminium which in turn provides superior corrosion resistance as the Cr passivates rather than forms soluble ions.

At 80°C the two gold coatings displayed large shifts in corrosion potential before static corrosion. Thin gold reduced by 0.72 V and thick gold reduced by 1.07 V. Therefore at elevated temperatures anodic dissolution occurs more readily. At 55°C the thick gold coating out performed the thin gold coating whereas the reverse was true at 80°C . Both gold coatings displayed an increase in corrosion current, suggesting a higher rate of corrosion. Corrosion potential values decreased after static corrosion testing with both exhibiting a similar value. In static corrosion testing at 80°C the corrosion current values increased by a large amount to $103.45 \mu\text{Acm}^{-2}$ and $117.83 \mu\text{Acm}^{-2}$ for the thin and thick gold coating respectively. The increase in corrosion potential and current can be attributed to exposed aluminium after the static corrosion test. In the SEM analysis it was observed that pits form on the gold samples. Exposed gold would reduce the corrosion potential and increase the corrosion current.

For the static corrosion test, both gold coatings performed worse than the 55°C test. The thick gold coating displayed a high corrosion current than the thin gold coating at 80°C up to 30 minutes. After 1 hour at 80°C the corrosion current of the thin gold coating increased to a higher value than the thick gold coating. Both however had a similar value differing by $50 \mu\text{Acm}^{-2}$ at the end of test.

Overall at 80°C the CrC coating provided the lowest corrosion currents for both LSV tests and the lowest current during the static corrosion test. In addition the EDX analysis could not identify any oxide formation on the CrC sample. This suggests that the CrC coating provided the best protection of the

aluminium substrate.

5.2.6 Inductively Coupled Plasma - Optical Emission Spectroscopy

The Al ion contamination from the solutions collected from the corrosion tests are shown in 5.7. The anodic dissolution of aluminium occurs in pits resulting in the formation of Al^{3+} ions, these form complexes in solution which can be detected through ICP-OES [162]. It is thought that the higher the concentration of these complexes the more aggressive the corrosion was in that system. Furthermore, ion contamination in membranes can result in reduced performance, this should be considered when selecting bipolar plate materials and coatings. Under 55°C corrosion the CrC sample displayed the least amount of ion contamination, the remaining samples were ranked as follows $\text{TiC} < 99\% < \text{thick gold} < \text{thin gold} < \text{TiN}$. All samples saw an increase in ion concentration for the 80°C test, this suggests that more dissolution and corrosion of the samples occurred at 80°C than 55°C . Interestingly the static corrosion results for the CrC sample saw a reduction in current at the elevated temperature but no reduction in ion contamination was observed. Again for the 80°C corrosion test the CrC sample exhibited the lowest Al ion concentration with 0.897 ppm, the other samples were ranked as follows $\text{thin gold} < 99\% < \text{thick gold} < \text{TiC} < \text{TiN}$. At both temperatures, under $0.9 V_{NHE}$, the TiN coating performs the worst with the highest amount of Al leaching. This trend is repeated in the 24 hours at OCV test where TiN again displayed the highest Al ion count. The CrC sample exhibited the lowest Al ion count at both 55°C and 80°C and the second lowest after 24 hours at OCV.

Table 5.7: Table of Al ion contamination present in solution after 1 hour at 0.9 V_{NHE} in $55^{\circ}C$, $80^{\circ}C$ and 24 hours at OCV in $80^{\circ}C$ 1 mM sulphuric acid solution. All values in ppm.

	1 hour at 0.9 V_{NHE}		24 hours at OCV
Sample	$55^{\circ}C$	$80^{\circ}C$	$80^{\circ}C$
99%	1.160	2.267	14.111
TiN	1.746	2.743	14.378
TiC	1.153	2.542	12.126
CrC	0.489	0.897	12.570
Thin gold	1.438	2.216	12.685
Thick gold	1.374	2.422	13.671

5.3 Conclusion

PVD coatings have been successfully deposited upon aluminium substrates. All coatings reduced the contact resistance of bare aluminium sample. However only CrC, thick and thin gold samples sufficiently reduced the contact resistance to an acceptable level. The corrosion resistance of the samples was not sufficient. All samples displayed high corrosion currents, while observation of the samples clearly showed corrosion products and coating failure. The CrC sample appeared to provide the best corrosion protection, followed by the thick then thin gold coating. This could suggest that a chromium interlayer is superior to a titanium interlayer in terms of corrosion resistance. However the chromium interlayer exhibited a higher concentration through EDX than the titanium interlayer of the TiC and gold samples. Therefore the thickness of interlayer needs to be considered also. Conversely the TiN sample displayed the highest concentration of coating but also high levels of corrosion. This could be attributed to the cracked surface observed, suggesting that thicker layers may require optimisation to prevent cracking.

Pitting corrosion appeared to be the primary cause of corrosion for the gold and CrC coatings. Pitting was likely due to defects in the coating. ImageJ analysis was successfully applied to SEM images and could be used as a measure to quantify the degree of pitting for aluminium samples in future work. ImageJ analysis and observation of the SEM revealed that the CrC sample provides superior corrosion protection. In addition the CrC sample exhibited the lowest corrosion current during static tests at both 55°C and 80°C .

Future work should investigate aluminium alloys, as it is alloys that would

be adopted in commercial applications.

Chapter Six

Ex situ Testing of PVD Coated Al6082 and High Purity Aluminium Bipolar Plates

6.1 Introduction

As discussed in the previous chapter, aluminium alloys should be investigated as potential substrates for bipolar plates. For this work Al6082 was investigated as it is widely utilised in the automotive and aerospace industries, this is due to the low mass and high strength to weight ratio of the material [189, 190]. For this reason, Al6082 samples were coated with TiC, TiAu and CrC to assess the viability of the substrate with current PVD coatings as a bipolar plate material. The aim of this work was to understand if the samples could achieve DoE interfacial contact resistance and corrosion targets. The coatings were produced by Teer coatings and were modified from the previous chapter due to the change of substrate. For this reason the coatings have been applied to both 99.0% pure aluminium and Al6082 as to investigate the differences between the performance of the pure and alloy substrates.

6.2 Materials Characterisation

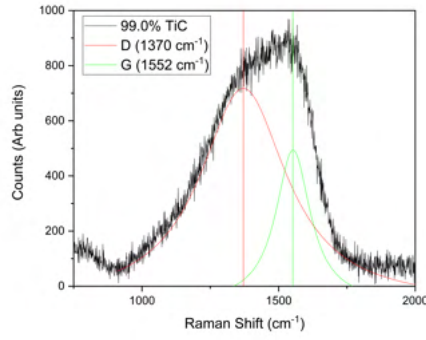
6.2.1 Raman

Figure 6.1 displays Raman spectra of the TiC and CrC samples, along with the D and G bands found through Lorentzian deconvolution. It can be seen from the spectra that the two bands overlap. This suggests deposition of an amorphous carbon layer on the surface. The band positions, intensities and relative intensities have been presented in table 6.1. All deconvolutions of the Raman spectra exhibited a high R^2 value with the lowest being 0.980, this suggests an accurate fit for the data. When investigating the nature of the carbon coating it was found that all samples displayed a G band between 1600 cm^{-2} and 1510 cm^{-2} with an intensity ratio between 0.25 and 2. This suggests that coatings are either a nanocrystalline or amorphous carbon [177]. The G band position will move from 1600 cm^{-2} to 1510 cm^{-2} and the intensity ratio (I_D/I_G) will decrease to 0 as nano-crystalline carbon become amorphous [177]. The G band intensity remains the same through the transition from nanocrystalline to amorphous carbon but the D band will reduce. Hence the decrease in the intensity ratio [177]. According to literature, calculated intensity ratios from nanocrystalline to amorphous follow the order 99.0% CrC > 99.0% TiC > alloy CrC > alloy TiC. The I_D/I_G intensity ratios of the CrC coatings are both lower than that of the TiC coating for each substrate. In addition the 99.0% pure aluminium samples both have higher intensity ratios than the alloy sample. This suggests that there is a different growth behaviour of the carbon on Ti and Cr but the difference is much smaller than changing to an alloy substrate. This could be a result of the substrate heating up in a different manner as thermal

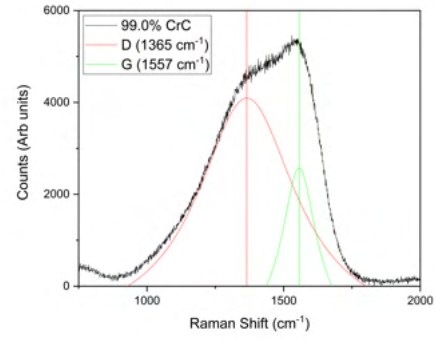
properties would be primarily governed by the bulk material. In section 2.3.2 it was discussed how the temperature of the substrate can govern the nature of the carbon layer.

Table 6.1: Table of Raman spectroscopy results. D and G band positions and intensities found through Lorentzian deconvolution of spectra.

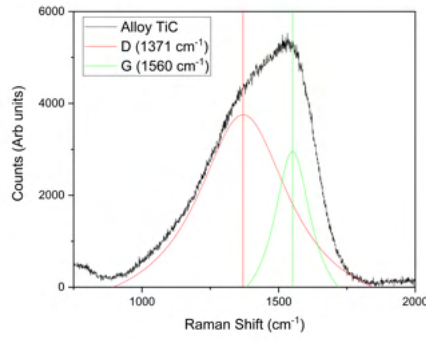
Sample	D band cm^{-1}	G band cm^{-1}	I_D	I_G	I_D/I_G	R^2
99.0% TiC	1370	1552	717	494	1.451	97.97
99.0% CrC	1365	1557	4093	2572	1.591	98.81
Alloy TiC	1371	1560	3753	2957	1.269	98.71
Alloy CrC	1371	1560	4998	3590	1.392	98.73



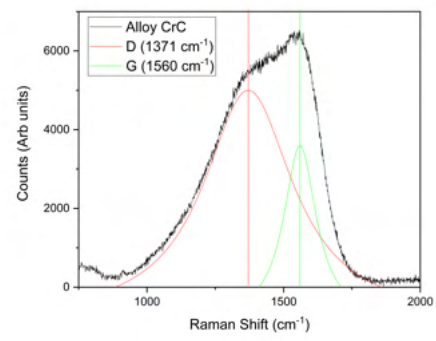
(a) 99.0% TiC



(b) 99.0% CrC



(c) Alloy TiC



(d) Alloy CrC

Figure 6.1: Raman spectrums collected from carbon coated samples with overlay of deconvoluted D and G band positions; (a) 99.0% TiC (b) 99.0% CrC (c) Alloy TiC (d) Alloy CrC.

6.2.2 Energy Dispersive X-ray

EDX measurements were carried out on fresh, and samples corroded at 55°C and 80°C . The results can be seen in table 6.2. Bare Al6082 alloy has a surface oxide layer with 5.5 wt.% oxygen concentration. After corrosion at 55°C the oxygen concentration increases to almost 50 wt.%, this shows growth of the oxide layer or build up of corrosion product. Both oxide layer and build up of corrosion product indicate corrosion of the substrate, which is detrimental to fuel cell performance. Therefore, oxygen concentration can be a good indicator of the performance of a sample. It was intended that the addition of coatings will prevent the formation of this oxide layer as this will significantly degrade the performance of a fuel cell.

It can be seen in table 6.2 that the TiC coating was successfully deposited on both the 99.0% and alloy substrates. Neither sample appears to have an oxide layer as no oxygen was detected. The composition is roughly the same for the coating between the two substrates but the lower detection of aluminium on the alloy sample could be the result of a thicker coating. The elements used for alloying in Al6082 alloy account for a maximum of 5% by weight. Therefore, it is not expected that this change in aluminium concentration is a result of the alloying elements. After corrosion at 55°C the alloy sample displays no oxygen content whereas the 99.0% sample surface is composed of 17% oxygen. This however may not be representative of the area as only a small area is tested in EDX measurements. At 80°C both samples appear to perform in a similar manner, both samples show signs of oxidation or corrosion product build up.

The CrC coatings on both substrates appear to be almost identical with an equal composition of Al, Cr and C as can be seen in table 6.2. Oxide layers

also appear to have been removed. At 55°C the alloy sample out-performed the 99.0% sample, as can be seen from the lower degree of oxidation of the sample. Both samples however display large concentrations of oxygen suggesting the failure of the coating to protect the bipolar plate. The alloy sample exhibits a higher concentration of oxygen at 80°C than 55°C , whereas the 99.0% displays a lower concentration. This is an unexpected result and suggests the 99.0% sample is more stable in 80°C than 55°C . The CrC 99.0% sample displayed the lowest level of oxidation for any sample at 80°C .

From table 6.2 it can be seen that both TiAu coatings display around 12 wt.% carbon, which decreases after corrosion. Carbon content could be a result of debris on the sample. The composition of the coating on each substrate was largely the same and no oxygen was measured on the fresh samples. After corrosion at both 55°C and 80°C the titanium and gold concentrations decreased for both samples, while the oxygen content increased.

From the EDX analysis it appears as if all coatings fail to prevent the oxidation of the substrate. The alloy samples appear to be more effective at preventing corrosion at lower temperatures whereas the 99.0% samples appear to be more effective at higher temperatures. The alloy TiC and 99.0% CrC samples exhibit the lowest oxygen concentrations after 55°C and 80°C degree corrosion respectively.

Table 6.2: Table of elemental concentrations as wt.% and at.% measured by EDX. Data shown for fresh ~~after 144 hrs.~~ samples with data for samples corroded at $55^{\circ}C$ and $80^{\circ}C$

Sample	Corroded	Al	Ti	Cr	C	Au	O
Al6082	Fresh	76.33/63.55	0.00/0.00	0.00/0.00	14.41/26.95	0.00/0.00	5.50/7.72
	$55^{\circ}C$	42.97/31.75	0.00/0.00	0.00/0.00	2.39/3.96	0.00/0.00	49.16/61.25
	$80^{\circ}C$	44.55/32.85	0.00/0.00	0.00/0.00	2.82/4.67	0.00/0.00	47.93/59.60
99.0% TiC	Fresh	43.66/26.98	4.64/1.61	0.00/0.00	51.28/71.21	0.00/0.00	0.00/0.00
	$55^{\circ}C$	32.74/20.82	5.86/2.10	0.00/0.00	40.51/57.86	0.00/0.00	17.11/18.35
	$80^{\circ}C$	21.07/13.33	4.95/1.76	0.00/0.00	24.74/35.15	0.00/0.00	45.24/48.26
Alloy TiC	Fresh	30.42/17.92	6.21/2.06	0.02/0.01	59.90/79.26	0.00/0.00	0.00/0.00
	$55^{\circ}C$	71.96/67.23	16.50/8.69	0.09/0.04	11.45/24.03	0.00/0.00	0.00/0.00
	$80^{\circ}C$	21.33/13.71	4.53/1.64	0.00/0.00	20.86/30.13	0.00/0.00	48.74/52.84
99.0% CrC	Fresh	18.98/12.33	0.00/0.00	24.87/8.38	54.00/79.79	0.00/0.00	0.00/0.00
	$55^{\circ}C$	18.76/12.68	0.00/0.00	15.76/5.53	26.98/40.97	0.00/0.00	34.40/39.21

	80°C	12.88/8.01	0.00/0.00	18.72/6.04	49.90/69.73	0.00/0.00	13.79/14.47
Alloy CrC	Fresh	19.31/12.46	0.00/0.00	24.43/8.18	54.46/78.92	0.00/0.00	0.00/0.00
	55°C	17.01/11.45	0.00/0.00	21.62/7.55	35.17/53.20	0.00/0.00	23.66/26.87
	80°C	15.87/10.71	0.00/0.00	20.76/7.27	31.21/47.31	0.00/0.00	29.74/33.84
99.0% TiAu	Fresh	65.47/61.99	19.38/10.34	0.00/0.00	12.78/27.17	1.42/0.18	0.00/0.00
	55°C	52.89/44.62	14.93/7.09	0.00/0.00	9.95/18.85	1.02/0.12	20.20/28.74
	80°C	42.86/34.87	12.13/5.56	0.07/0.03	3.37/6.15	0.90/0.10	37.83/51.89
Alloy TiAu	Fresh	44.05/35.22	21.64/11.92	0.06/0.03	11.28/24.77	1.59/0.21	0.00/0.00
	55°C	44.83/36.14	10.21/4.64	0.00/0.00	6.21/11.24	0.72/0.08	33.44/45.46
	80°C	44.05/35.22	11.51/5.18	0.00/0.00	6.45/11.59	0.79/0.09	34.26/46.20

6.3 Interfacial Contact Resistance

Table 6.3 shows the contact resistance results for the samples over a range of compression forces. DoE resistance values are given at 140 Ncm^{-2} , this value will be used for the comparison of coatings [79]. For the coatings on the 99.0% pure aluminium the TiAu coating produced the lowest contact resistance with a value of $1.3 \text{ m}\Omega\text{cm}^2$ followed by the CrC sample, $4.3 \text{ m}\Omega\text{cm}^2$, then the TiC sample, $12.6 \text{ m}\Omega\text{cm}^2$. The CrC and TiAu samples both out-perform DoE targets which is defined as $10 \text{ m}\Omega\text{cm}^2$, whereas the TiC sample was in excess of the target [79]. From figure 6.1 it can be seen that the intensity of the D and G bands of the carbon coating on the TiC layer were lower than that of the other carbonaceous coatings under the same conditions. This suggests that the carbon layer is thinner than the other layers which could result in a higher ICR [191].

Table 6.3: Table of interfacial contact resistance measurements with units of $\text{m}\Omega\text{cm}^2$.

Sample	Compression force Ncm^{-2}					
	100	120	140	160	180	200
99.0% TiC	16.3	14.2	12.6	11.6	10.8	10
99.0% CrC	5.3	4.8	4.3	4.1	3.9	3.7
99.0% TiAu	1.4	1.4	1.3	1.25	1.2	1.2
Alloy TiC	6.0	5.1	4.5	4.0	3.7	3.4
Alloy CrC	3.8	3.5	3.1	2.8	2.6	2.5
Alloy TiAu	1.5	1.1	1.1	1.0	1.0	1.0

The alloy samples all out-perform the equivalent 99.0% pure sample and followed the same trend as the 99.0% samples: Alloy TiAu < Alloy CrC < Alloy TiC. All alloy samples exceed the DoE target.

6.4 Electrochemical Corrosion

Ex situ corrosion testing was carried out on the coated and uncoated samples to assess the effectiveness of the coatings. Both the Al6082 and pure aluminium were tested as controls. Each sample was investigated using LSV analysis carried out before and after an electrochemical accelerated stress test (AST) as per methodology section.

6.4.1 Uncoated Substrates

Results for the linear sweep voltammograms (LSVs) are displayed in table 6.4. The LSV data after corrosion for the pure aluminium sample could not be accurately measured due to the dissolution of the sample. This was not an issue for the alloy sample, due to the increased thickness of the sample. This does not lead to any conclusions related to the corrosion properties of either material but is merely a note on the different physical characteristics of each sample.

At 55°C the pure aluminium displayed a more noble corrosion potential of $-0.670 V_{\text{Ag}/\text{AgCl}}$ compared to $-0.711 V_{\text{Ag}/\text{AgCl}}$ for the alloy sample. The pure aluminium also exhibits a lower corrosion current of 1.6 mAcm^{-2} as compared to 39.5 mAcm^{-2} . This suggests that under these conditions the pure aluminium is less

susceptible to corrosion. This is a large current difference, with the alloy corroding at a rate almost 25 times faster. Both corrosion potentials are very electronegative which suggests a high susceptibility to corrosion in the simulated conditions. The alloy sample exhibits a similar corrosion potential after AST. Suggesting that the relative rate of forward and reverse reactions are the same albeit at a slower rate. This could be due to a loss in surface area after corrosion, as products build up on the surface limiting active area as discussed in section 2.1.4.

Corrosion potentials decreased as the temperature increased for both pure and alloyed substrates. The 99.0% pure aluminium displayed a larger change in corrosion potential than the alloy sample. The corrosion potential of the 99.0% pure sample was lower than the alloy sample at 80°C. The corrosion current of the 99.0% sample also increased to values greater than that of the alloy sample, as seen in table 6.4. This result could mean that the base substrate material should be selected according to the operating conditions of the stack.

Table 6.4: Table of corrosion potential and current values for the uncoated substrates before and after *ex situ* accelerated stress tests carried out at 55°C and 80°C .

Substrate	Temperature ($^{\circ}\text{C}$)	Before corrosion		After corrosion	
		E_{corr} (V)	I_{corr} (mAcm^{-2})	E_{corr} (V)	I_{corr} (mAcm^{-2})
Al6082	55	-0.71	39.5	-0.71	4.1
Al6082	80	-0.79	182.2	-0.82	84.5
99.0%	55	-0.67	1.6	n/a	n/a
99.0%	80	-0.87	157.7	n/a	n/a

The results of the 80°C corrosion test indicate the current flow at OCV for the alloy is higher than that of the pure aluminium, 182.2 mAcm^{-2} compared to 157.7 mAcm^{-2} , respectively.

The alloy sample allowed for LSV tests to be carried out after the accelerated stress test for each temperature. The corrosion potential decreased by a small amount, 0.03 mV for the 80°C test and remained unchanged for the 55°C test. The corrosion current for each test decreased. In the 55°C test the current changed from 39.5 mAcm^{-2} to 4.1 mAcm^{-2} from the initial state to the final state, respectively. The 80°C test exhibited a decrease from 182.2 mAcm^{-2} before corrosion to 84.5 mAcm^{-2} after corrosion. However, the decrease in current flow could be attributed to a reduction in electrochemically active surface area. Stansbury et al. suggested the build up of corrosion product on the surface of the sample after corrosion testing is responsible for limiting the exposed surface area [3]. This cor-

rosion product could block the surface from carrying out either anodic or cathodic reactions and therefore limit the contribution to the corrosion current flow.

Table 6.5: Table of corrosion current measured throughout the static corrosion testing for the uncoated substrates at $55^{\circ}C$ and $80^{\circ}C$. Units in $mAcm^{-2}$.

Substrate	Temperature ($^{\circ}C$)	Current density at time ($mAcm^{-2}$)				
		Initial	30 min	1 hr	2 hr	4 hr
Al6082	55	0.94	1.00	1.040	1.06	1.06
Al6082	80	1.66	1.79	1.88	1.91	1.89
99.0%	55	0.88	0.92	0.93	1.15	n/a
99.0%	80	1.17	1.33	1.39	1.12	n/a

Accelerated stress tests were carried out on the bare substrates to form an understanding of how the materials may behave inside the fuel cell environment. All samples exhibited an initial increase in current, then stabilisation. This behaviour had been mentioned in literature for aluminium tested under similar conditions [192]. The work of Barranco et al. displayed maximum current values of around $0.5 mAcm^{-2}$, this is almost half the lowest current value measured in this work. Barranco et al. carried out tests in more acidic conditions with the addition of 2 ppm HF, however a lower potential and temperature was used [192]. Nevertheless, the behaviour found here is similar to that which Barranco et al. found, with bare aluminium alloy and the thinnest Al-CrN coated alloy tested [192]. A.K. Sfikas et al. tested the electrochemical behaviour of aluminium alloys in sulphuric acid, the tests were carried out in 1 M sulphuric acid at $25^{\circ}C$ [193]. At all potentials ($-36 mV_{Ag/AgCl}$ to $60 mV_{Ag/AgCl}$) 6 of the 7 chronoamperometry

results displayed the same behaviour in current response with an initial sharp increase and then a slow decrease that starts to plateau throughout the test [193]. Barranco et al. associated this increase in current with solution on the surface causing the growth of aluminium oxide, as the corrosion of the CrN surface increases, the presence of defects may increase. Increased defect count would result in more solution reaching the aluminium substrate, Barranco et al. suggested this would result in oxide growth and would then result in an initial drop in the current density–time transient.

Sfikas et al. is in agreement with this and goes onto suggest that the sharp increase reflects a fast rate of oxidation [193]. After this stage the current tends to decay at a decreasing rate with time, this was attributed to the formation of surface films. All samples tested here appeared to display high levels of noise in the data set, this was also true of the data Sfikas et al. collected. This noise implied instability in the formed surface layers and metastable pitting. Metastable pitting and stable pit formation rely on diffusion limitation into the pit which maintains the harsh environment [194]. Pits are more likely to become stable at higher potentials, like those used in this work [194]. The current past the peak was associated with a dynamic equilibrium set up by the varying surface films formed on the aluminium [193]. All bare samples displayed this same behaviour.

Increased current flow was observed at elevated temperature, this can be attributed to favourable kinetics which are present at increased temperatures. For the 55°C tests both the alloy and 99.0% samples displayed an increase in current up to what appeared to be a diffusion limited current value. The alloy sample produced a higher current and maintained this up to the 2 hour mark where

the 99.0% sample was then greater. This suggests that the stable potential of the 99.0% sample was higher than that of the alloy sample. This could be an indicator for decreased corrosion resistance of the 99.0% sample. However upon inspection of this sample there are pits that have corroded through the sample; leading to corrosion then propagating from behind the sample. This would lead to an increased surface area which would lead to higher current densities, this phenomena was noticed in tests as short as 1 hour. Had the 99.0% sample been thicker it is possible the current values would have been lower from 1 hour onwards. For the 99.0% sample examined at 30 minutes no holes were seen through the area to the other side.

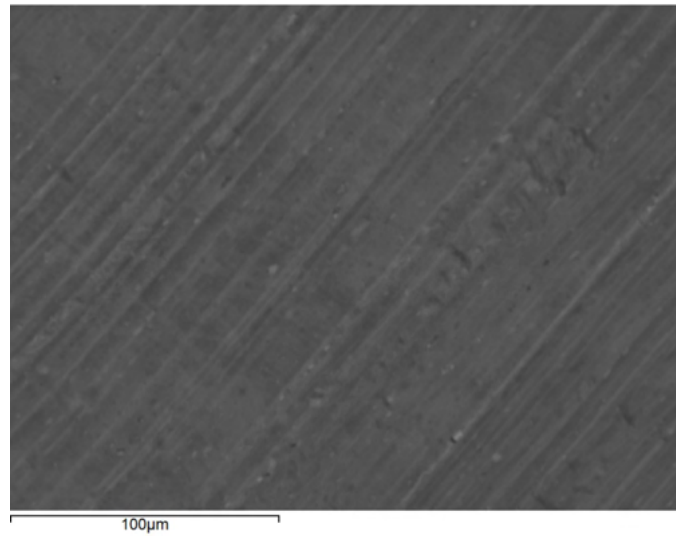
Inspection of the samples and current values show higher rates of corrosion at the elevated temperature. A larger increase in initial current value was seen for the alloy sample when comparing the two temperatures. In both cases the alloy exhibits higher current values. Throughout the entire time period the alloy produces a larger current than the 99.0% sample for the 80°C test. The noisy data attributed to metastable pitting was again observed for both samples and was confirmed with a high degree of pitting of the samples. It is evident that the elevated temperature leads to a higher corrosion rate, this was clearly seen on the 99.0% by the increased number of pits that penetrated through the entirety of the 1 mm sample and increased corrosion product on the surface of the sample. The chronoamperometry and corrosion current results suggest that the alloy substrate will corrode at a faster rate than the 99.0% pure sample.

Scanning Electron Microscopy and Energy Dispersive X-ray Analysis of Uncoated Samples

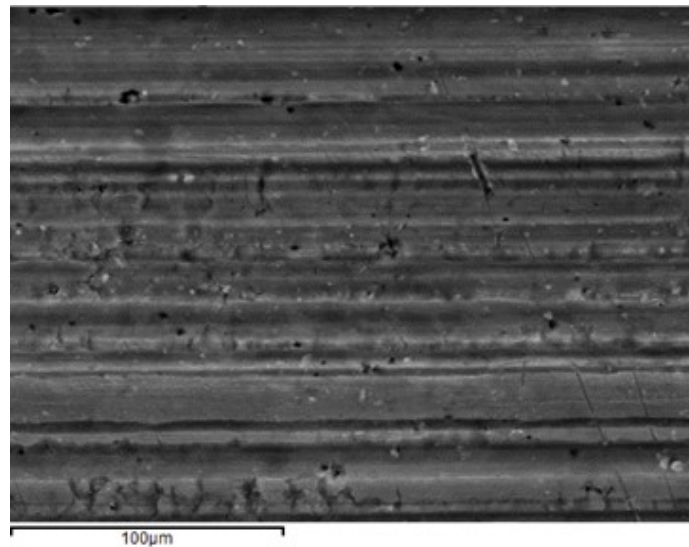
Comparing the 99.0% pure and alloy substrates prior to corrosion in figures 6.2a and 6.2b, it can be seen that both display straight parallel grooves through the sample. The grooves are a result of the rolling process which is carried out during the production of the sample. The alloy sample appears to have more defects upon the surface.

Both substrates display large amounts of degradation after corrosion testing as can be observed in figures; 6.3, 6.4, 6.5 and 6.6. At 55°C the predominate source of corrosion appears to be pitting corrosion which is shown in 6.3, this is similar to the pitting behaviour seen in the work of Comez et al. [195]. The EDX map of oxygen shows small amounts of oxygen around the large pit with the addition of small amounts of sulphur. Two smaller defects exist at the top of the image and show rings of high oxygen concentration around a small pit. Reboul et al. states that oxygen reduction at cathodic sites is the second step in the formation of pits. The area of high oxygen concentration could be the cathodic region to the anodic pit that is forming at the centre of the area [162]. When the temperature is increased to 80°C the density and size of pits increases. Furthermore, as displayed in figure 6.4, intergranular corrosion can be observed with some evidence of exfoliation occurring [196]. The EDX map of oxygen shows areas of high oxygen concentration around the pit orifice, similar to what had been observed at 55°C .

The alloy sample displayed large amounts of corrosion with copious amounts of a white precipitate build-up on the surface. By observing the sulphur EDX map



(a) 99.0%



(b) Al6082.

Figure 6.2: As received a) 99.0% pure aluminium and b) Al6082 alloy before accelerated stress testing.

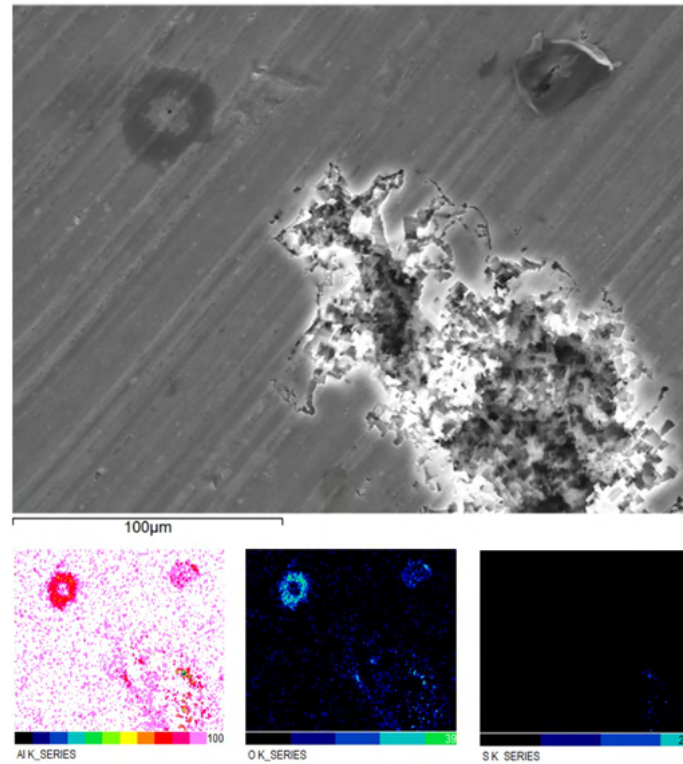


Figure 6.3: As received 99.0% pure aluminium after accelerated stress testing at 55°C for 1 hour.

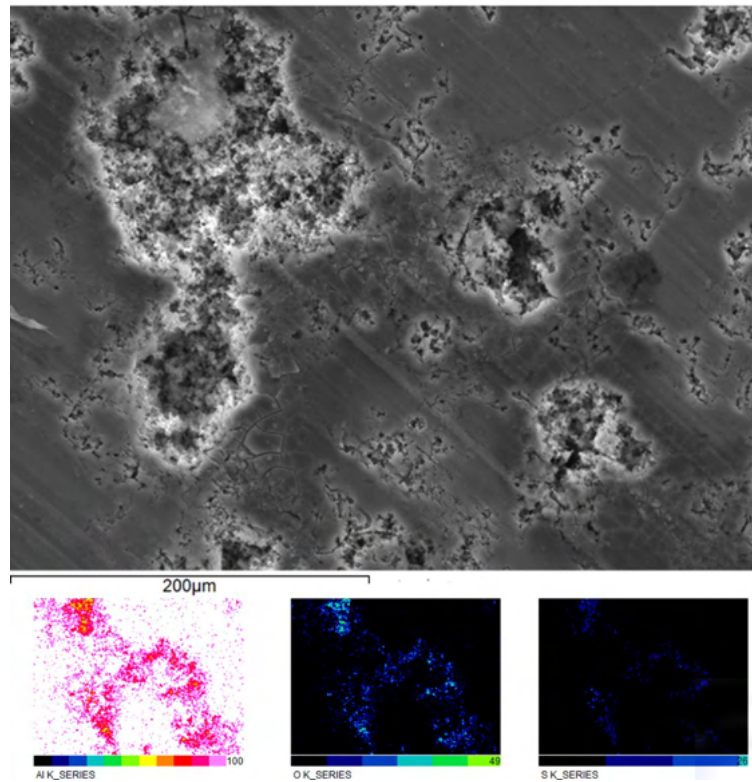


Figure 6.4: As received 99.0% pure aluminium after accelerated stress testing at 80°C for 1 hour.

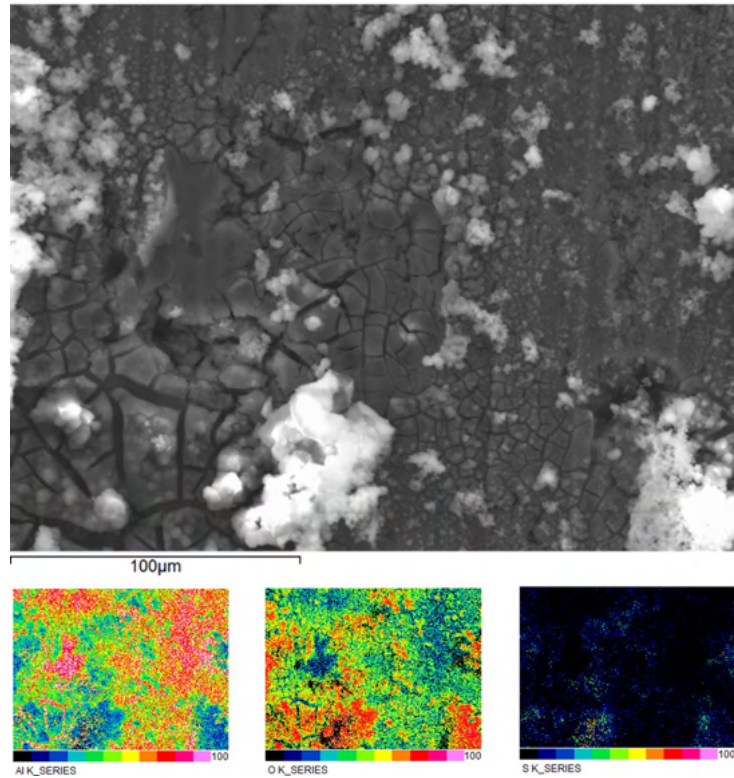


Figure 6.5: As received Al6082 aluminium after accelerated stress testing at 55°C after 4 hours.

in figure 6.5 it can be seen that the precipitate displayed a large proportion of sulphur content, this also coincides with high oxygen contents. The electrochemical corrosion testing was carried in a sulphuric acid solution, one of the corrosion products in this acid is $\text{Al}_x(\text{SO}_4)_y(\text{OH})_z$ [197, 198]. It is likely that this salt is $\text{Al}_2(\text{SO}_4)_3$ but was not confirmed as part of this work [198]. Pits and a high degree of intergranular corrosion can be seen on this sample. Comparing figures 6.3 and 6.5 it appears that the alloy sample suffered more severely from intergranular attack than the 99.0% sample and appears to have formed more corrosion product. The 99.0% sample on the other hand appears to have more severe pitting.

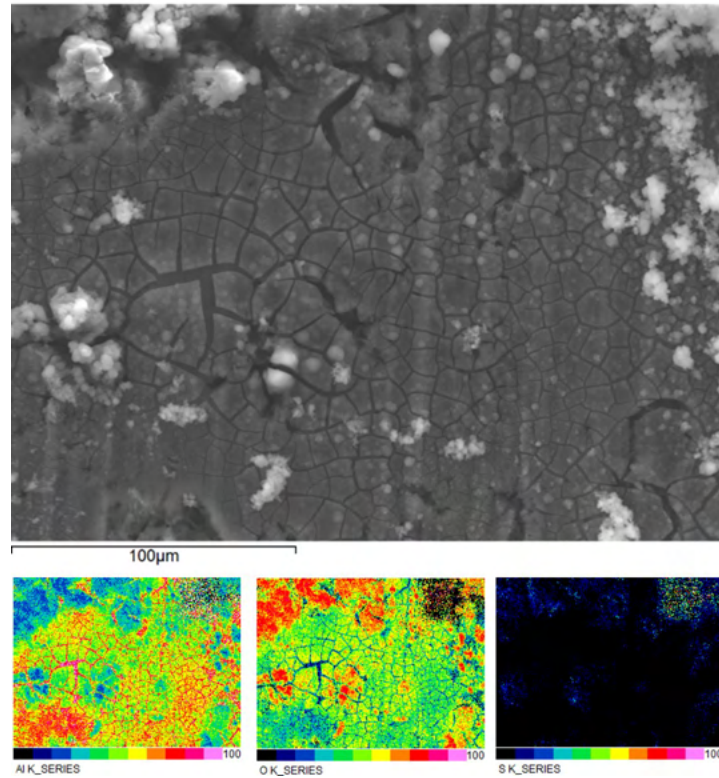


Figure 6.6: As received Al6082 aluminium after accelerated stress testing at 80°C after 4 hours.

The alloy sample, corroded at 80°C appears to display the same corrosion mechanisms as those seen in the test at 55°C , see figure 6.6. Intergranular corrosion can be seen across the surface with white oxygen/sulphate containing precipitate observed.

6.4.2 Coated Substrate

Corrosion at 55°C

Table 6.6 displays the corrosion parameters of the PVD coated alloy and high purity substrates as measured at 55°C. All samples display a more noble corrosion potential than that of the highest performing bare substrate before corrosion testing. The most noble potential measured for the bare substrates was -0.67 $mV_{Ag/AgCl}$ before corrosion, whereas for the coated samples the least noble potential before corrosion was -0.59 $mV_{Ag/AgCl}$. Furthermore, the corrosion potentials of the coated samples measured after the accelerated stress test are all more noble than those measured from the bare substrate before or after accelerated stress testing. This suggests that all coatings have decreased the susceptibility of the plates to corrosive attack.

The lowest corrosion current measured from the bare substrates was 1.6 $mAcm^{-2}$, this was the high purity aluminium tested before static corrosion. All coated high purity aluminium samples exhibited a lower corrosion current than the bare sample showing that the rate of corrosion had been reduced as a result of the coating. In addition, as seen in the bare substrate study the high purity aluminium exhibits lower corrosion currents than the alloy substrate. This is observed for all samples before and after accelerated stress testing. The TiC and CrC coated alloy samples exhibited corrosion currents equal to and higher than the bare high purity substrate respectively. This means the rate of corrosive attack at the corrosion potential for each sample is higher than that or equal to the bare high purity sample. However, all coated alloy samples exhibited a lower corrosion current

than the bare alloy before static corrosion testing. The highest current from the coated alloy samples was 4.47 mAcm^{-2} compared to 39.5 mAcm^{-2} for the bare sample. This shows that the coatings initially reduce the rate of corrosion, most likely attributed to the reduced exposure of aluminium and the reduced corrosion rate of the coatings relative to bare aluminium. After static corrosion the corrosion current of the bare alloy sample is much lower than that of the coated samples with a value of 4.1 mAcm^{-2} compared to the lowest value of 73.62 mAcm^{-2} for the coated samples. Initially in the case of the coated samples, the underlying substrate would only be exposed through flaws in the coating. However after static corrosion the surface had been degraded, leading to more of the alloy substrate being exposed, which could lead to galvanic coupling between the more noble coatings (TiC, CrC and TiAu) and less noble substrate material (Al6082).

Table 6.6: Table of corrosion potential and current values for the coated substrates at 55°C .

Substrate	Coating	Before corrosion		After corrosion	
		$E_{corr} (V_{Ag/AgCl})$	$I_{corr} (\text{mAcm}^{-2})$	$E_{corr} (V_{Ag/AgCl})$	$I_{corr} (\text{mAcm}^{-2})$
Al6082	TiC	-0.37	1.60	-0.63	73.62
99.0%	TiC	-0.50	1.32	-0.65	6.49
Al6082	CrC	-0.59	4.47	-0.65	79.01
99.0%	CrC	-0.20	0.43	-0.60	10.19
Al6082	TiAu	0.00	1.09	-0.63	120.23
99.0%	TiAu	0.01	0.48	-0.54	36.64

When comparing the coated samples the TiAu coating displayed the most

noble corrosion potentials with values of 0.0 $V_{Ag/AgCl}$ for both the alloy and high purity samples. The TiAu 99.0% sample exhibited the highest corrosion potential post corrosion for all the samples tested at 55°C. The carbon containing coatings followed the trend of 99.0% TiC < Al6082 CrC < Al6082 TiC < 99.0% CrC, going from the most susceptible to the least susceptible to corrosion. The TiC coated alloy sample was less susceptible than the equivalent 99.0% pure coated sample, this was the only case in all testing.

Examining the corrosion potentials post static corrosion showed a large increase in the susceptibility of the samples to corrosion. Both gold samples displayed a reduction in corrosion potential in excess of 500 mV while the carbon based coatings exhibited more modest reductions in corrosion resistance. The samples follow the trend 99.0% TiC / Al6082 CrC < Al6082 TiC < Al6082 TiAu < 99.0% CrC < 99.0% TiAu, going from the most susceptible to corrosion to the least. With the exception of the 99.0% TiC sample the 99.0% pure coated samples exhibited lower susceptibility to corrosion as seen in the bare substrate tests. The TiAu 99.0% sample displayed the highest nobility both before and after corrosion suggesting superior resistance to corrosion relative to the alloy equivalent and all CrC/TiC samples.

The corrosion current of the TiAu and CrC coatings on 99.0% are the lowest exhibited in testing, the corrosion currents are 0.48 $mAcm^{-2}$ and 0.43 $mAcm^{-2}$ respectively. Both coatings show an excellent improvement in current density, however both are far in excess of the DoE target of < 1 μAcm^{-2} . The remaining samples follow the trend of Al6082 TiAu < 99.0% TiC < Al6082 TiC < Al6082 CrC, going from the lowest rate of corrosion to the highest. No trend was observed

between Cr and Ti interlayers. However, the TiAu coating does appear to display relatively low rates of corrosion as compared to the other samples with 99.0% CrC also producing low rates of corrosion.

Post static corrosion testing the alloy samples again exhibit higher rates of corrosion as compared to the high purity samples. Both TiAu coated samples display the highest rates of corrosion for each substrate material. Both substrates also display the same trend: $\text{TiC} < \text{CrC} < \text{TiAu}$ going from the lowest rate of corrosion to the highest. This is in contrast to the susceptibility of the samples to corrosion which followed the reverse trend for the 99.0% pure samples.

From the LSV analysis it can be seen that static corrosion at 55°C results in an increase in corrosion rate and a decrease in corrosion resistance for all samples. This highlights that the sample had been degraded through the accelerated stress test.

Table 6.7 and figure 6.7 show the corrosion current throughout the corrosion test. All samples display a behaviour of an initial increase in corrosion current with time and then a plateau in current. However, the TiAu and TiC samples exhibit a more gradual increase in current and only start to plateau after around 3 hours of corrosion testing. The remaining samples only required around 30 minutes to reach a steady state value. For all samples the current measured at this plateau is in excess of the DoE target $<1 \mu\text{Acm}^{-2}$ [79].

As seen in the LSV analysis and bare substrate study, the 99.0% pure substrates out perform the alloy substrates. The exception to this is the TiC coated sample, which like in the LSV analysis, does not follow this trend. The

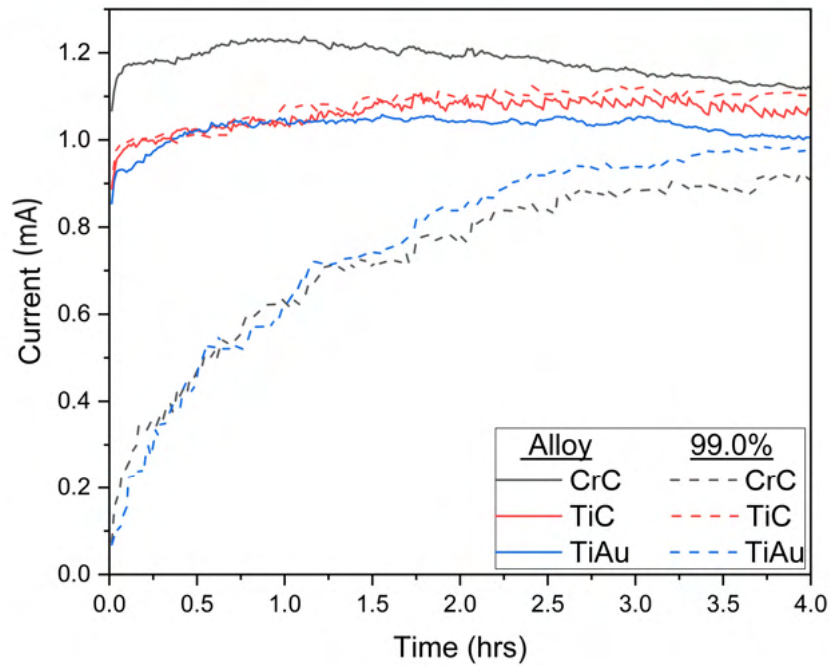


Figure 6.7: Graph of corrosion current throughout the static corrosion testing for the coated substrates at 55°C .

LSV analysis before corrosion testing suggested that the two TiAu coatings and the 99.0% CrC sample were the least susceptible to corrosion and displayed the lowest corrosion rate. The static test suggests the 99.0% substrate coated with TiAu and CrC produced the highest corrosion resistance in the simulated fuel cell conditions. The alloy coatings followed the trend of $\text{TiAu} < \text{TiC} < \text{CrC}$, going from lowest corrosion current to highest corrosion current. This highlights the discrepancy between substrates with the CrC coating displaying both the highest and the lowest current throughout the 55°C static corrosion test. In both cases the TiAu coating displays good reductions in the corrosion current relative the

Table 6.7: Table of corrosion current measured throughout the static corrosion testing for the coated substrates at $55^{\circ}C$. Units of $mAcm^{-2}$.

Substrate	Coating	Initial	30 min	1 hour	2 hour	4 hour
Al6082	TiC	0.89	1.02	1.03	1.09	1.07
99.0%	TiC	0.89	1.01	1.08	1.09	1.09
Al6082	CrC	0.07	1.20	1.23	1.19	1.12
99.0%	CrC	1.07	0.47	0.63	0.78	0.91
Al6082	TiAu	0.85	1.02	1.05	1.04	1.01
99.0%	TiAu	0.07	0.46	0.62	0.85	0.99

other coatings and the bare substrates.

Static corrosion of the 99.0% TiC displayed noise, this was likely due to pit initiation and the formation of metastable and stable pits. Pit repassivation can also cause decreases in current. The data points in this work were collected every 50 s and an area of 1 cm^2 was used. This meant that analysis of the current response produced by individual pits was not possible. Pistorius et al. utilised micro-electrodes in the region of $50\text{ }\mu m$ to analyse the current response of individual pits, pit initiation and stability was achieved in the region of 15 s. Furthermore, the current measured for that work was in the range of 1 nA to 10 nA, which would be lost to noise in this work [194].

Corrosion at 80°C

Table 6.8 displays the corrosion current and corrosion potentials of the coated samples in an 80°C solution. The bare alloy substrate had a corrosion potential of $-0.792 V_{Ag/AgCl}$ and a corrosion current of $182.2 mAcm^{-2}$ as per table 6.4. The TiC, CrC and TiAu coated alloy samples had corrosion potentials of $-0.609 V_{Ag/AgCl}$, $-0.482 V_{Ag/AgCl}$ and $-0.528 V_{Ag/AgCl}$ respectively. This highlights that all the coatings on the substrate decreased the susceptibility of the sample to corrosion. Furthermore, the coated samples: TiC, CrC and TiAu produced corrosion current values of $0.628 mAcm^{-2}$, $0.411 mAcm^{-2}$ and $136.36 mAcm^{-2}$, respectively. All values are below that of the bare alloy substrate, which displayed a corrosion current of $182.2 mAcm^{-2}$. Indicating that the coatings have also reduced the rate of corrosion.

From table 6.4 the corrosion potential and corrosion current of the 99.0% aluminium substrate was $-0.875 V_{Ag/AgCl}$ and $157.7 mAcm^{-2}$, respectively. The corrosion potential of the coated samples was in the range of $-0.306 V_{Ag/AgCl}$ to $-0.381 V_{Ag/AgCl}$, this was approximately 500 mV higher than that of the bare sample, which shows a considerable increase in corrosion resistance. Likewise, the corrosion current of the coated 99.0% samples were all lower than $4 mAcm^{-2}$, therefore the coating resulted in a large decrease in the corrosion current of the substrate.

The corrosion potentials of the coated samples under 80°C conditions were as follows: Al6082 TiC < Al6082 TiAu < Al6082 CrC < 99.0% TiC < 99.0% CrC < 99.0% TiAu. This highlighted a trend of alloy being more susceptible to corrosion relative to the 99.0% substrate when at 80°C. The TiC again appears to be the most susceptible coating as it had the least noble potential for both Al6082

and 99.0% substrates. The corrosion potential for the 99.0% TiC sample at 80°C was more noble than at 55°C . This was also the case for the Al6082 CrC sample.

Both TiC coated samples and the Al6082 CrC sample displayed a decrease in corrosion current when tested at the elevated temperature. The corrosion currents before static corrosion followed the trend $\text{Al6082 TiAu} < 99.0\% \text{ TiAu} < \text{Al6082 TiC} < 99.0\% \text{ CrC} < \text{Al6082 CrC} < 99.0\% \text{ TiC}$. This shows the reverse to what was displayed in the 55°C tests for the alloy sample. In the 55°C tests the lowest rates of corrosion were observed for the TiAu coatings whereas at 80°C the TiAu coating exhibited the highest corrosion current. The two carbon containing coatings displayed currents below 1 mAcm^{-2} , whereas the gold coatings displayed current flows of 3.52 mAcm^{-2} and 136.36 mAcm^{-2} for the 99.0% and Al6082 samples, respectively.

Post static corrosion testing the corrosion potentials decreased for all samples, showing a reduction in corrosion resistance. The corrosion potentials follow the trend of $\text{Al6082 CrC} < \text{Al6082 TiC} < 99.0\% \text{ TiC} < \text{Al6082 TiAu} < 99.0\% \text{ CrC} < 99.0\% \text{ TiAu}$ from the lowest to highest potential. Similar to what was seen in the 55°C tests, the TiAu coating on both substrates and the 99.0% CrC samples displayed the highest corrosion potentials. This suggests the highest resistance to corrosion. This demonstrated a change in the materials from the initial BOL LSV to the EOL LSV. The TiC and CrC coatings exhibited degradation which resulted in a loss of corrosion resistance.

The corrosion currents measured post static corrosion increased for all samples. The trend follows $\text{Al6082 TiAu} < 99.0\% \text{ TiAu} < \text{Al6082 TiC} < 99.0\% \text{ TiC} < 99.0\% \text{ CrC} < \text{Al6082 CrC}$ from the highest to lowest corrosion currents. Here

Table 6.8: Table of corrosion potential and current values for the coated substrates at $80^{\circ}C$.

Substrate	Coating	Before corrosion		After corrosion	
		E_{corr}	I_{corr}	E_{corr}	I_{corr}
		($V_{Ag/AgCl}$)	($mAcm^{-2}$)	($V_{Ag/AgCl}$)	($mAcm^{-2}$)
Al6082	TiC	-0.609	0.63	-0.753	133.66
99.0%	TiC	-0.381	0.24	-0.722	100.00
Al6082	CrC	-0.482	0.41	-0.768	48.84
99.0%	CrC	-0.339	0.56	-0.660	48.86
Al6082	TiAu	-0.528	136.36	-0.662	230.62
99.0%	TiAu	-0.306	3.52	-0.547	149.60

the corrosion rate at OCV follows a clear trend with the gold coating performing the worst and the CrC performing the best. All currents are far greater than were measured in the $55^{\circ}C$ tests except in the case of the Al6082 CrC sample, which displayed a reduction from $79.01 mAcm^{-2}$ in the $55^{\circ}C$ test to $48.84 mAcm^{-2}$ in the $80^{\circ}C$ test. In addition, the Al6082 CrC sample exhibited the lowest corrosion current in the post corrosion $80^{\circ}C$ tests. Overall from the LSV analysis carried out at $80^{\circ}C$ the CrC coating appears to display the best performance when considering the initial and final parameters.

Table 6.9 and figure 6.8 display the current response from the sample during the accelerated stress test. All the samples appear to reach a steady state except the CrC alloy and TiC 99.0% samples. Both samples appear to be increasing in

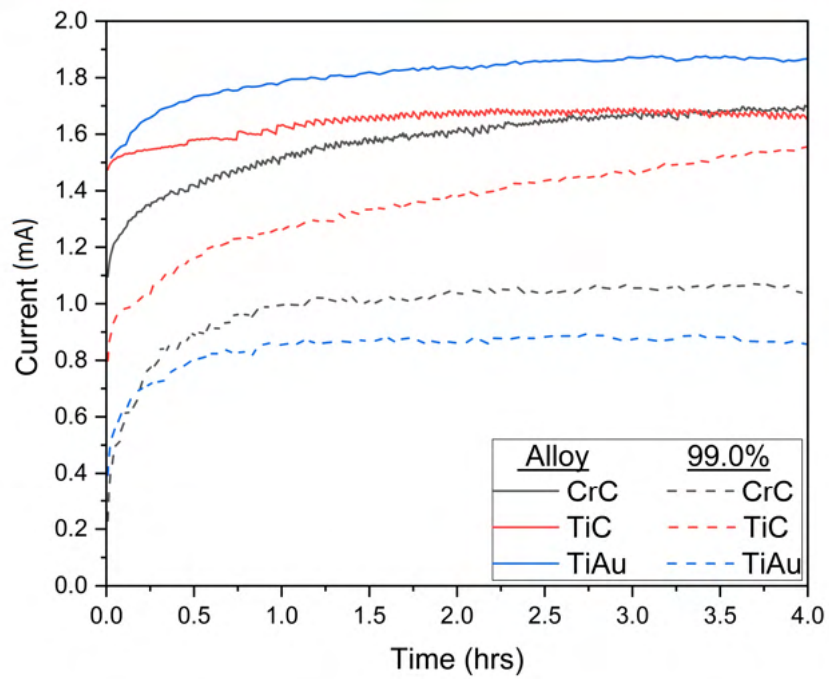


Figure 6.8: Graph of corrosion current throughout the static corrosion testing for the coated substrates at 80°C .

Table 6.9: Table of corrosion current measured throughout the static corrosion testing for the coated substrates at 80°C . Units of mAcm^{-2} .

Substrate	Coating	Initial	30 min	1 hour	2 hours	4 hours
Al6082	TiC	1.47	1.58	1.63	1.67	1.65
99.0%	TiC	0.80	1.15	1.26	1.37	1.56
Al6082	CrC	1.10	1.42	1.52	1.61	1.70
99.0%	CrC	0.23	0.88	0.99	1.03	1.03
Al6082	TiAu	1.52	1.73	1.78	1.83	1.87
99.0%	TiAu	0.39	0.80	0.86	0.87	0.86

current to the end of the test. As seen previously, all samples start with an increase in current, but the rate of increase decreases shortly after with a plateau in current occurring. The current produced by all the coated Al6082 samples were lower than that of the bare substrate. This suggests an increase in corrosion resistance.

Additionally, the coated 99.0% samples exhibited a decrease in corrosion current relative to the bare substrate. The bare substrate produced a current density of 1.17 mAcm^{-2} at BOL which increased to 1.39 mAcm^{-2} after 1 hour of accelerated stress testing. This compares with an initial current of 0.799 mAcm^{-2} and 1.26 mAcm^{-2} after 1 hour of corrosion testing for the TiC coated 99.0% sample. Which was the worst performing for the coated 99.0% samples.

All samples displayed an increase in current relative to the 55°C test except 99.0% TiC, 99.0% CrC and 99.0% TiAu. The TiC and CrC samples exhibited a lower corrosion current at the start of the test. However, after 30 minutes, corrosion currents at 80°C exceeded those measured at 55°C . This suggests that, the sample is less chemically stable in the hotter conditions. It is possible that variances in the coating quality of the tested area could be responsible for the lower starting current. The TiAu sample displayed lower corrosion currents at 55°C until 4 hours of AST. After 4 hours large amounts of corrosion product had built up on the surface. The build up of this product could reduce the rate of corrosion due to reduced diffusion or a reduction in active area. The current produced under 80°C was higher than that of the 55°C sample up to 4 hours. Higher rates of corrosion would in more corrosion product upon the surface.

All 99.0% samples exhibited a lower corrosion currents at all times than the alloy samples at 80°C . This is a strong indicator that regardless of the coating

material applied the substrate had a strong influence on the corrosion current. It is possible that the coatings are of a lower quality on the alloy than the 99.0% sample. This could occur due to the alloying elements affecting the potential distribution across the sample during coating. Inhomogeneous coating could result in localised defects in the coating. These could result in solution reaching the substrate surface more readily and therefore more aggressive corrosion could occur. Corrosion of the bare substrates indicated that the rate of corrosion of the Al6082 alloy was higher than that of the 99.0% substrate, seen in table 6.5. Therefore it would be expected that an equal number of defects in either substrate would result in a higher corrosion current for the alloy substrate.

The alloy samples followed the trend of $\text{CrC} < \text{TiC} < \text{TiAu}$ going from the lowest corrosion current to the highest, until 3.5 hours, as can be seen in figure 6.9. After 3.5 hours the corrosion current for CrC is greater than that of TiC. This is the reverse of what was seen in the 55°C test, where the TiAu coating exhibited the lowest corrosion current and the CrC the highest. This suggests that one coating may not be superior at all conditions, therefore coatings could be optimised for specific operating conditions. By the end of the test TiC and CrC produced approximately the same current with a difference of around 0.05 mAcm^{-2} . The current density of the TiAu coating is approximately 0.15 mAcm^{-2} greater than the next highest coating (CrC). This suggests lower corrosion resistance.

The coated 99.0% samples increased in current density from 30 minutes until the end of the test following the trend $\text{TiAu} < \text{CrC} < \text{TiC}$, from table 6.9. It can also be seen that prior to this, the CrC sample out-performs the other coatings, up to around 15 minutes, from table 6.9 and figure 6.8. At this point

stability is not achieved, therefore the relevance of this performance difference is inconclusive. Once stability is achieved the difference between the TiAu and CrC samples is relatively constant whereas the TiC sample exhibits a continuous increase in corrosion current. The TiAu exhibits superior performance for the 99.0% substrate. In both the $55^{\circ}C$ and $80^{\circ}C$ tests the CrC and TiAu coatings on 99.0% aluminium were superior. After 4 hours of static corrosion testing at $55^{\circ}C$ the CrC sample out performed the $80^{\circ}C$ sample by 0.08 mAcm^{-2} . Whereas at $80^{\circ}C$ the TiAu sample out performed the CrC sample by 0.15 mAcm^{-2} . Furthermore, the 99.0% aluminium samples stabilised close to the end of the $55^{\circ}C$ test (around 3.5 hours), whereas for the same samples at $80^{\circ}C$ stabilisation occurred in around 30 minutes.

Scanning Electron Microscopy and Energy Dispersive X-ray Analysis of Coated Samples

Surface morphology of the TiAu and CrC coated layers were imaged with SEM and presented in figures 6.9 and 6.10, respectively. The long parallel grooves were still present and no significant changes can be seen after the ion etching and coating processes. The coatings applied were in the nanometric scale and as such were unlikely to significantly change the surface morphology.

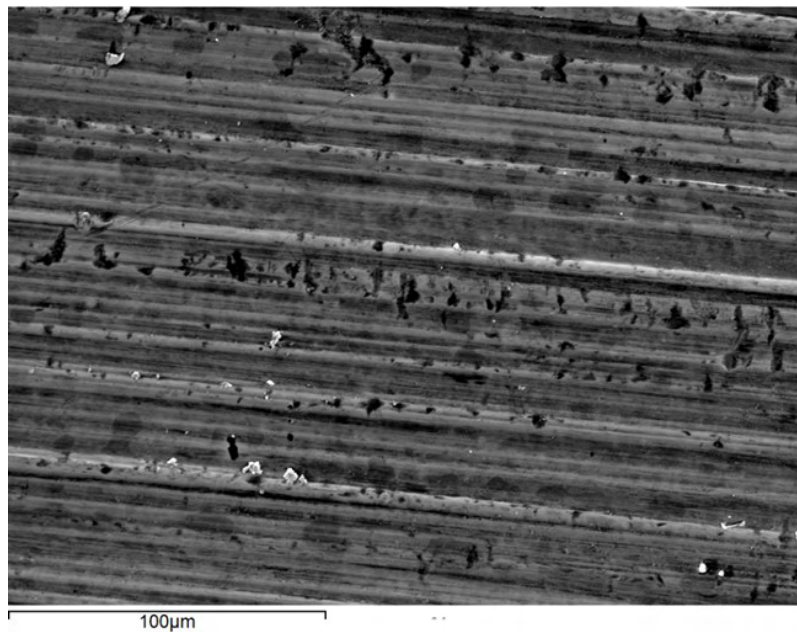


Figure 6.9: TiAu coated 99.0% aluminium substrate, imaged prior to accelerated stress testing.

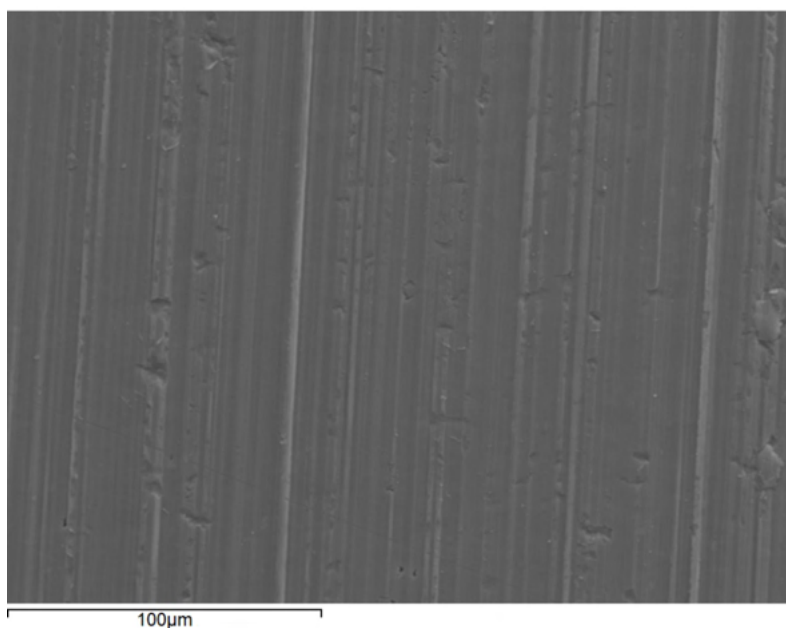


Figure 6.10: CrC coated 99.0% aluminium substrate, imaged prior to accelerated stress testing.

TiC

All samples after corrosion show significant signs of degradation. The 99.0% TiC sample in figure 6.11 exhibits pitting corrosion with large orifices. Intergranular corrosion can be observed in a perimeter around the pits. In addition, high oxygen concentration can be observed at these locations. These are thought to be cathodic regions which balance the reactions of the anodic attack at the grain boundary edge [162, 196]. An area of high oxygen also exists at the pit edge which was a result of the cathodic reaction [162]. The SEM image and EDX map of carbon show less corrosion in the areas of high carbon concentration, figure 6.11. Insignificant salt formation can be observed at these locations despite the high degree of corrosion.

The TiC coated sample exhibited more corrosion when tested at 80°C. Pits, intergranular and exfoliation corrosion can be observed on the sample in figure 6.12. A large amount of corrosion product can be seen, with more sulphur present. It can be seen that the corrosion product exists on most of the surface in the imaged area. Areas that do not show corrosion product, appear to be regions where exfoliation have occurred and are closer to the pit orifice. Under both conditions it appears failure of the coating had occurred.

In figure 6.5, the uncoated alloy substrate exhibited intergranular corrosion and a high concentration of corrosion product. When the alloy substrate was coated the surface morphology remained unchanged for all samples. The TiC coating is displayed in figure 6.13. The corrosion behaviour of the TiC coated alloy differed from the base substrate and the equivalently coated 99.0% sample. Figure 6.14 highlights coating failure. Delamination of the coating occurred with the underlying aluminium displaying intergranular corrosion. The EDX map of

titanium, highlights the loss of coating.

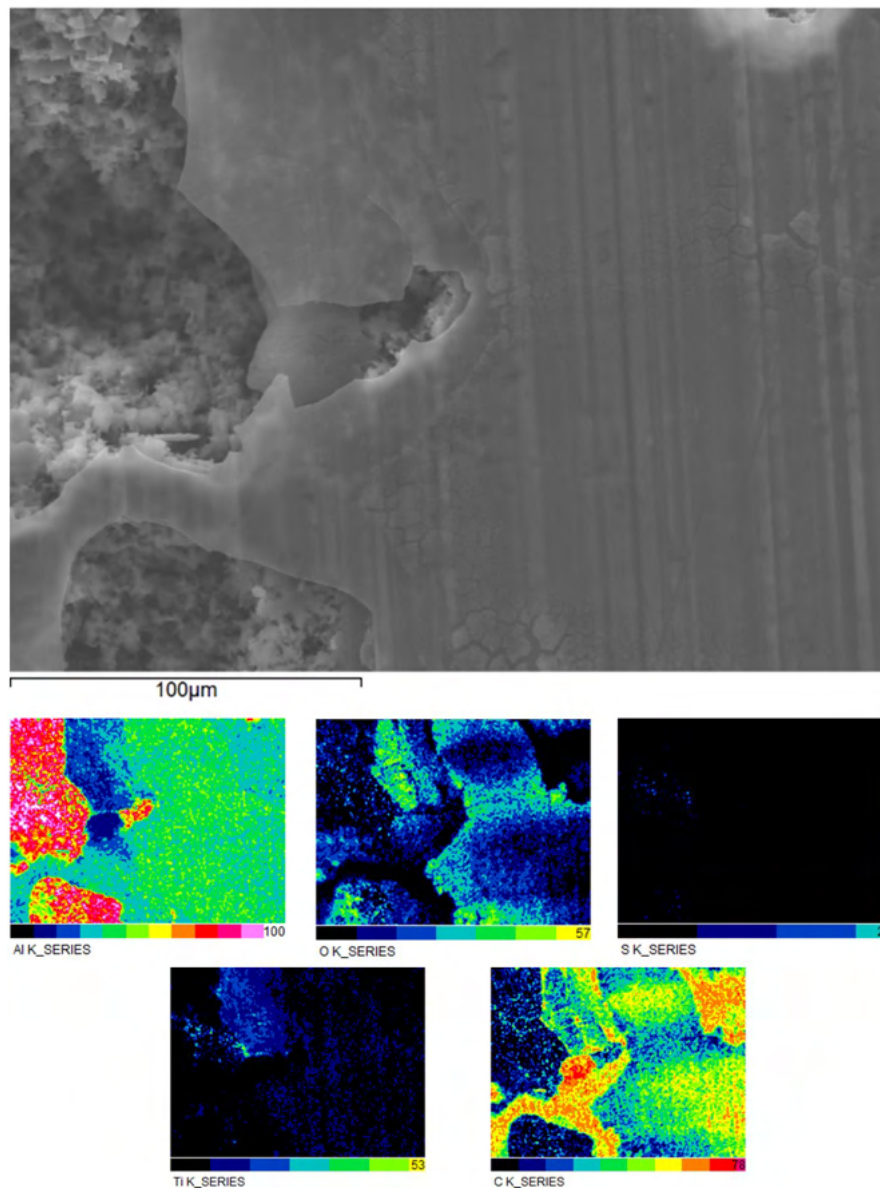


Figure 6.11: TiC coated 99.0% pure aluminium substrate imaged post accelerated stress testing at $55^{\circ}C$ after 4 hours.

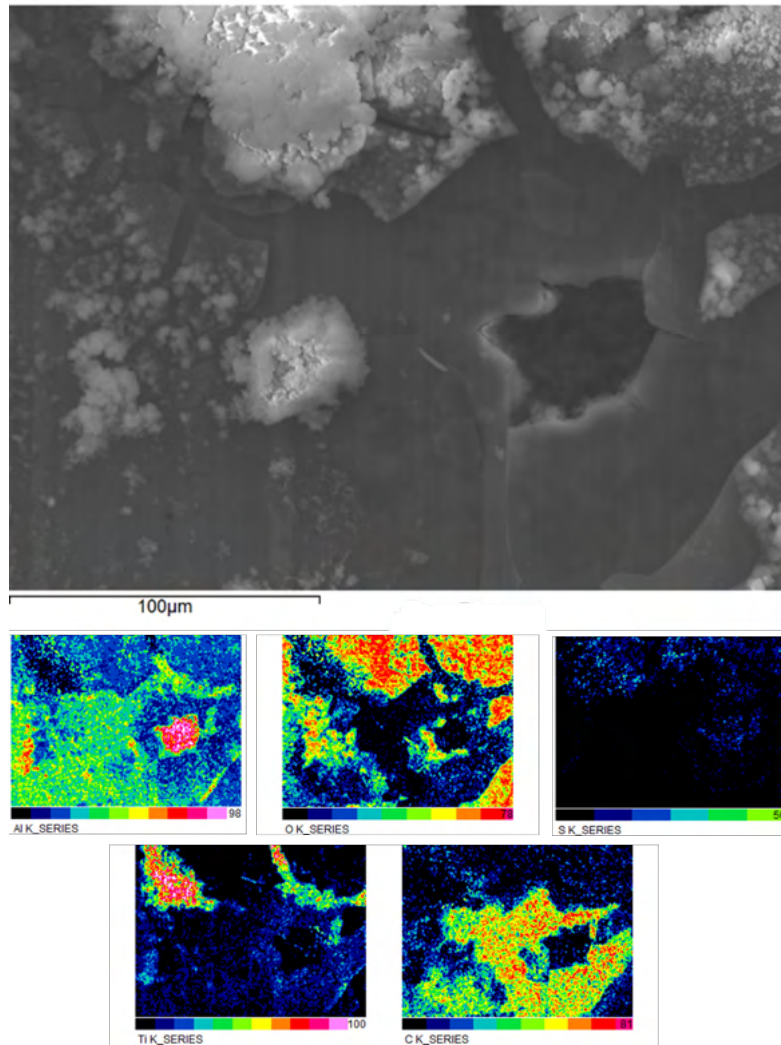


Figure 6.12: TiC coated 99.0% pure aluminium substrate imaged post accelerated stress testing at 80°C for 4 hours.

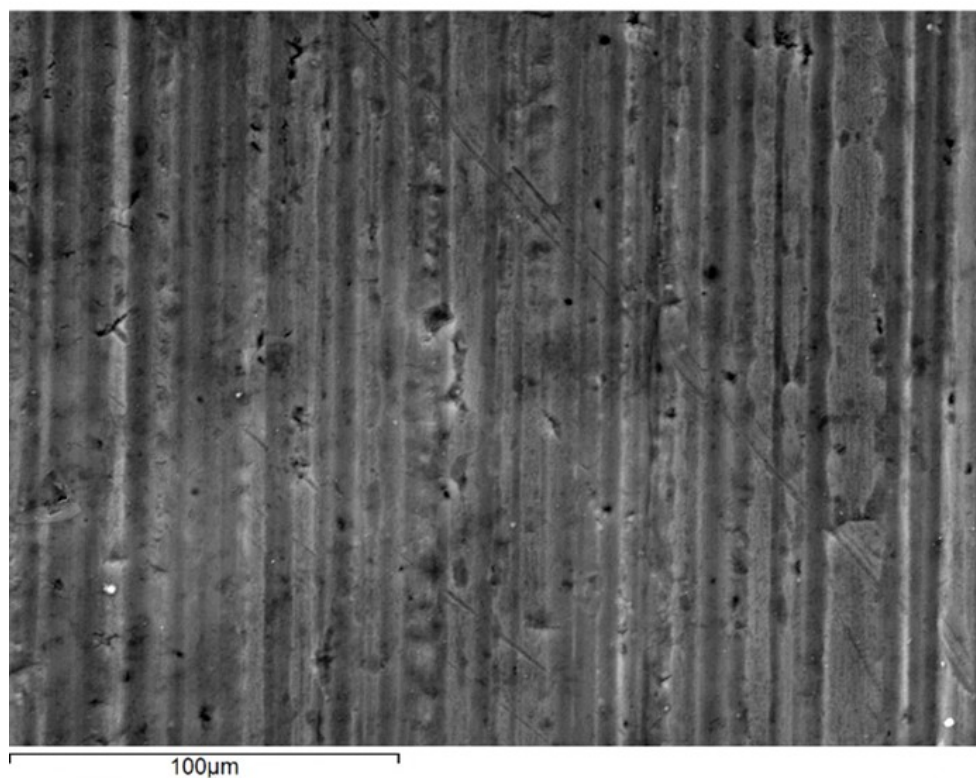


Figure 6.13: TiC coated Al6082 aluminium substrate, imaged prior to accelerated stress testing.

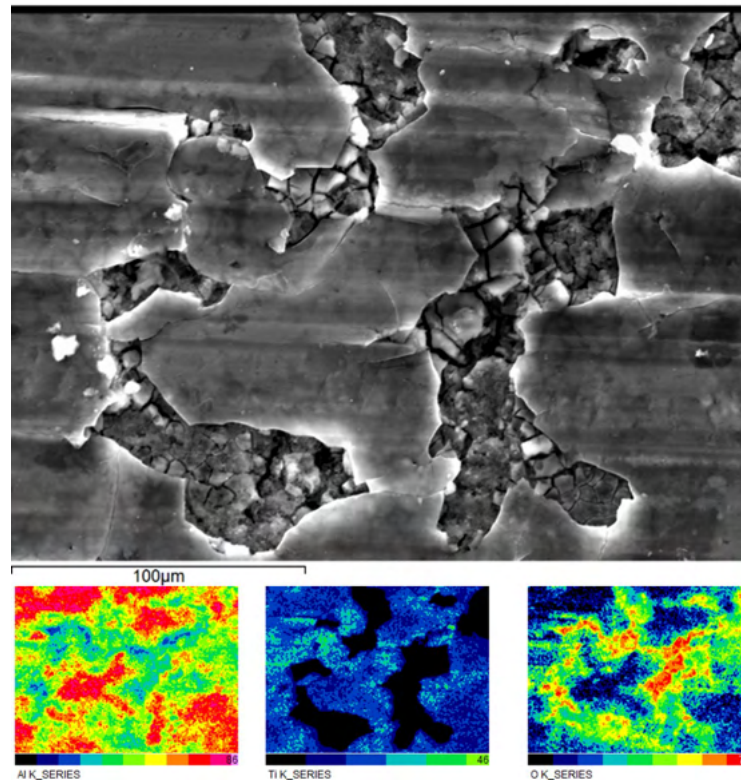


Figure 6.14: TiC coated Al6082 aluminium substrate, imaged post accelerated stress testing at 55°C after 4 hours.

CrC

When the 99.0% substrate is coated with CrC the morphology does not change significantly as can be seen in figure 6.10. This is likely due to the low thickness of the coating. After corrosion at 55°C , corrosion product, intergranular and exfoliation corrosion can be observed. In figure 6.15, exfoliation corrosion is present, displayed by large pieces of detached material. Pits could be observed but coating material had remained across the entrance of the pit. The EDX map of aluminium shows the areas of high aluminium concentration present in the pit, figure 6.15. These areas are dark in the EDX maps of both chromium and carbon (the coating materials), indicating that the coating is not present in these regions. This suggests that defects in the coating or exfoliation of the coating have led to the formation of a pit in the aluminium substrate. Galvanic corrosion also occurs with the substrate in electrical and ionic contact with the coating. Aluminium is used as a sacrificial anode due to the low electrode potential of the metal, the coating used on the substrate was more noble than the aluminium substrate due to a higher electrode potential [199]. Galvanic coupling can occur between the aluminium and the coating, which will enable or accelerate the corrosion of the substrate. The CrC sample corroded at 80°C exhibited the same corrosion phenomena as the 55°C sample. Figure 6.16 shows SEM and EDX images of an exposed pit with high oxygen concentration in and around the pit. Sulphur was observed within the pit suggesting corrosion product formation.

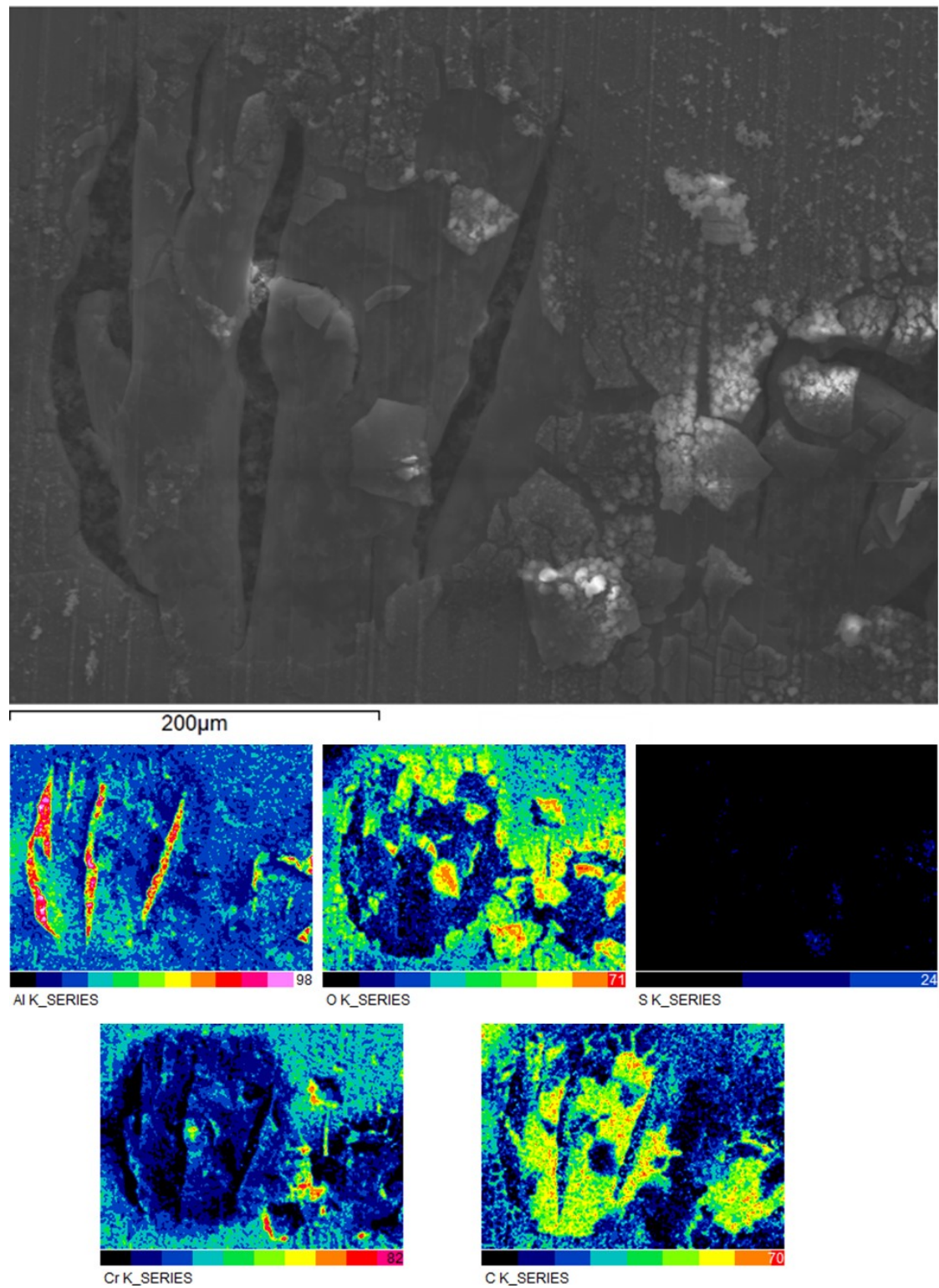


Figure 6.15: CrC coated 99.0% pure aluminium substrate imaged post accelerated stress testing at 55°C after 4 hours.

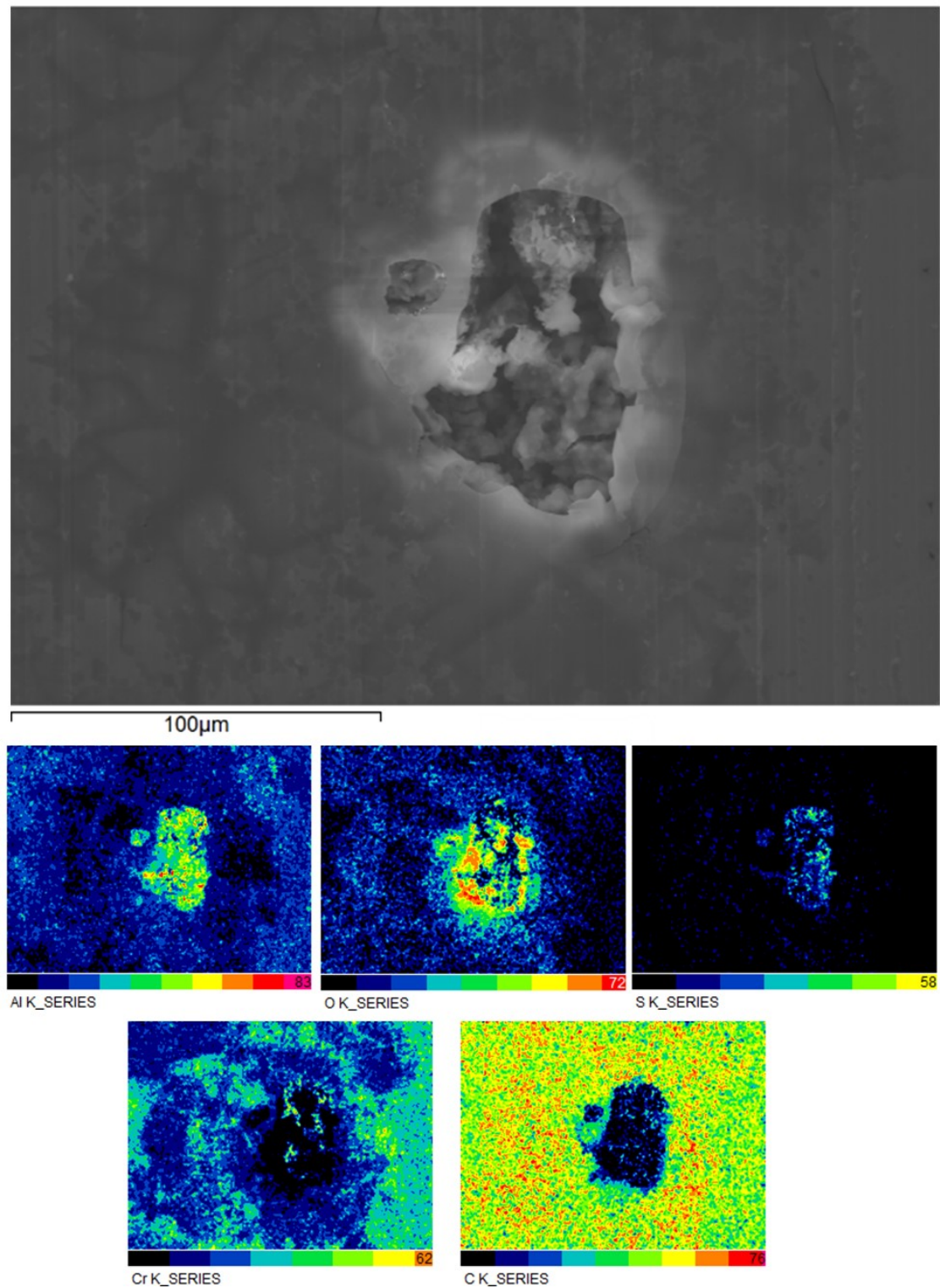


Figure 6.16: CrC coated 99.0% pure aluminium substrate imaged post accelerated stress testing at 80°C after 4 hours.

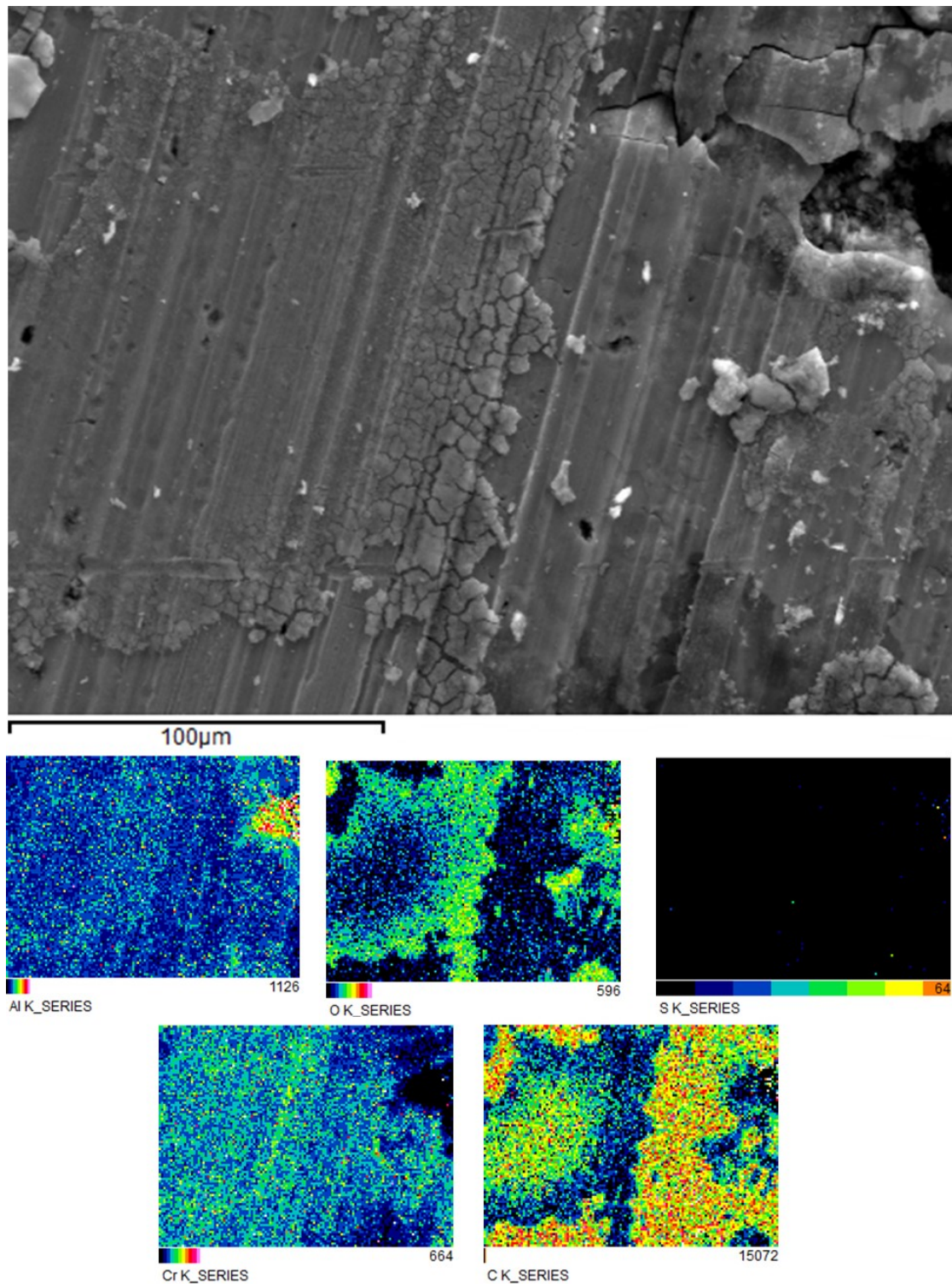


Figure 6.17: CrC coated Al6082 aluminium substrate imaged post accelerated stress testing at 55°C after 4 hours.

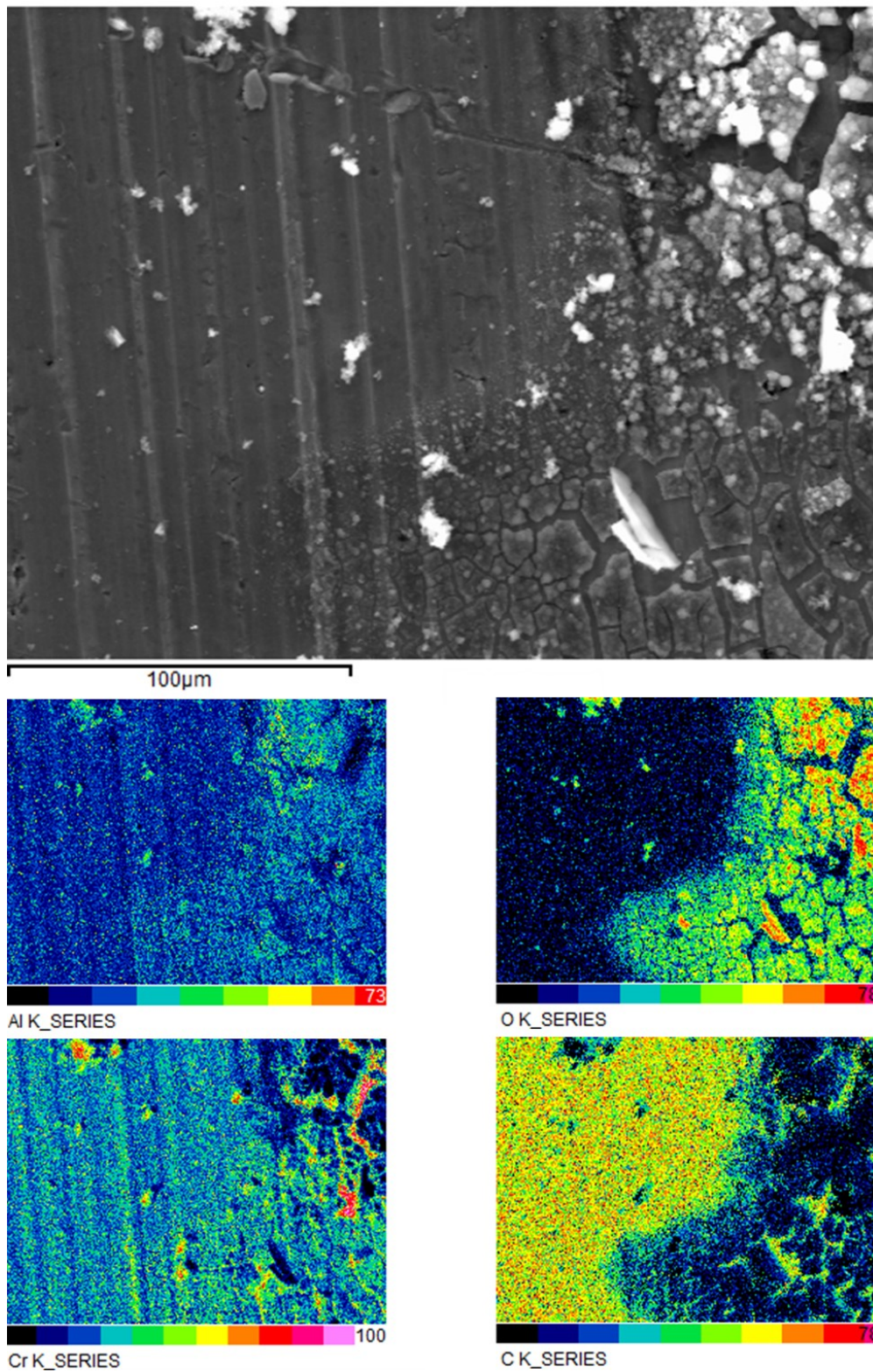


Figure 6.18: CrC coated Al6082 aluminium substrate, imaged post accelerated stress testing at 80°C after 4 hours.

The CrC alloy samples also displayed a large number of pits across the surface, figure 6.17. The phenomena was displayed across large areas of the surface. The raised area was highly oxygenated and cracked. It is likely that this area suffered severely from intergranular corrosion where exfoliation then occurred. This process causes deterioration of the surface. A small amount of corrosion product can be observed in this area, with a low detection of sulphur. Figure 6.18 shows a significant increase of corrosion product when the temperature of corrosion increased to 80°C . Intergranular and exfoliation corrosion appeared to have increased but, the number of pits observed was reduced. It is possible that the large amounts of corrosion product make the identification of pits difficult.

TiAu

The TiAu 99.0% sample corroded at 55°C displayed similar behaviour to the previous samples. An area of high oxygen concentration exists outside the pit as seen by the EDX map in figure 6.19. Pits also formed across the surface. The area of high oxygen concentration appears similar to that seen in figure 6.15 where the surface was broken up into small pieces. However the TiAu sample displays less exfoliation relative to the CrC sample. Pitting was severe on the TiAu 99.0% sample, perforating the sample during the 55°C 4 hour corrosion test. Minimal corrosion product could be observed by eye on the sample, additionally low sulphur content is detected by EDX spectroscopy, figure 6.19. More exfoliation can be seen when the temperature was increased to 80°C , figure 6.20. Furthermore, a build up of corrosion product can be observed while pits also form at this temperature.

The corroded alloy samples coated with the TiAu also suffered from cor-

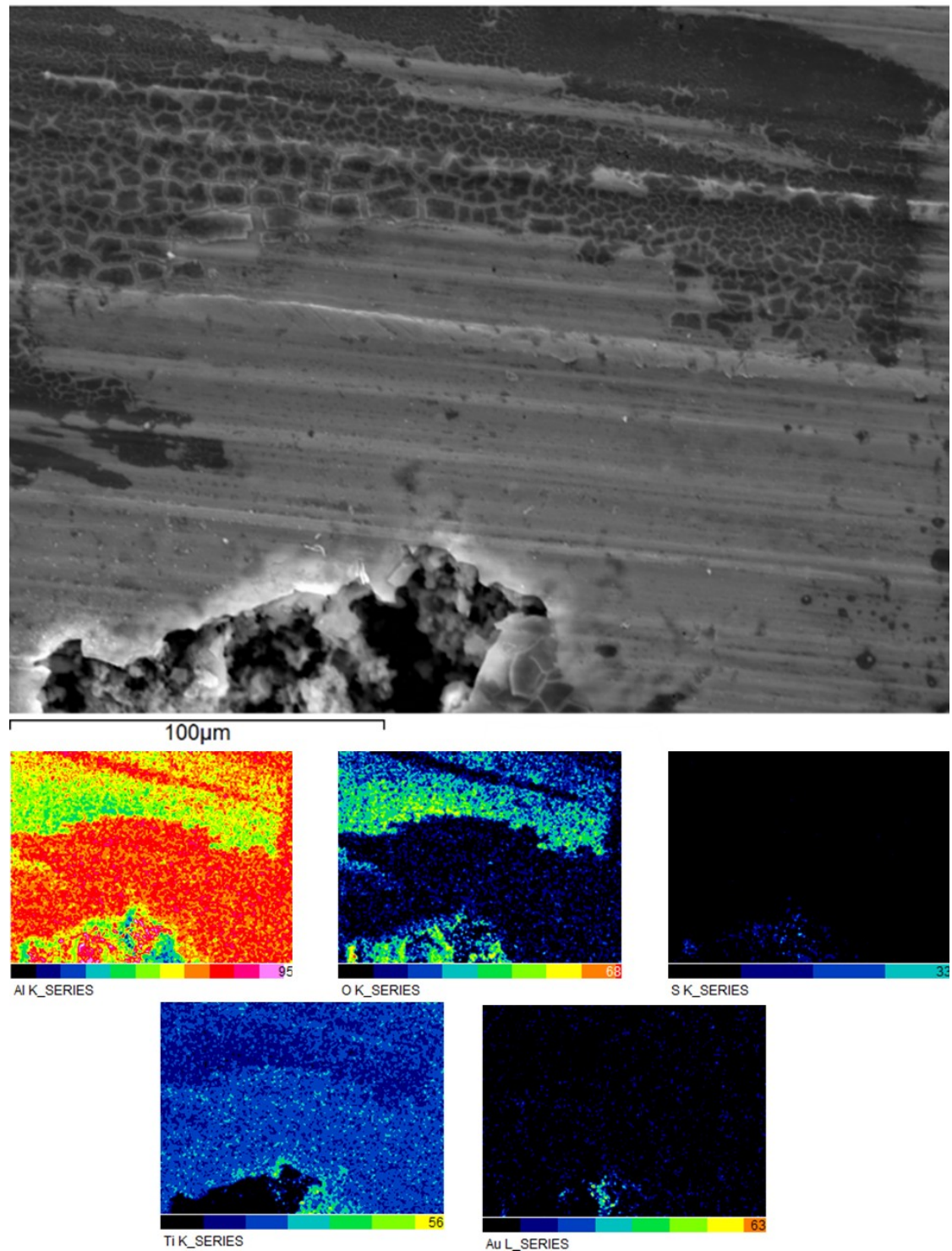


Figure 6.19: TiAu coated 99.0% pure aluminium substrate imaged post accelerated stress testing at 55°C after 4 hours.

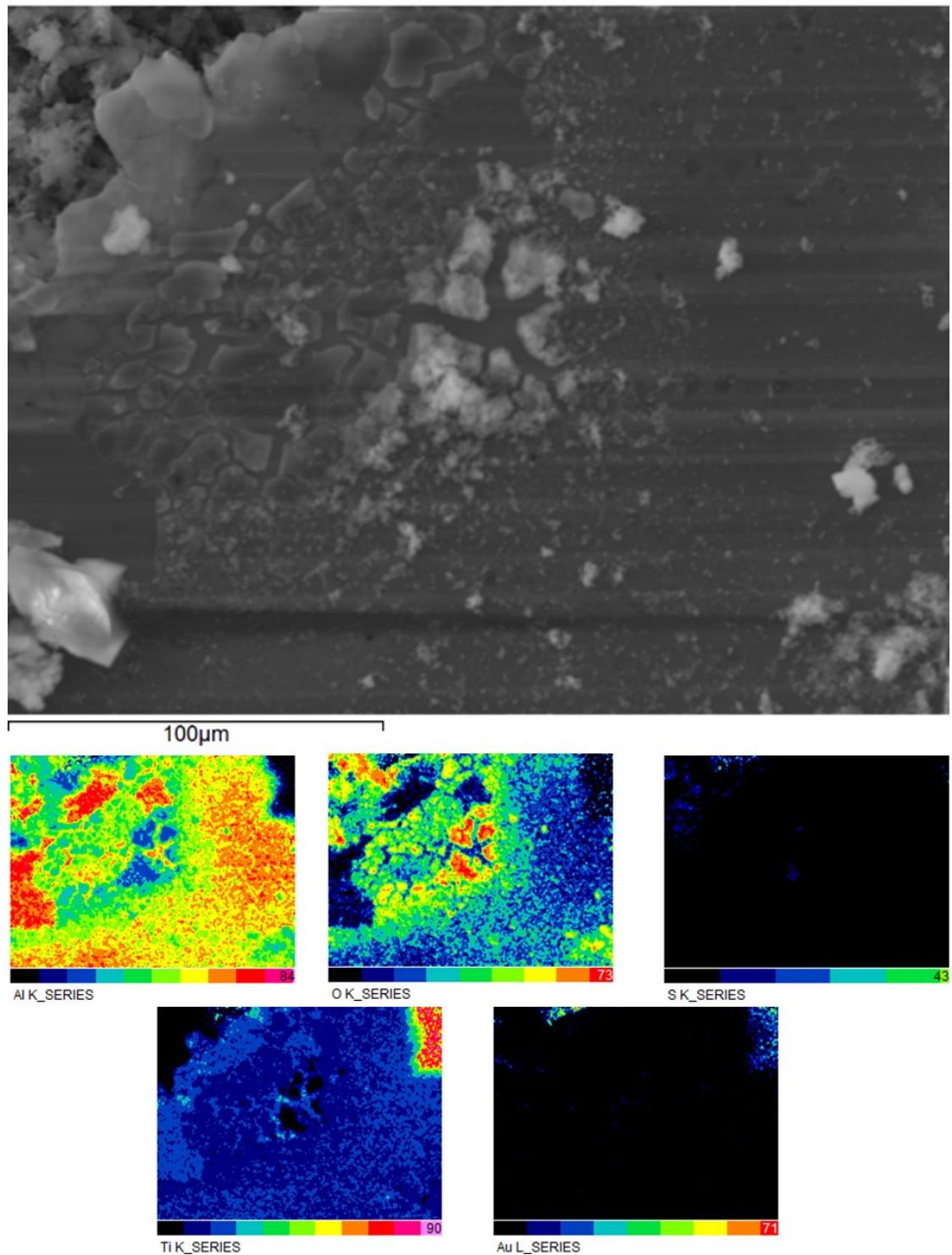


Figure 6.20: TiAu coated 99.0% pure aluminium substrate imaged post accelerated stress testing at 80°C after 4 hours.

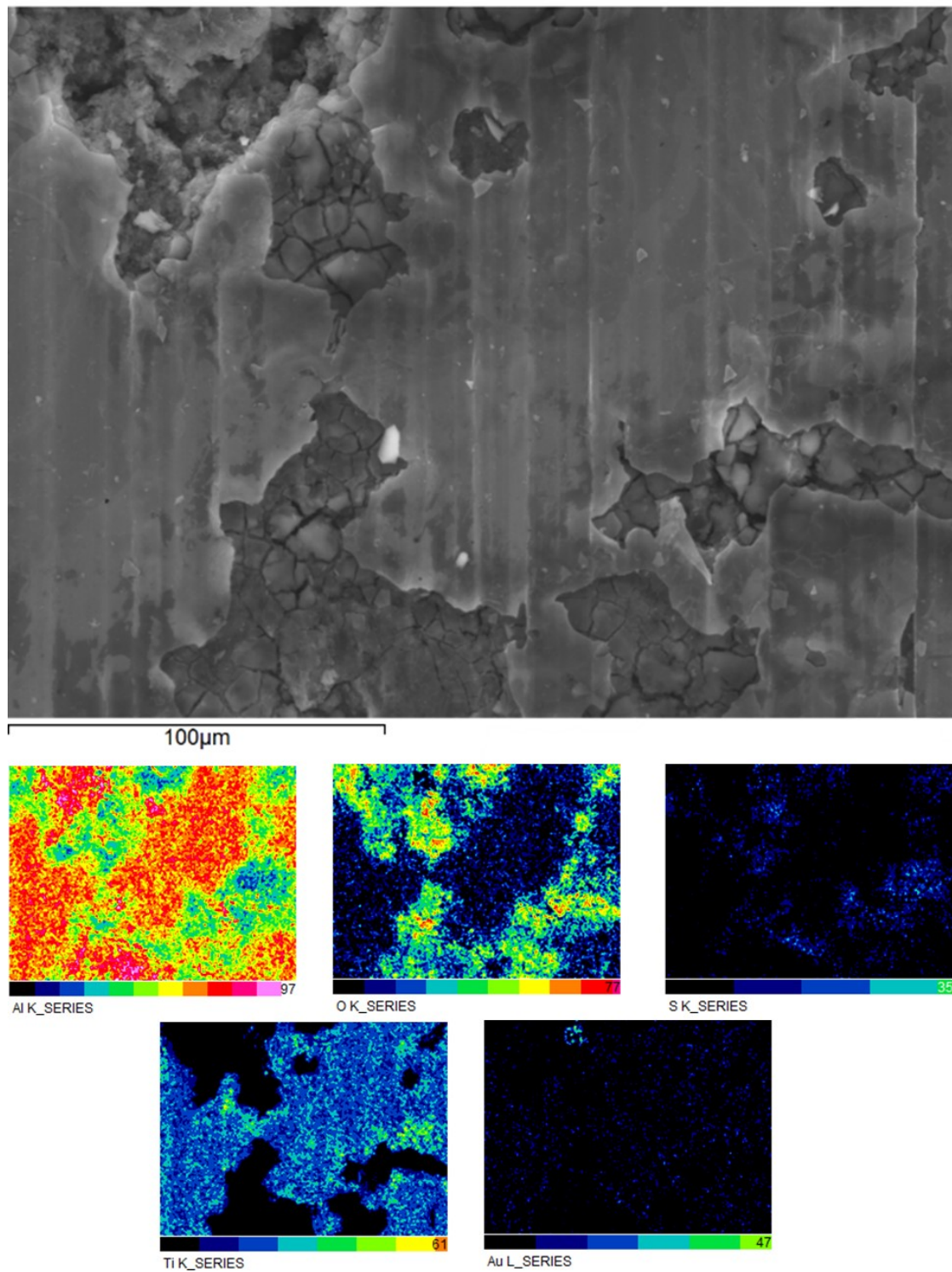


Figure 6.21: TiAu coated Al6082 aluminium substrate imaged post accelerated stress testing at 55°C after 4 hours.

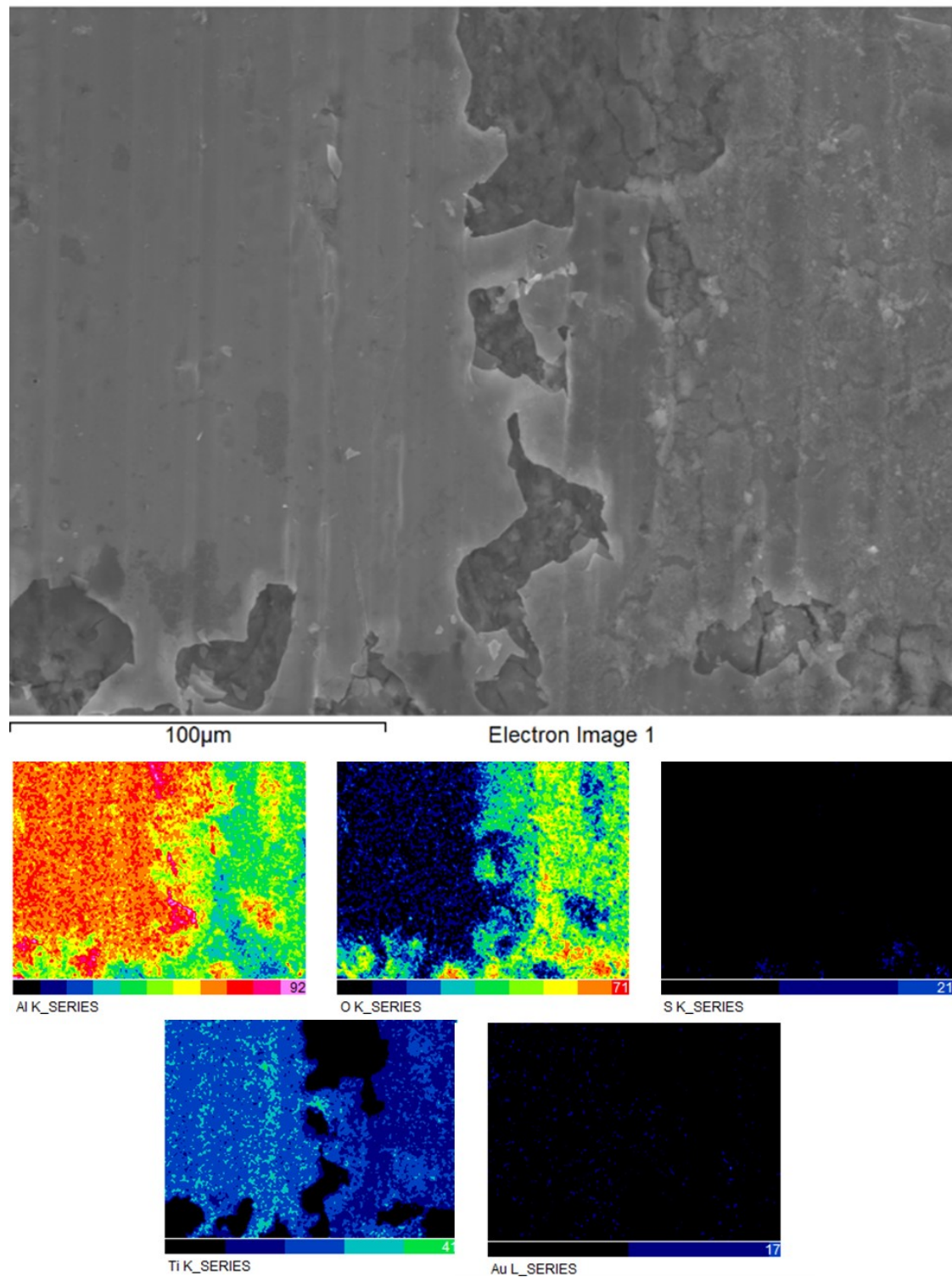


Figure 6.22: TiAu coated Al6082 aluminium substrate, imaged post accelerated stress testing at 80°C after 4 hours.

rosion. A similar behaviour to the alloy TiC sample was observed at 55°C . The coating appears to delaminate leading to intergranular and pitting corrosion on the substrate. On the surface there does not appear to be direct corrosion, like that seen at other conditions or for the CrC sample under the same conditions. Both these samples are alloy substrates with a Ti interlayer. This suggests that these samples undergo an alternative corrosion mechanism to the other samples. When the temperature was increased to 80°C this delamination behaviour was still observed. Pits however became larger and corrosion product could be seen. In addition, figure 6.22 shows an oxide layer on the surface of the sample. The oxide layer that formed at 55°C appeared on the substrate and not the coating. This highlights the aggressive conditions of the 80°C test.

6.5 Conclusion

Ex situ potentiostatic corrosion testing found that Al6082 is more susceptible to corrosion than bare 99.0% pure aluminium. The alloy substrate also produced high levels of corrosion product at pit sites. However 99.0% pure aluminium, is soft and ductile, which limits its applications. Despite increase corrosion on Al6082, relative to 99.0% pure aluminium, the alloy would be selected by automotive and aerospace manufacturers due to the superior mechanical properties [189, 190, 200, 201].

Titanium gold, titanium carbon and chromium carbon were all successfully deposited on high purity aluminium and Al6082. All samples, except the TiC 99.0% aluminium sample, exhibited excellent contact resistance with values between 1 and 5 $m\Omega cm^2$. Displaying between a 90% and 50% reduction when compared to the DoE target. The use of an alloy substrate resulted in a reduction of the contact resistance for all coatings. The contact resistance performance of the coatings on the alloy Al6082 followed the trend: TiAu < CrC < TiC, from lowest to highest contact resistance. The same trend was observed on the 99.0% substrate.

The corrosion current of all samples however exceeded DoE targets with values of 880 $\mu A cm^{-2}$ or greater, compared to DoE targets of 10 $\mu A cm^{-2}$. Dissolution of the substrate can be seen to some degree for all samples, highlighting the failure of the coating. Earlier in this work stainless steel substrates were seen to passivate, which although detrimental to performance would not result in significant failure events occurring in a fuel cell system. Bipolar plates of less than 0.1 mm have been utilised in systems, dissolution of these plates could result in

hydrogen and air mixing which would present safety concerns [13].

From the results in this chapter it would suggest that none of the coatings are currently suitable for aluminium bipolar plates as all fail to sufficiently protect the substrate in the simulated environment. However, literature had shown that there is a discrepancy between the performance of materials used *in situ* and *ex situ*. Therefore single cell testing should be conducted to fully understand the feasibility of PVD coated aluminium as a bipolar plate substrate.

Chapter Seven

In situ Testing of PVD Coated Al6082 Bipolar Plates

7.1 Introduction

The previous chapter investigated the corrosion resistance of PVD coated aluminium substrates by *ex situ* corrosion testing; all samples appeared to severely degrade under these simulated conditions. This chapter investigated the performance and durability of PVD coated aluminium through *in situ* testing.

Literature has demonstrated that the conditions and degradation observed via *ex situ* testing does not closely match that seen in *in situ* testing. For this reason the TiC, CrC and TiAu coatings investigated in the previous chapter were deposited upon Al6068 bipolar plates and tested as a single cell. The aim of this work was to investigate the discrepancy between *in situ* and *ex situ* test conditions. An understanding of the *in situ* performance of PVD coated Al6068 was also achieved.

7.1.1 Polarisation Curve

There are three regions of a fuel cell polarisation curve; activation (or charge transfer), ohmic and concentration (mass transport) regions [202–204]. Tang et al. found that charge transfer resistance accounted for 90% of the voltage drop at low current density (0.2 Acm^{-2}) and 0% at high current density [204]. The oxygen reduction reaction is primarily responsible for the losses in the activation region due to the slow kinetics of the reaction [204]. Ohmic resistance, which is primarily attributed to an increase in the protonic resistance of the membrane, accounts for between 15 and 35% of the voltage losses, depending on the current density [204]. This resistance is strongly related to the humidification of the membrane [205]. Work carried out by Tang et al. displayed mass transport losses at around 0.8 Acm^{-2} , at this current mass transport losses represent 15% of the total losses [204]. The losses due to mass transport linearly increased with current density representing 80% of the losses at high current density (2 Acm^{-2}). However, mass transport losses are dependent upon the test conditions and equipment design.

Losses in the OCV are a result of hydrogen cross over. The mass transport losses that occur at high current densities are the result of reduced diffusion of reactants to the catalyst. This is more prominent in the cathode due to the low reactant concentration of oxygen in air, 20% oxygen content. BPP degradation could play a role in this if the water contact angle changes as the plate corrodes, this could result in partial or complete blockages of channels. The ohmic region of the polarisation curve is where the resistance dominates the losses of the cell. As previously mentioned, this is dominated by the ionic resistance in the membrane but the interfacial contact resistance of the BPP also contributes to the total

resistance.

In this work the same flow field design, CCM and GDL was used, test conditions and cell compression were also kept constant.

7.1.2 Electrochemical Impedance Spectroscopy

In situ impedance measurements are a valuable tool to characterise the performance of an individual cell or stack [206]. Equivalence circuits can be made by fitting impedance spectra. Equivalence circuits allow for the analysis of individual components within the system [206]. Furthermore conditions of the system can be adjusted to improve the validity of the equivalence circuit and further the analysis of each component. These adjustments include changes to the operating conditions of the system; humidity, temperature, pressure, catalyst loading, ionomer loading, membrane thickness etc., potentiostatic measurements, galvanostatic measurements [206].

When using potentiostatic measurements, the applied overpotential to the system has to be chosen with consideration of the desired results [206]. At low overpotentials the main contributor to impedance is interfacial charge transfer resistance, this resistance varies with potential [207]. Medium overpotentials incorporate impedance information from the proton conductivity, water and reactant gas transport [207]. At high overpotentials in air, the low oxygen concentration can become the dominant contributor to impedance. Under these conditions oxygen diffusion in the catalyst layer and the gas diffusion layer can be investigated [207]

A single semicircle is indicative of no diffusion limitation whereas two semicircles suggest finite diffusion [208]. A Warburg-impedance (45° straight line) is observed at low frequencies when a situation of infinite diffusion occurs [208].

The total ohmic resistance of the system can be determined by the high frequency intercept on the real axis (the left side of the Nyquist plot) [206, 209]. The total ohmic resistance is the sum of the bulk and contact resistances that arise from the membrane, anode and cathode catalyst layers, GDLs and bipolar plates [206, 209].

The charge transfer resistance of the oxygen reduction reaction is equal to the diameter of the semicircle seen in Nyquist plots [206, 210]. Cathode catalyst properties such as loading, surface area and utilization determine this value [210].

Each coated bipolar plate was tested at 55°C and 80°C . The data will be presented in the same manner for all plates. The first graph in each of the following sections will be the polarisation curves collected with the graphitic cathode bipolar plate before and after the AST test. It will also display the polarisation curves collected after 0, 12 and after 120 hours of accelerated stress testing. The following figure will be comprised of the polarisation curves collected at 0, 12 and 120 hours with another graph which will be a Nyquist plot (imaginary resistance plotted against the real resistance) for the same testing intervals.

7.2 Titanium Carbon

7.2.1 55°C Cell Testing

The MEA was hydrated with the carbon plates, the OCV increased from 0.87 V before hydration to 0.92 V after hydration. After activation a current density of 1.32 Acm^{-2} was achieved at 0.60 V. When the graphitic cathode plate was replaced with the TiC plate the OCV was 0.90 V and the current at 0.60 V was 1.22 Acm^{-2} . The initial performance of the TiC plate was worse than that of the graphitic plate at 0.60 V, seen in figure 7.1. This could be attributed to the plate producing a higher contact resistance between the current collector and GDL. As shown by the steeper gradient in the ohmic region, shown in figure 7.1.

Comparing the polarisation curves of the MEA tested before AST and the polarisation curves at 0 and 12 hours of AST testing, all polarisation curves display increased losses due to mass transport, as shown by the steep decrease in potential at higher current densities [202, 204].

Figure 7.2a shows the polarisation curves collected from the AST test using the TiC plate. It can be seen that between 0 and 12 hours the performance decreases by a small amount at low to medium current densities but has increased at higher current densities. Suggesting the membrane was well humidified in the initial test and that little degradation has occurred to any of the components. The current density at 0.60 V after 0, 12 and 120 hours was 1.22, 1.08, 0.65 Acm^{-2} respectively. From figure 7.2a it can be seen that the loss in performance has occurred across the entire polarisation curve. The OCV at 120 hours was 0.89 V

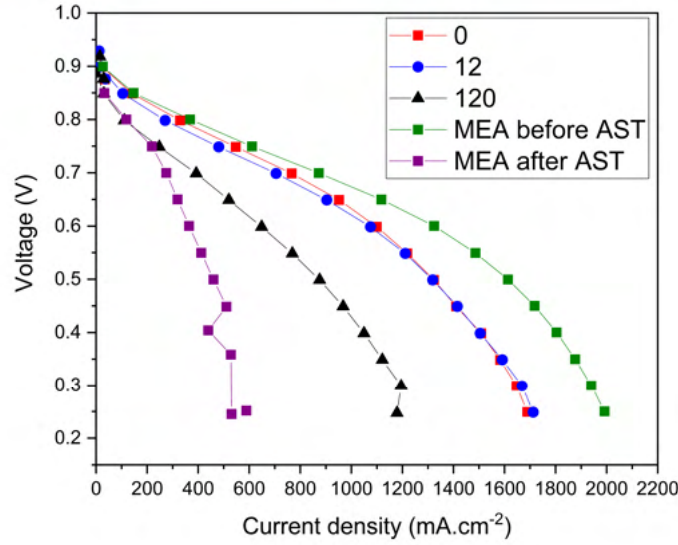
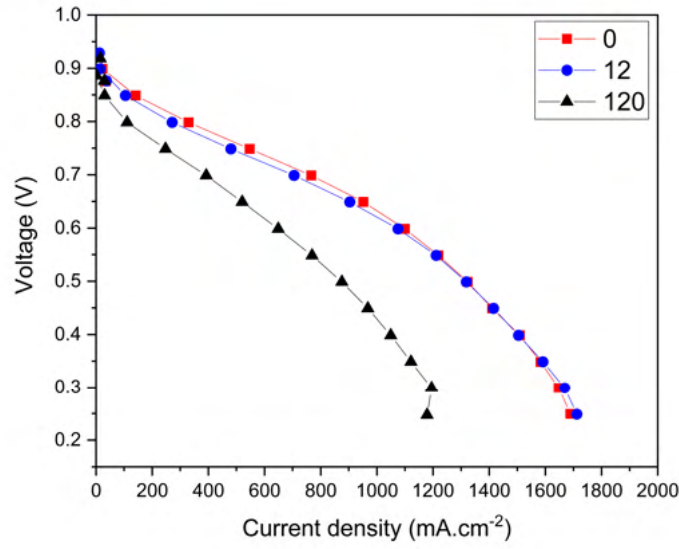


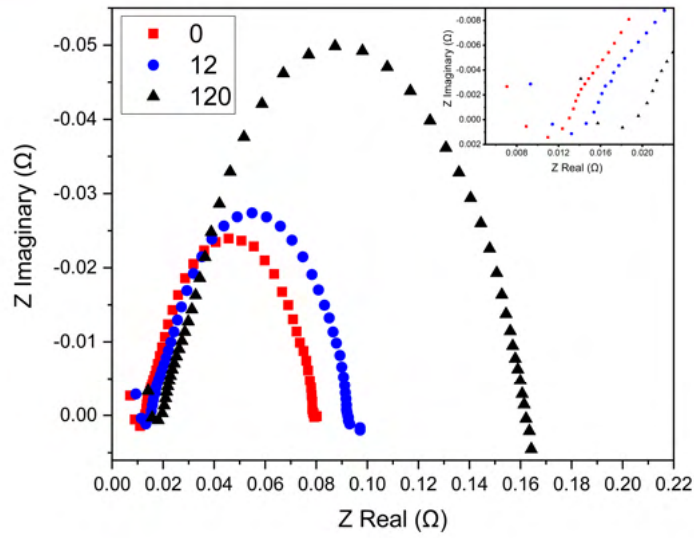
Figure 7.1: Polarisation curves of the TiC coated cathode after 0, 12 and 120 hours of the accelerated stress testing with the curves from the same MEA tested with carbon plates before and after the AST, all at 55°C.

which is a decrease of 10 mV from the start of the test. This loss results from increased H_2 cross over or catalyst poisoning.

Figure 7.2b shows the EIS data collected throughout the accelerated stress test. The leftmost (high frequency region) intercept of the semicircle with the x-axis is the high frequency resistance (HFR). This is the total ohmic resistance of the cell. The TiC plate contributes to the total ohmic resistance with both the bulk and interfacial resistances. Bulk resistances are magnitudes smaller than interfacial resistances and would remain unchanged throughout the test. The interfacial resistance however could increase if the surface of the plate changes, this could be oxide growth due to corrosion. It can be seen that the curves shift to



(a)



(b)

Figure 7.2: TiC sample. a) Polarisation curves after 0, 12 and 120 hours of accelerated stress testing b) Nyquist plots from impedance measurements taken after 0, 12 and 120 hours of accelerated stress testing. All test carried out at 55°C.

the right throughout the test, this shows that the resistance of the cell increases, figure 7.2. Table 7.1 displays the HFR measurements taken from the Nyquist plots. The HFR increases from the start of the test to the end with values of 13.0, 15.1 and 19.8 m Ω . The HFR of the graphitic plate was lower than that of the TiC plate with a value of 9.9 m Ω at beginning of life. The HFR for the graphitic plate after the AST test was 12.1 m Ω , suggesting the MEA resistance increased by 2.2 m Ω . This suggests that the TiC plate increased in contact resistance by 4.6 m Ω throughout the test.

Table 7.1: Table of the HFR measurements acquired from the extrapolation of the Nyquist plots for the samples tested *in situ*.

Sample	Temperature ($^{\circ}C$)	High frequency resistance (m Ω)		
		0	12	120
TiC	55	13.0	15.1	19.8
	80	20.7	21.5	21.0
CrC	55	13.8	16.3	17.4
	80	21.6	22.6	27.8
TiAu	55	18.5	18.0	19.2
	80	9.8	22.8	25.1

The performance of the cell at beginning of life was superior using the graphitic plate. However at the end of life the TiC performance was superior. The degraded MEA performed worse with the graphitic plate than the degraded TiC plate. It is possible that the MEA was damaged by moving it from one cell to another, this could be caused by the humidity cycling but such a performance

loss would not be expected from one cycle. An MEA will undergo many humidity cycles when utilised in the automotive sector. Alternatively, mechanical damage of the cell could occur from disassembly and reassembly.

Table 7.2 displays the EDX data collected on the TiC plate before and after the AST test. The land of a plate is responsible for the electrical contact between the bipolar plate and the GDL. For the TiC plate the measure of carbon on the surface decreased from 64.9 wt.% to 41.1 wt.% after the AST test. This suggests some of the carbon coating has been removed during the test and could explain the increase seen in the HFR. The oxygen concentration decreases by a small amount which suggests that the TiC coating has prevented oxide formation on the aluminium plate. The same behaviour could be seen in the channel of the plate.

7.2.2 80°C Cell Testing

Figure 7.3 displays the initial and final polarisation curves from the metallic plates. In addition the polarisation curves are included of the same MEA tested with the carbon plates, both before and after the AST test. Comparatively the polarisation curves of the initial states in the metallic and carbon plates are very similar. The carbon plates and metallic plate produced an OCV of 0.85 V and 0.86 V respectively. At 0.60 V the metallic plate produced 1.59 Acm^{-2} whereas the carbon plates produced 1.52 Acm^{-2} . The carbon plates appear to have more losses in the activation region, in the ohmic region there appears to be a steeper gradient for the metallic plate suggesting a higher cell resistance. A higher contact resistance between the GDL and coated plate could be responsible for increased losses in

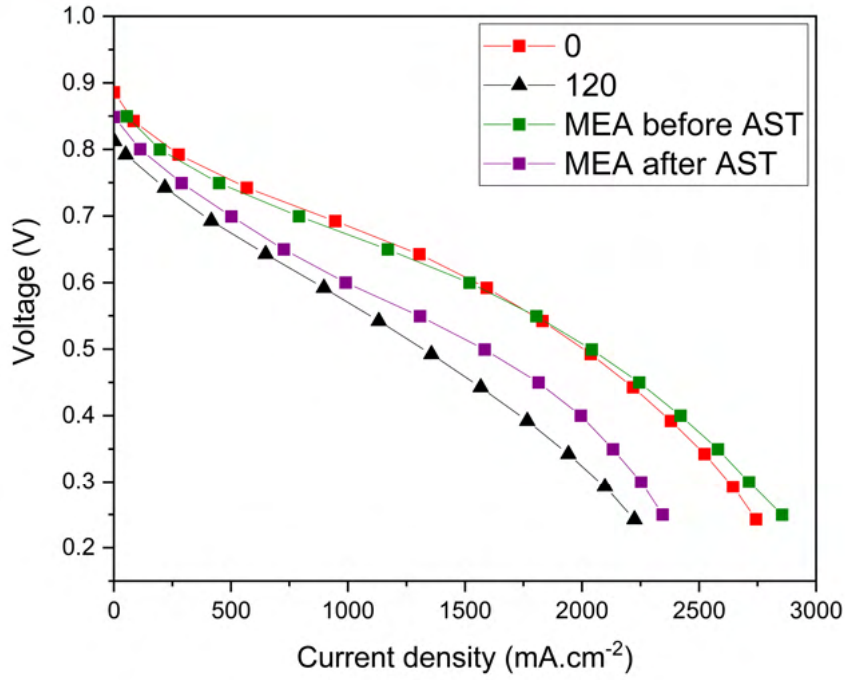


Figure 7.3: Polarisation curves of the TiC coated cathode at beginning of life and after 120 hours of the accelerated stress testing. Polarisation curves of the same MEA are displayed before and after accelerated stress testing with carbon plates. All tests carried out at 80°C .

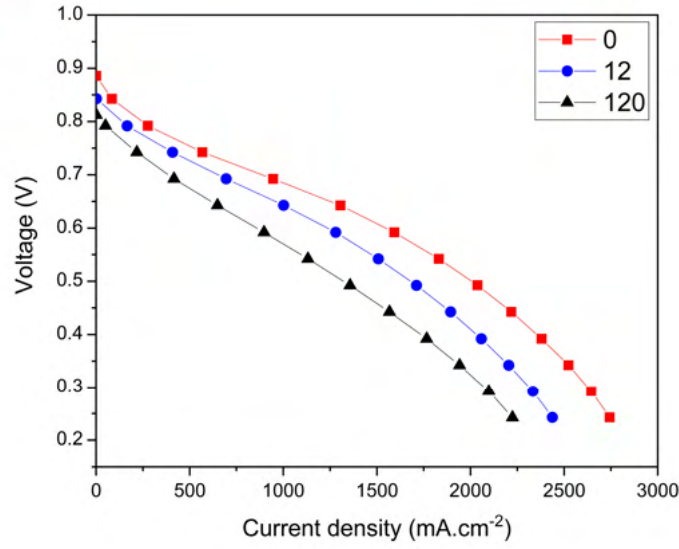
this region. The carbon plate achieved a higher limiting current than the metallic plate due to the increase in mass transport losses and higher ohmic resistance of the metal plate.

Over the first 12 hours the performance degrades quickly as can be seen in figure 7.4a). The current produced at 0.60 V reduced from 1.59 Acm^{-2} to 1.28 Acm^{-2} , the OCV reduced by 0.02 V and a steeper gradient in the ohmic region could be seen. Oxide formation could be responsible for the losses observed in the

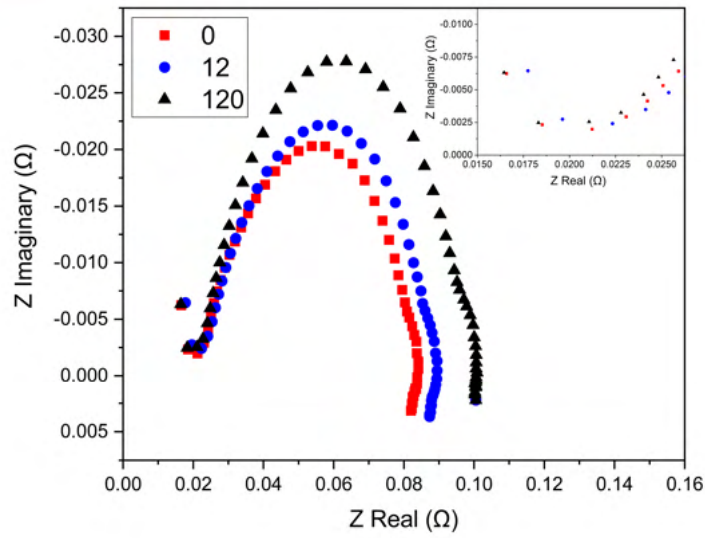
ohmic region however oxide formation was not confirmed by EDX. Further losses can be seen in the OCV after 120 hours with a reduction to 0.81 V, displaying a reduction in OCV of 0.05 V from BOL to EOL. Between 12 and 120 hours of AST, the OCV drops by 0.03 V. The polarisation curve at 120 hours, displays little behaviour associated with mass transport losses. This is likely due to high ohmic losses. Comparing the polarisation curve after AST (120 hours) in the metallic plates to that in the carbon plates (MEA after AST) in figure 7.3 it can be seen that the gradient in the ohmic region differs, as seen before AST also.

The compression of the cell was controlled between tests and as such each MEA should be at a consistent compression. Therefore the changes in this region should be a result of the change in interfacial contact resistance between the plates. This is an assumption as it cannot be measured with the setup and as such should be taken into consideration when comparing results. However, all the results during the AST were taken without disassembling the cell and as such cell compression will remain constant, the membrane will swell from hydration but the membrane was hydrated prior to the AST and as such should not swell further. In both cases, before and after AST, it appears that the carbon plates exhibit a lower resistance. Furthermore the TiC plate appears to show signs of degradation as seen by the steep polarisation curve at 120 hours of AST. An increase in the concentration of oxygen however could not be seen from the EDX data, this is likely due to the Joel 6060 device used.

The AST carried out 80°C displayed a percentage decrease in performance at 0.60 V of 43.6% from the start to the end of the test. The 55°C test exhibited a 46.8% decrease in performance at 0.60 V. Between the two tests the difference is



(a)



(b)

Figure 7.4: TiC sample. a) Polarisation curves after 0, 12 and 120 hours of accelerated stress testing b) Nyquist plots from impedance measurements taken after 0, 12 and 120 hours of accelerated stress testing. All test carried out at 80°C.

3.2%, this would be considered within the range of error of the test. For the TiC *in situ* test there was no significant change in the rate of degradation of the TiC cathode plate with temperature. This is in contradiction to the *ex situ* testing that was carried out.

Table 7.2: Table of the EDX measurements carried out on the TiC bipolar plate before and after *in situ* AST. Measurements taken on both the land and channel for each operating temperature. Here the measurements taken for the plates tested at 80°C after AST were measured using the Joel 6060 device.

Element	Temperature	Before AST (wt.%)		After AST (wt.%)	
	(°C)	Land	Channel	Land	Channel
Al	55	7.7	30.3	10.7	42.3
	80			3.09	100
Ti	55	21.0	11.3	38.3	18.7
	80			1.4	0
C	55	64.9	55.8	41.1	35.9
	80			95.51	0
O	55	1.2	0.7	0.9	0.2
	80			0	0

7.3 Chromium Carbon

7.3.1 55°C Cell Testing

Figure 7.5 shows the first and last polarisation curves from the AST along with the MEA tests carried out with the graphitic plates before and after AST. The carbon plate began with a lower OCV compared to the the CrC plate. However the current density at 0.60 V was greater for the carbon plate with 1.17 Acm^{-2} compared to 1.09 Acm^{-2} for the CrC plate. From figure 7.5, it can be seen that the CrC test exhibited greater losses in the ohmic region than the carbon plates before AST. This suggests the CrC plate has a higher contact resistance than the graphitic plate. The OCV remained constant throughout the AST test with a value of 0.93 V. This suggests that there was little degradation to the membrane [211, 212].

Figure 7.6a) shows the polarisation curves collected at 0, 12 and 120 throughout the AST. Polarisation curves at 0 hours and 12 hours of corrosion testing display similar gradients but lower activation losses for the 0 hours curve. The 12 hour curve appears to display more mass transport losses. The high frequency resistance increase between the two curves from $13.8 \text{ m}\Omega$ at 0 hours to $16.3 \text{ m}\Omega$ at 12 hours, as can be seen in 7.1. This shows that the resistance of the cell has increased. The polarisation curve at 120 hours AST displays a similar gradient but greater losses in the activation region. Suggesting a higher charge transfer resistance in the the cathode, figure 7.6a) [206]. The EIS data from figure 7.6b) shows a small change in the HFR but large increases in the height and width of the semi circle. The width of the semicircle is indicative of the charge transfer

resistance which can be seen to increase throughout the AST. The increase in charge transfer resistance could explain the changes seen in the activation region of the polarisation curves. The HFR increased from 13.8 m Ω to 17.4 m Ω at 120 hours, indicating a loss of cell conductivity. The EDX measurements carried out on the land locations showed little change to the composition, suggesting that the increase in resistance is not due to the CrC coated cathode plate.

The performance of the cell at 0.60 V degraded with time as follows: 1.09 Acm^{-2} in the initial state, 1.02 Acm^{-2} after 12 hours and 0.925 Acm^{-2} at the end of AST. This meant that the performance of the cell degraded by only 15% throughout the degradation test. It is possible that the relatively unchanged surface meant that no ions leached from the plate and poisoned the membrane or catalyst layer, this results in less of a performance loss from the membrane.

Finally the MEA was tested in the graphitic plates after AST, the OCV for the cell was 0.9 V. The OCV was consistent throughout the AST. However, the polarisation curve displayed a steep gradient and quickly reaches a limiting current of 0.726 Acm^{-2} , as seen in figure 7.5. This value is less than 50% that of the 120 hours polarisation curve. It is possible that the MEA was damaged when it was moved between cells.

7.3.2 80°C Cell Testing

In figure 7.7 it can be seen that the MEA performance of the carbon plate was superior to that of the CrC plate. The current density at 0.60 V for the carbon plates was 1.48 Acm^{-2} compared to 1.09 Acm^{-2} for the CrC plate, and degradation

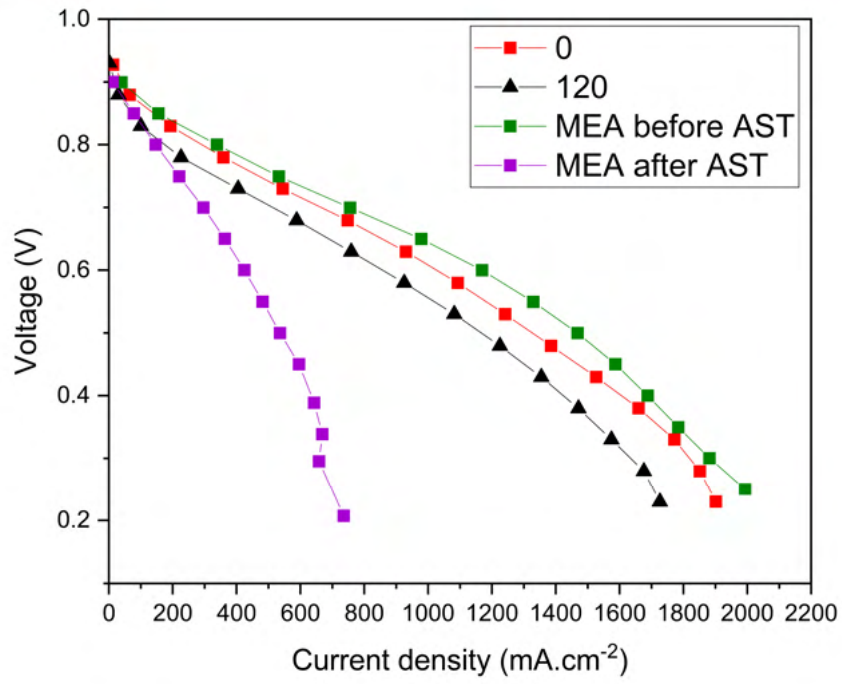
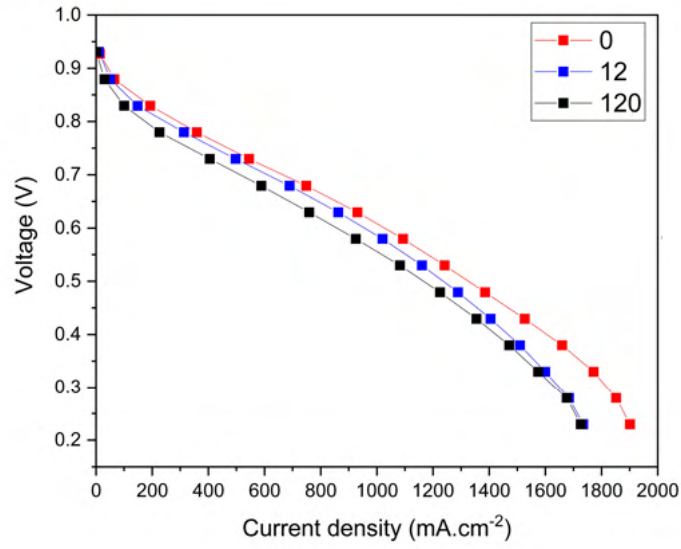
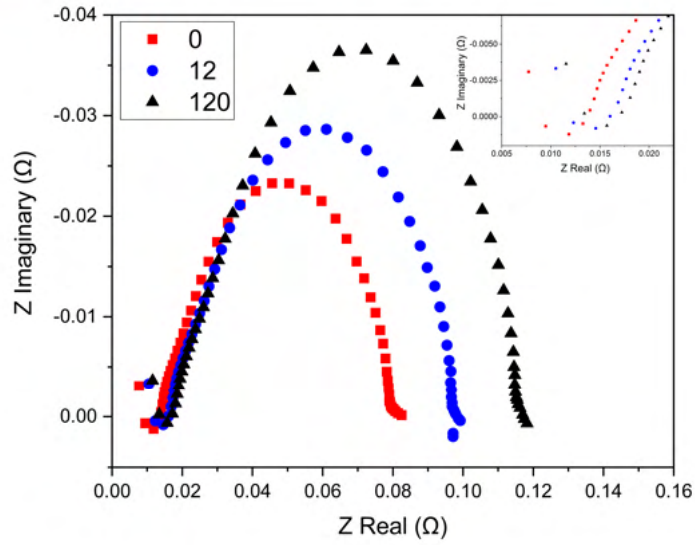


Figure 7.5: Polarisation curves of the CrC coated cathode plate after 0 and 120 hours of the accelerated stress testing with the curves from the same MEA tested with carbon plates before and after the AST. All tests carried out at at 55°C .



(a)



(b)

Figure 7.6: CrC sample a) Polarisation curves after 0, 12 and 120 hours of accelerated stress testing b) Nyquist plots from impedance measurements taken after 0, 12 and 120 hours of accelerated stress testing. All tests carried out at 55°C.

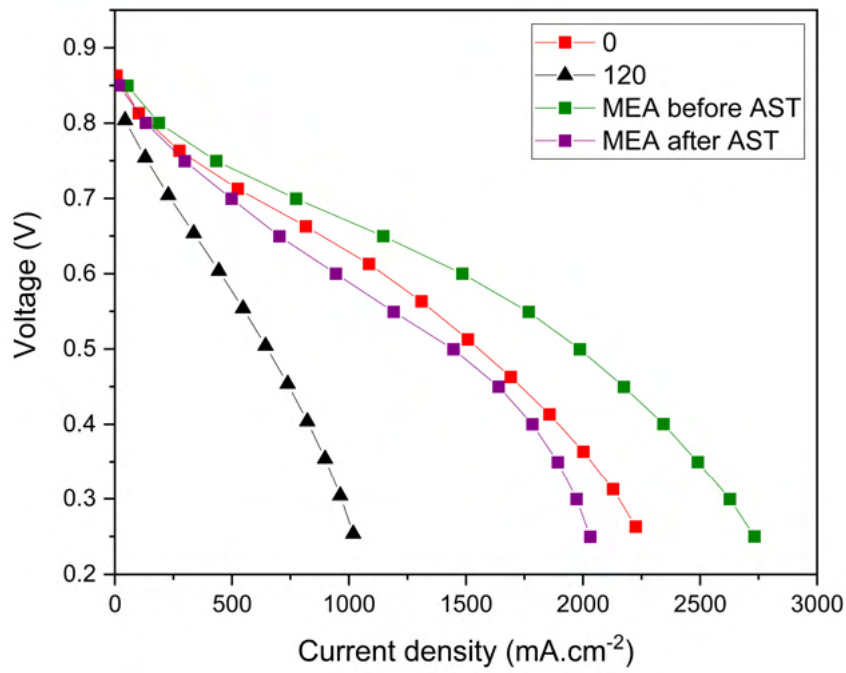


Figure 7.7: Polarisation curves of the CrC cathode plate after 0, 12 and 120 hours of the accelerated stress with the curves from the same MEA tested with carbon plates before and after the AST. All tests carried out at 80°C .

Table 7.3: Table of the EDX measurements carried out on the CrC bipolar plate before and after *in situ* AST. Measurements taken on both the land and channel for each operating temperature. Here the measurements taken for the plates tested at 80°C after AST were measured using the Joel 6060 device.

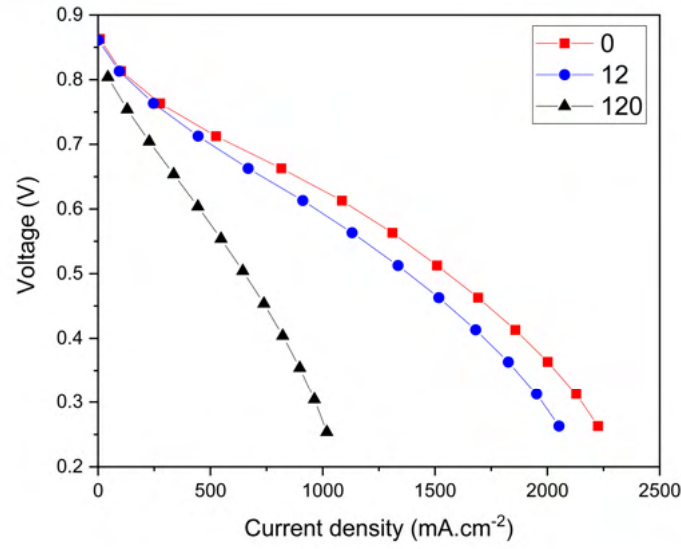
Element	Temperature	Before AST (wt.%)		After AST (wt.%)	
	($^{\circ}\text{C}$)	Land	Channel	Land	Channel
Al	55	0.7	15.8	0.60	14.8
	80			1.6	51.85
Cr	55	48.6	41.0	48.2	41.8
	80			2.14	48.15
C	55	47.6	41.6	47.7	41.9
	80			78.39	0
O	55	0.1	0.4	0.60	0.3
	80			17.87	0

could be observed after 12 hours. In figure 7.8a) it can be seen that the performance degrades between 0 and 12 hours, this suggests the MEA was hydrated, it also suggests degradation of the cell. The current density at 0.60 V decreased from 1.09 Acm^{-2} to 0.91 Acm^{-2} in the first 12 hours of AST. From table 7.1 it can be seen that the HFR increased by $1 \text{ m}\Omega$ over this time. The HFR increased to $27.8 \text{ m}\Omega$ after 120 hours of AST. The current density decreased to 0.444 Acm^{-2} .

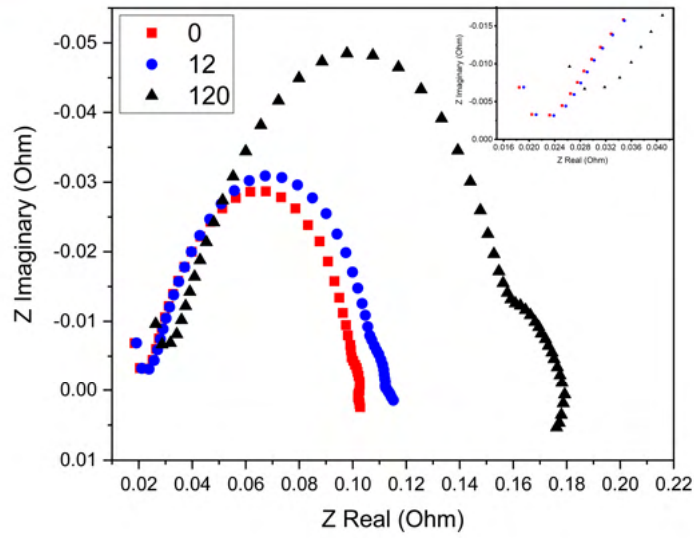
The degradation of the cell can be attributed to both the bipolar plate contact resistance increasing and MEA degradation. The charge transfer resistance

increased between 12 and 120 hours of AST, as seen by the increase in diameter of the semicircle present in figure 7.8b). The increase in HFR could be attributed to the oxidation of the bipolar plate, this is seen in table 7.3 where the oxygen content of the land increased to 17.9%. Oxidation would increase the ohmic resistance due to the increased interfacial contact resistance between the plate and the GDL. For the other samples oxygen was not detected when using the Joel 6060 device. It was thought that the sensitivity of the device or beam strength was responsible for the lack of oxygen detection. This suggests that excessive oxygen would need to be present in order to be detected. The channel did not indicate the presence of oxides.

The MEA was tested with carbon plates after AST, shown in figure 7.7. It can be seen that the cell performance is greater with the carbon plate. The performance loss at 0.60 V between the two polarisation curves carried out with a carbon cathode was 36% whereas the performance loss throughout the AST using the CrC plate was 59%. This indicates that a large amount of the performance loss was associated with the CrC cathode plate. The HFR for the CrC plate after 120 hours of AST at 80°C was the highest seen throughout testing.



(a)



(b)

Figure 7.8: CrC sample. a) Polarisation curves after 0, 12 and 120 hours of accelerated stress testing b) Nyquist plots from impedance measurements taken after 0, 12 and 120 hours of accelerated stress testing. All test carried out at 80°C.

7.4 Titanium Gold

7.4.1 55°C Cell Testing

Figure 7.9a) shows the polarisation curves collected during the 55°C AST test of the TiAu coated plate. It can be seen that the performance of the cell increases between the initial state and 12 hours after the start of the AST test. An increase in performance could also be seen in figure 7.9b) where the charge transfer resistance decreased, recovery was likely due to changes in the catalyst layer. The HFR of the sample also decreases by 0.5 $m\Omega$. This suggests insufficient humidification of the membrane at the start of testing.

In figure 7.10 the performance of the 12 hour polarisation curve was plotted in place of the initial curve as it was the highest performance achieved with the TiAu plate at 55°C. This was done as the gains were likely related to the MEA hydration rather than a feature of the TiAu cathode plate. The performance difference between the cell with carbon plates and TiAu plates were minimal, the OCV for each was 0.90 V and 0.93 V respectively. The most significant difference occurred in the ohmic region where the TiAu plate out performed the carbon plate, figure 7.10. This is indicative of lower ohmic resistance, which could be the result of lower contact resistance between the plate and the GDL. Although, it is possible that the MEA was never fully conditioned when using the carbon plate and this limited performance.

The OCV of the cell was stable throughout the degradation test with an initial value of 0.93 V which decreased to 0.92 V at 120 hours. Suggesting mem-

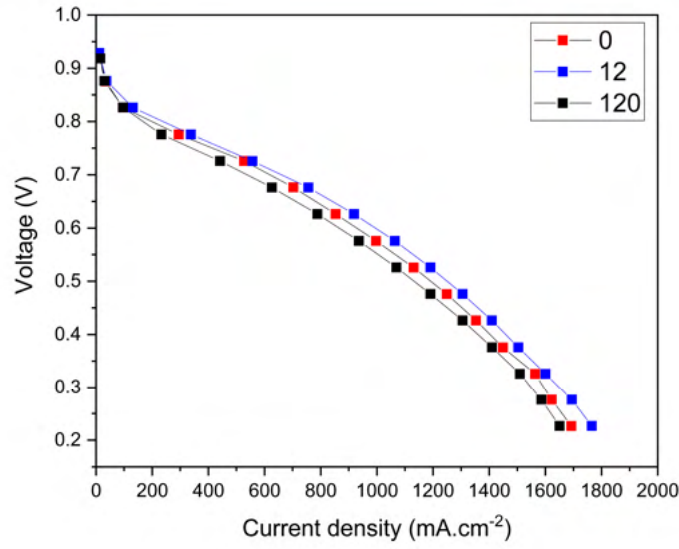
brane stability throughout the test. The current density at 0.58 V was as follows 1.00 Acm^{-2} , 1.06 Acm^{-2} and 0.94 Acm^{-2} for the initial, 12 hour and 120 hour states respectively. The performance between the initial and 12 hour state displays an increase, suggesting that the membrane was not fully conditioned. The performance loss at 0.58 V was 6.1% suggesting only a minor loss in performance. Figure 7.9b) suggests the performance loss is due to the change in charge transfer resistance. Furthermore the polarisation curves appear to be parallel in figure 7.9a) from around 0.75 V (outside of the activation region). This suggests that the resistance of the cell and the mass transport losses are not degrading throughout the test.

The degraded MEA was tested with the carbon plate, an OCV of 0.90 V and a current density of 0.79 Acm^{-2} at 0.60 V (0.89 Acm^{-2} at 0.55 V) was measured. The end of AST performance of the MEA with the gold plate displayed a superior OCV, of 0.92 V, and a superior current density of 0.94 Acm^{-2} . Suggesting that much of the degradation of the cell was in the MEA.

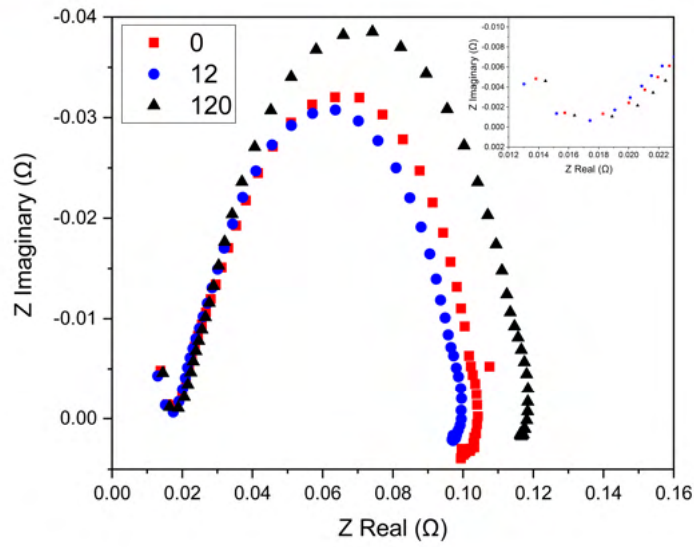
The HFR increased from 18 m Ω to 19.2 m Ω over the AST. Total cell degradation resulted in a 1.2 m Ω increase in resistance. The degradation of the MEA shown by the cell test with carbon plates after AST, suggests little degradation to the TiAu coated plate. The EDX data shown in figure 7.4 shows a high concentration of gold on the land; initially at 11.2%. Gold is critical for both reducing the contact resistance and increasing the corrosion resistance of the plate. The channel shows a lower concentration at 5%, this will be due to the recessed nature of the channel limiting deposition in these areas.

After the AST it can be observed that the gold concentration on the land

decreased to 4.49%, it is possible that little gold was lost. Oxidation of the plate had occurred which resulted in the composition changing, with oxygen representing a larger proportion. At the initial state the land surface of the plate consisted of 1.2% oxygen, this increased to 17.69% after the test. The cell exhibited an increase of 1.2 m Ω throughout the AST, therefore the oxidation of the plate did not result in a large increase in ohmic resistance of the cell. Oxidation of the channel also occurred. However, the effect on performance from the oxidation of the channel is not well understood. The channel is not responsible for interfacial conductivity of the plate and as such will affect performance less than oxidation of the land. Corrosion resistance of the channel is still of importance as metal leaching can adversely affect the membrane [213].



(a)



(b)

Figure 7.9: TiAu sample. a) Polarisation curves after 0, 12 and 120 hours of accelerated stress testing b) Nyquist plots from impedance measurements taken after 0, 12 and 120 hours of accelerated stress testing. All test carried out at 55°C.

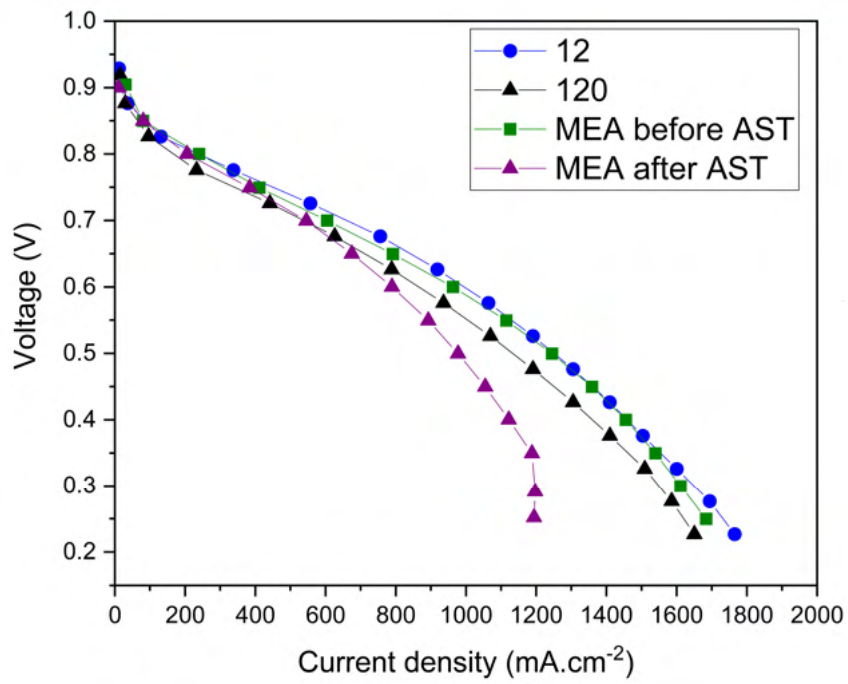


Figure 7.10: Polarisation curves of TiAu after 12 and 120 hours of the accelerated stress with the curves from the same MEA tested with carbon plates before and after the AST, all at 55°C .

7.4.2 80°C Cell Testing

In figure 7.11 it can be seen that the initial performance of the MEA was superior in with the TiAu plate. This performance increase can be seen in both the activation and ohmic region of the polarisation curve. Figure 7.12a) displays the polarisation curves collected during the AST. An error occurred during the 12 hour polarisation curve which affected the result, this did not occur at 24 hours. As such the 24 hour curve was used for analysis. The 24 hour curve displayed recovery relative to the 12 hour curve, the cell was not rebuilt in this time and as such changes to the cell were not expected, it is possible the reactant supply was interrupted during the polarisation test carried out after 12 hours.

In figure 7.12a) the loss of performance between the initial condition, 24 hours and 120 hours AST can be seen. The performance of the cell quickly declined, the loss in performance was observed in the EIS measurements, displayed in 7.12b). The HFR of the cell increased from 9.8 mΩ to 22.8 mΩ after 24 hours, the increase in resistance was responsible for some of the loss in performance of the cell. The HFR increased to 25.1 mΩ at 120 hours AST. Displaying an increase in resistance but at a slower rate than the first 24 hours. It could be possible that the plate passivates which decreases the rate at which performance is lost. This could not be proven by EDX however due to no oxygen being detected in the channel or land. This is thought to be due to the high beam strength penetrating deep into the sample, resulting in only a weak signal of the thin surface layer.

Beam strength has been found to vary the penetration and therefore the signal of the measured sample [161, 214]. Reneau et al. found that a 30 kV electron beam penetrated 2 μm in a sample of rock, whereas an accelerating voltage of 10 kV

penetrated $0.5\ \mu\text{m}$ [214]. Lee et al. wrote a monte carlo simulation to identify the dependency of penetration on accelerating voltage. In Al samples the penetration of the electron beam can be doubled by increasing the beam strength from 10 kV to 15 kV, this would result in a penetration of $1\ \mu\text{m}$ and $2\ \mu\text{m}$ respectively [161]. The Joel6060 device utilises a 30 kV electron beam compared to the 15 kV electron beam used in the Hitachi desktop SEM. This change in beam strength is likely the reason that the surface compositions cannot be identified on the plates tested at 80°C plates.

The current density of the plates at 0.58 V decreased throughout the test, seen in figure 7.12a). The initial performance of the the cell at 0.584 V was $1.84\ \text{Acm}^{-2}$, this reduced by 46% by the 24 hour mark to $0.99\ \text{Acm}^{-2}$. The reduction from initial to 120 hours of AST was 61%. With a final current density of $0.72\ \text{Acm}^{-2}$ after 120 hours of AST. The rate of performance loss decreases throughout the test. The same MEA however only displayed a 34% loss in performance when tested with the carbon plates before and after AST. This shows that the bipolar plate had degraded through the test.

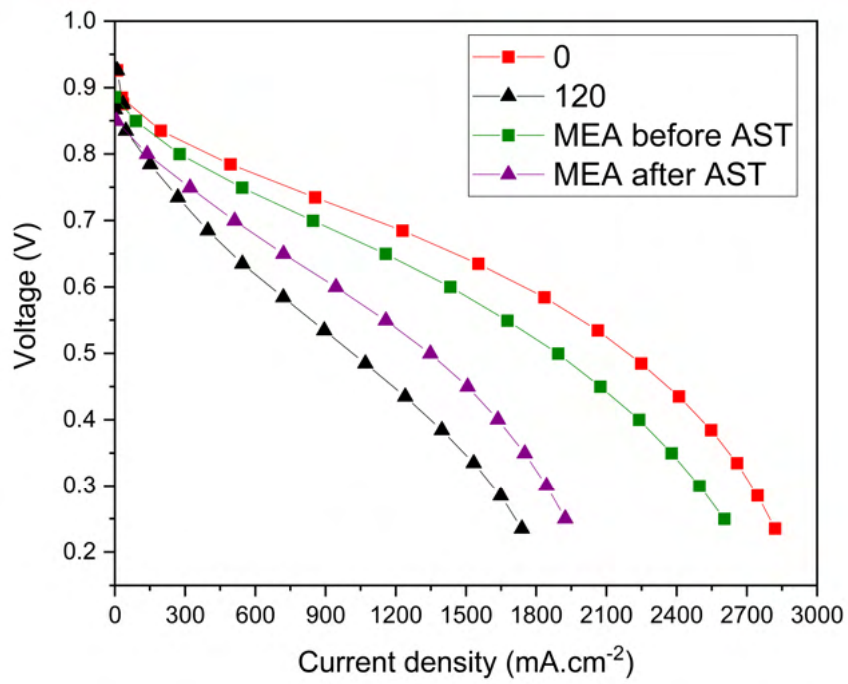
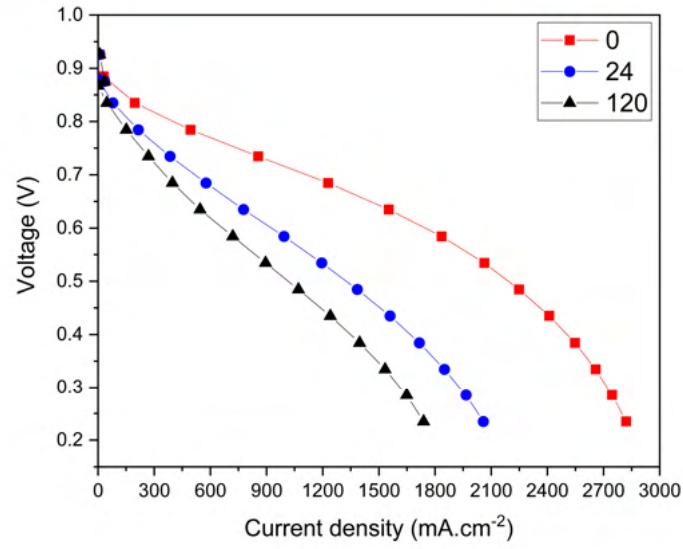
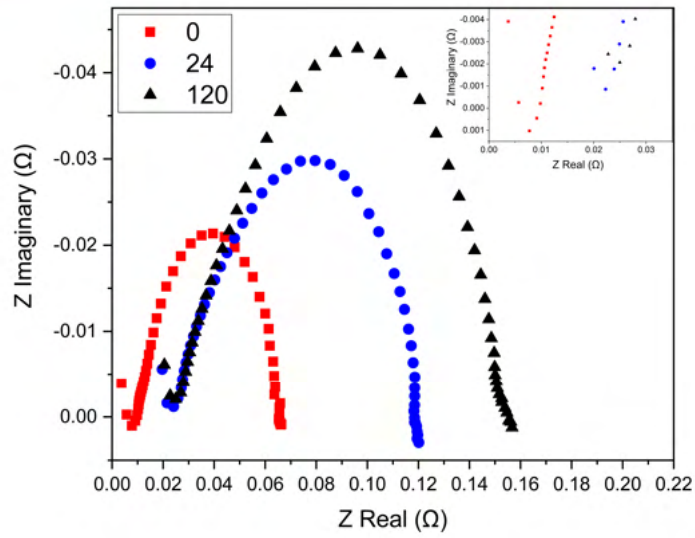


Figure 7.11: Polarisation curves of TiAu after 0, 12 and 120 hours of the accelerated stress with the curves from the same MEA tested with carbon plates before and after the AST, all at 80°C.



(a)



(b)

Figure 7.12: TiAu sample at 80°C. a) Polarisation curves after 0, 12 and 120 hours of accelerated stress testing b) Nyquist plots from impedance measurements taken after 0, 12 and 120 hours of accelerated stress testing.

Table 7.4: Table of the EDX measurements carried out on the TiAu bipolar plate before and after *in situ* AST. Measurements taken on both the land and channel for each operating temperature. The measurements taken after the 80°C AST were carried out using the Joel 6060 device.

Element	Temperature	Before AST (wt.%)		After AST (wt.%)	
	(°C)	Land	Channel	Land	Channel
Al	55	33.2	70.3	55.99	58.7
	80			75.85	100
Ti	55	55.0	24.3	21.82	21.9
	80			24.15	0
Au	55	11.2	5.0	4.49	4.3
	80			0	0
O	55	1.2	0.5	17.69	15.1
	80			0	0

7.5 Conclusion

Al6082 cathode BPPs have been prepared using CNC manufacturing. Coatings were successfully deposited using a plasma vapour deposition technique. It has been shown that despite the recessed nature of the channels the coating was still applied in these regions, albeit at reduced levels. Therefore it is possible that coatings can be successfully applied post plate forming, using line of sight deposition techniques.

Beginning of life performance (BOL) of the TiAu sample exceeded that of the graphitic bipolar plate highlighting the opportunity for increased performance of metallic coated materials over graphitic BPPs. Depending on the conditions the TiC and CrC samples could effectively match the BOL performance of the carbon plate also. If aluminium bipolar plates were utilised in a stack, the volumetric power density of the system could be increased relative to a system using carbon plates. The gravimetric power density could be increased relative to stainless steel bipolar plates.

However, end of life testing highlights the durability issues faced by metallic materials. At 55°C the TiAu and CrC plates displayed a small degradation in performance over the AST, with each showing a loss in performance of 6.1% and 15%, respectively. This includes degradation of the catalyst and membrane, which typically use similar duty cycles to accelerate degradation. At 80°C the TiAu sample out performed the the carbon plate at all current densities, this was not the case however after AST. Transferring the MEA back into the single cell tester using carbon bipolar plates highlighted the degradation of the MEA. The validity

of this test could have been improved with the use of a baseline sample. A baseline MEA should undergo the same AST test used for the aluminium BPPs. The MEA should then be removed and replaced back into the cell to investigate the change in performance caused by disassembly. This was not done as part of this work due to test stand availability and lack of commercial MEA supply. In addition further analysis could be carried out, such as: hydrogen crossover for membrane degradation and cathode CV testing for active area changes. The MEA could also be analysed using XRF to investigate metal leaching.

The plates displayed signs of performance loss in the cell but upon SEM and EDX analysis the substrate appeared to be far less corroded than the samples from *ex situ* testing. Highlighting the discrepancy between *in situ* and *ex situ* testing.

Coatings require optimisation due to the performance losses observed in this work. In addition difficulties were encountered when switching the MEAs between cells. With some results suggesting the MEA became damaged. Furthermore the repeatability of the testing has not been validated, the MEA performance differed greatly between samples when using the graphitic carbon plate. For this reason direct comparisons of the cell performance could not be made and percent changes were used. To increase the value of this work and the results, repeats should be carried out.

Chapter Eight

Conclusion

Bipolar plates present an opportunity to decrease costs and increase performance in PEM fuel cells. Material choices will be made upon the requirements of the application. The contact resistance and corrosion resistance of conductive polymer coatings were both improved relative to literature. Coatings achieved DoE corrosion current targets. The contact resistance was reduced but was still greater than DoE targets. In addition coatings were not competitive with alternative coating methods and materials. Considerable literature around polymer coatings for PEM fuel cell BPPs exist, none however achieved DoE contact resistance targets. In addition, aniline (the monomer of polyaniline), has many hazard statements including: toxicity, potential to cause an allergic reaction, causes serious eye damage and is suspected of causing both genetic defects and of causing cancer, among other hazards [155]. For this reason widespread adoption of the coating is unlikely due to the risk to both human and environmental safety. Moreover the coating did not prevent the formation of surface oxide on the metal sample. *Ex situ* testing showed that end of life performance of the plate would be unacceptable for industry requirements.

316 stainless steel was selected as a substrate for the polymer coatings. Stainless steel has been incorporated into commercial fuel cell systems, with carbonaceous PVD coatings. This work highlights that polymer coatings do not

currently provide competition to PVD coatings.

Aluminium is 40% as dense as stainless steel. By utilising aluminium the mass of stacks could be reduced. Aluminium was selected due to its low density and lower material cost as compared to titanium, another lightweight metal. High purity aluminium, 99.0%, was coated with TiN, CrC, TiC and two TiAu coatings with different gold loadings. All coatings reduced the contact resistance of the substrate. The CrC, thin and thick gold coatings achieved ICR values of 4.34, 3.36 and $1.05\text{ m}\Omega\text{cm}^2$ respectively, this exceeded the DoE target and displayed an improvement on the PANI TiN bilayered coatings.

All layers exhibited pitting corrosion with dissolution of the substrate occurring. The CrC sample exhibited the lowest corrosion current at all times throughout the 80°C corrosion test and up to 1 hour in the 55°C corrosion test. In addition the ImageJ analysis of the post mortem SEM images showed that the CrC sample displayed the smallest defect area.

The interlayer thickness was not determined in this work but EDX data shows large differences in the intensity of the signal for interlayers. In literature the thickness of PVD layers has been shown to be inversely correlated with pin hole defect density. The TiN and CrC samples exhibited the highest elemental intensities of the interlayers. The TiN sample however displayed cracks across the surface which could be responsible for the increased rate of corrosion relative to the CrC sample. In literature TiN has been identified to form a columnar structure, which leads to pores in the layer. Pores would allow for corrosive electrolyte to reach the aluminium substrate [215, 216]. The CrC sample did not display this same surface morphology. Therefore limiting the electrolyte penetration to the

surface. This work could have been improved with the addition of masking of the sample before coating. After coating, the mask could have been removed. Interferometry or stylus profilometry could then have been used to measure the step change between coated and uncoated regions. This was not possible during the work due to the coating being applied by an external company.

Pure aluminium was used in this work to investigate relatively low cost and lightweight materials. Pure aluminium however would not be used in the automotive or aerospace industry due to the superior properties of aluminium alloys. Thus TiC, CrC and TiAu coatings were coated on to a common automotive grade of aluminium, Al6082.

It was established that the uncoated aluminium alloy Al6082 more readily corrodes than the uncoated pure aluminium. This was attributed to the galvanic couples formed by the aluminium and alloyed elements in Al6082. TiC, CrC and TiAu coatings on Al6082 all resulted in lower ICR than the same coatings on the 99.0% pure aluminium substrate. The contact resistances of which were all below DoE targets, in the range of 1 to 5 $m\Omega cm^2$.

The corrosion currents of these materials were all in excess of the DoE target. Literature has shown that surface pretreatment and interlayer thickness can be optimised to decrease coating defects. Both of which could be investigated as ways to increase the corrosion resistance of PVD coated Al6082.

Literature had demonstrated that *ex situ* test conditions do not accurately replicate the conditions found in *in situ* tests. To validate PVD coatings on aluminium, samples should be tested *in situ*.

Al6082 single cell cathode plates were produced using CNC manufacture, plates were coated post forming. Coating was achieved on both land and channel regions. Reduced loading was detected in the channel. At 55°C the TiAu sample achieved performance parity with the graphitic carbon plates at beginning of life. The TiAu plates at 80°C out-performed the graphitic carbon plate at beginning of life. Demonstrating the opportunity for metallic plates to increase the power density of the system.

The end of life performance of the TiC and CrC samples show significant degradation of both the MEA and bipolar plate at both conditions. The TiAu and CrC sample displayed little degradation throughout the 55°C AST. In addition the TiC sample at 80°C is comparable at end of life to the carbon plate with the same degraded MEA. SEM analysis of the plates post AST showed little degradation when compared to the *ex situ* results of the previous chapter. This shows that *ex situ* testing does not sufficiently reflect the results of *in situ* testing.

8.1 Future Work

Polyaniline coatings are unlikely to be adopted by industry due to the hazards associated with the aniline monomer and high contact resistances of the coating. Therefore further investigation of this coating is of little value.

Future work should solely focus on aluminium alloys as 99.0% aluminium is not a viable material for bipolar plates. TiAu coatings displayed low contact resistances and was an effective barrier to corrosion in the *in situ* environment. Typically this coating would be ruled out by *ex situ* corrosion tests due to the high

current densities and sample dissolution observed, highlighting the necessity to investigate new *ex situ* accelerated stress tests that are more closely aligned with the electrochemical degradation observed from *in situ* testing. Multiple *ex situ* accelerated stress tests that mimic systems may be necessary to screen materials for specific use cases.

Transition layer thickness was identified as a key feature for the performance of coatings. This work failed to measure the coating thickness. A study to investigate a correlation between the number of pits and the transition layer thickness should be carried out. This study could identify if a minimum thickness of coating is required to prevent aluminium substrate dissolution. Material and production costs could be minimised by targeting the minimum layer thickness. In addition, defect density of coatings could be investigated by adjusting the substrate pretreatment. Pretreatment could include different chemical or mechanical polishing techniques, targeting different level of surface roughness. Ion cleaning is used to remove surface oxides. This step should be minimised while maintaining adequate oxide removal. Thereby minimising production costs.

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