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Titanium Nitride Polyaniline Bilayer Coating for Metallic Bipolar Plates used in Polymer Electrolyte Fuel Cells

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Abstract

Two materials, polyaniline (PANI) and titanium nitride (TiN), used for bipolar plate coatings (BPP) have each shown promise in improving the corrosion resistance and contact resistance, respectively, of metallic bipolar plates. 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's 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 coating 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. The optimized coating achieved DoE targets with potentiostatic corrosion currents of $\sim 0.024 \mu\text{Acm}^{-2}$ and ICR values of $11.2 \text{ m}\Omega \text{ cm}^2$. PANI polymerization was confirmed using FTIR and TiN loadings were investigated with EDX.

Keywords

Polymer electrolyte fuel cell (PEFC), Bipolar plate (BPP), Coating, Composite layer, Composite polymers, Polyaniline, Titanium Nitride (TiN)

1. Introduction

Transportation accounts for 14% of all greenhouse gas emissions on the planet, new renewable technologies for use in the transportation sector are being investigated at ever increasing rates in the hope of stifling carbon emissions [1]. Vehicles powered by hydrogen in an electrolytic fuel cell are one option to prevent the carbon emissions of vehicles. Hydrogen fuel cells produce a DC electrical current by electrochemically reacting gaseous hydrogen with air or more specifically oxygen [2]. A hydrogen fuel cell stack is comprised of many individual fuel cells connected in series via bipolar plates (BPPs). BPPs provide structural support for the cell, electrical conduction for the electrons, deliver the reactant gases to the cell and remove the produced water out of the cell. BPPs have also been used to aid in heat rejection from the cell whereby intermittent cells in a stack can be machined with cooling channels. Both the GDL and bipolar plate work to remove the produced water from the cell, poor removal of water can lead to flooding which reduces the cell's performance and efficiency. BPPs account for about 80% of the weight, most the volume and 45% of the total cost of a PEFC stack, making cost reduction of BPP essential for commercial viability [3-5].

Traditionally BPPs have been made from high density graphite. Graphite provides excellent corrosion resistance and has a very low interfacial contact resistance with the carbon paper used as a GDL. However graphite is costly to process and machine, it is brittle and thick plates are required to provide the necessary mechanical requirements of the stack [6]. Researches are searching for potential replacements for graphitic plates with metallic substrates being readily investigated. Stainless steels and other metallic materials such as; aluminium and titanium have seen much research due to their superior properties in terms of material costs, manufacturability, mechanical properties and electrical conductivity [7, 8]. The use of metallic materials allows for the production of thinner plates, thereby improving the volumetric power density of the fuel cell stack [6, 9]. Metallic BPP's also have good thermal conductivity which is essential for the thermal management of high power stacks [10, 11].

Metallic plates however do suffer in the high potentials and acidic environment found in the PEFCs (pH's of 3.4 and transient potentials reaching 0.8V [12]). A passive oxide layer forms on the surface of the stainless steel in the presence of oxygen, which although offers additional corrosion protection in aggressive environments [13], it causes the contact resistance to greatly increase, reducing the performance of the stack. For this reason, coatings for metallic bipolar plates that provide an effective barrier to the harsh conditions have seen extensive research. Moreover coatings need to achieve and maintain a low contact resistance as to avoid electrical losses in the stack. BPPs are expected to have an ICR of less than $10 \text{ m}\Omega\text{cm}^2$ and cathodic corrosion resistances of less than $1 \mu\text{Acm}^{-2}$ according to the DoE 2020 targets [2]. Coatings of SS plates need to achieve these performance targets, if PEFC stacks are to be commercially viable.

As metallic BPPs alone do not satisfy DOE targets, research has focused on coating development to improve both the corrosion properties and interfacial contact resistance. Many different techniques exist for applying coatings, including; physical vapour deposition (PVD), chemical vapour deposition (CVD), electroplating and electrophoretic deposition [14-17]. When comparing the coating methods in terms of scalability and cost, it can be noted that physical and chemical vapour deposition methods require batch production which could limit mass production and increase cost [18]. Electroplating and electrophoretic deposition are two such techniques which can be used as part of a

continuous production line, and both of which can provide uniform coatings on complex shapes [19].

Progress in the development of metallic BPPs by coating them with transition metal nitrides was reported in the literature [11, 20, 21]. Metal nitrides, most notably chromium nitride and titanium nitride [21-23], have been investigated due to their effective corrosion protection and improved interfacial conductivity. Group 4 (periodic table) metal nitrides, namely titanium, are typically used for coatings on cutting tools due to their hardness and their chemical and thermal stability [24, 25]. Titanium remains metallic in the nitride matrix due to the electron structure in the metals d-orbital, the metallic structure results in titanium nitride showing good electrical conductivity [25]. Furthermore, the resistance to oxidation results in TiN maintaining its conductivity in the aggressive conditions such as those found in PEFCs. Deposition of titanium nitride in industry is typically achieved via PVD although other methods involving CVD or plasma nitriding are also popular [26]. Pugal Mani coated 316L with TiN, TiAlN and a composite layer of TiN/TiAlN via a cathodic arc evaporation system [20]. The TiN sample showed adequate corrosion potentials and low corrosion currents. The TiN also showed the lowest ICR with values around $1\text{m}\Omega\text{cm}^2$.

In addition, vast research has been committed to conductive polymers for PEFC BPP coatings because of their chemical stability and their relatively high conductivity and redox functions [27, 28]. Polymers also offer low cost in terms of application processes and materials. Polyaniline and Polypyrrole are two such conductive polymers. Both are chemically stable and researchers have found that polymer coatings can reach corrosion current requirements of PEFCs in *ex-situ* corrosion tests, effectively providing a barrier for the BPP [29, 19]. Joseph et al reported that the increased thickness of the polyaniline coating leads to increased pin hole defects [30]. Thicker coatings also increase the ICR of the samples. Polymer coating can be applied by employing various methods, for instance; Joseph et al. painted polyaniline onto the surface of the substrate by dissolving the polyaniline in xylene [31, 32] whereas electrochemical polymerization was used by other researchers to apply the polymer coating [12, 20, 31, 33]. However the interfacial contact resistance between polymer coatings and GDL's is high and results in high electrical losses.

In order to combine the benefits of multiple materials, composite bilayered materials were developed. Zhang et al chose polyaniline due to its excellent corrosion properties and looked to improve upon its poor conductivity by combining the coating with gold nanoparticles and carboxyl group functionalised carbon nanotubes [34]. The composite coating satisfied DoE corrosion targets and had a much reduced ICR of $16.6\text{m}\Omega\text{cm}^2$, thereby showing how the combination of coatings can symbiotically improve the coating. Surbhi et al also used a polymer coating, which was doped with titanium nitride (TiN) [29]. This coating also produced an effective barrier to corrosion products that satisfied DoE corrosion targets. ICR values of the composite polymer coating were also reduced relative to pure polymer coating.

This work looks to further the development of polymer-metallic composite coatings by optimizing a thin titanium nitride (TiN) polyaniline composite layer using low temperature plating solutions. This was then modified to produce a bilayered coating with an electrodeposited surface layer of TiN. The coatings were characterized to confirm the deposition of PANI and TiN, and then examined for their corrosion resistance and ICR. The aim here is to reduce the ICR achieved in the literature to values within the DoE target while maintaining the reported corrosion resistance.

2. Experimental

2.1 Coating process

An electroplating three-electrode cell was designed and 3D printed using TinkerCAD software and a MakerBot Replicator 2 FDM printer respectively. Two platinum mesh counter electrodes were used to get a homogenous coating on both sides of the sample simultaneously. The AISI 316 stainless steel (SS) sample (30x50 mm) is placed in the centre housing equidistant from the two counter electrodes with the reference electrode fixed to the edge of the cell. The SS sample is the working electrode in the three electrode setup. A silver/silver chloride was used as a reference electrode for this work.

Before coating, the samples were first wiped with ethanol to remove grime off the surface. They are then acid washed in 50% sulphuric acid solution to remove the passivation layer on the SS surface, after 10 minutes the samples were removed and immersed in deionized water, rinsed and dried under a nitrogen stream.

The coating electrolyte was prepared in a 0.1M sulphuric acid solution. Aniline monomer (Sigma Aldrich) concentration was fixed at 0.1M, and TiN nanoparticles (SkySpring Nanomaterials Inc. (97+% purity and 20nm particle size)) were added for the composite coating, the loading was set at 0.5gL^{-1} . The solution was sonicated for 10 minutes and then cooled to a temperature of 5°C in an ice bath, then shaken by hand, 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). Static potentials were also used to create a TiN surface layer (in the bilayer coatings). A list of samples and coating parameters are shown in table 1. For the CV cycles, the potential was swept from -0.18 to $+1.00$ $\text{V}_{\text{Ag}/\text{AgCl}}$ at a scan rate of 50mVs^{-1} and a potential step of 5mV for 5 cycles. After plating, samples were removed from the cell, rinsed with DI water and then dried under a nitrogen stream.

Table 1: Samples and their coating procedure

Sample name	CV cycles	Time potential held static at 0.5V / s
Bare SS	0	0
PANI	5	0
PANI 150s	5	150s
PANI TiN	5	0
PANI TiN 150s	5	150s
PANI TiN 300s	5	300s
PANI TiN 450s	5	450s
PANI TiN 600s	5	600s
TiN 600s	0	600s

2.2 Coating characterization

2.2.1 Fourier-transform infrared (FTIR)

FTIR spectroscopy measurements were carried out to confirm the electropolymerisation of aniline using a Bruker Lumos device in the reflectivity setup. The ATR crystal was wiped clean before every measurement and background scans were carried out using 64 scans on the gold reference plate. For the 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, using the solutions reported in section 2.1. 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.

2.2.2 Energy dispersive X-ray (EDX)

EDX measurements were carried out using a JOEL JSM6060LV scanning electron microscope (SEM) equipped with EDX. A 5kV beam was used to achieve surface measurements to quantify the surface loading of titanium of the samples.

2.3 Interfacial contact resistance

The ICR measurements were taken between the samples and two gas diffusion layers (Toray 60) following the method described in [29]. An Instron 584 microtester was used to control the compression force on the samples. The carbon paper GDL's are pre-cycled by compressing to 300Ncm^{-2} between two gold plated copper pins with a surface area of 1cm^2 and then cycling between 250N and 300N for 2 hours at a rate of 50Ns^{-1} . Pre-cycling is conducted as the GDL's have irregular compressible behaviour which can alter the measured ICR values [35].

SS samples are placed between two pre-cycled GDL's, this is then loaded onto the microtester between the two plated pins. The samples are then compressed from 20 to 300N in 20N steps, 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 ICR value is then calculated from the overall measured resistance as explained in [29]. The ICR was measured for the samples before and after the corrosion test to assess the stability of the coating.

2.4 Electrochemical corrosion

Metal samples were loaded into the corrosion three-electrode electrochemical cell with a sample exposed area of 1cm^2 . A pH3 sulphuric acid solution is used as an electrolyte and the cell temperature was maintained at 80°C to simulate the PEFC environment. Reference and counter electrodes of mercury/mercury sulphate (MSE) and platinum mesh respectively were used. The cell was then connected to the potentiostat (IVIUM compactstat). A potentiodynamic test was then carried out in nitrogen atmosphere by means of linear sweep voltammetry; sweeping the potential from -0.5 to $1V_{\text{SHE}}$ at a sweep rate of 10mVs^{-1} for 11 cycles. This experiment was then repeated after the potentiostatic corrosion test. After the LSV the gas line was swapped to bubble the solution with air for 20 minutes in preparation for the potentiostatic corrosion test. Amperometric detection was used to hold a constant potential of $0.9V_{\text{SHE}}$ for 24 hours.

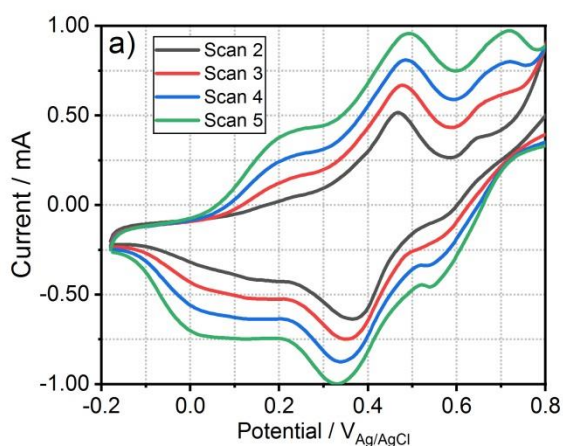
3. Results and Discussion

3.1 Coating and Characterisation

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 [29]. The reduced porosity enhances the corrosion resistance of polyaniline coatings. Previous work showed thicker coatings cause a more porous structure [20]. By controlling the temperature and initiating electroplating experiments at 5°C , thinner coatings can be achieved. The CV scans carried out at 5°C didn't show the traditional peaks seen in

electropolymerisation of aniline. Figure 1a shows the CV cycles produced in a solution of 0.1 gL^{-1} TiN and 0.1M aniline at 25°C . The peaks observed here are due to the higher number of reactions 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 weren't observed at 5°C because the current flowing was minimal. Three redox peaks can be seen within the CV potential window (-0.18 and $1V_{\text{SHE}}$) 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 $0.5 V_{\text{SHE}}$. 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 [29]. It is possible that the TiN gets trapped in the structure as the aniline polymerises, another possible mechanism could be the TiN electrophoretically depositing at sites across the PANI surface, claiming nucleation sites and slowing the polymerisation of the PANI. The surface layer of TiN was achieved via holding a static potential of 0.5V .

Figure 1b shows the FTIR spectrum of the 25 cycle PANI and 25 cycle PANI TiN. The intensity of the peaks is indicative to the amount of substance present. 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 the TiN could encourage the nanoparticle to deposit at these sites. The peak observed at around 700cm^{-1} is typically attributed to stretching of the Sulphur Oxygen double bond [36]. The PANI was polymerized in sulphuric acid which can cause the PANI coating to be doped with sulphate ions. The peaks at 823cm^{-1} and 1149cm^{-1} show the out of plane vibration and in-plane vibration of the carbon hydrogen bond, 1149cm^{-1} also corresponds to the vibrational mode of the positively charged nitrogen hydrogen structure present in PANI [37, 38]. The shoulder at 1268cm^{-1} and peak at 1309cm^{-1} correspond to the vibrational modes of the carbon nitrogen bonds. The peak at 1309cm^{-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 [39].



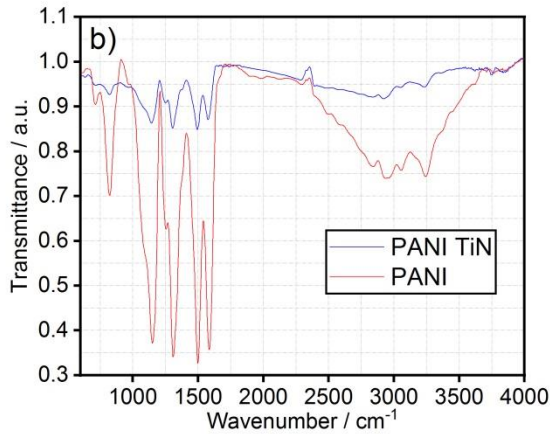


Figure 1: (a) CV cycle of a 0.1M polyaniline and 0.1g/L solution at room temperature (approx. 25°). (b) FTIR spectrums of 25 cycle PANI and PANI TiN samples.

The peaks observed at 1500cm^{-1} and 1588cm^{-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 2000cm^{-1} are typical of PANI in its conducting 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 CVs, the TiN loading can be increased and a bilayered coating formed (see table 2). Initially up to 300 seconds the TiN loading stays around the 6% by weight but increasing the time held static to 450 second and 600 seconds causes the weight % to increase to 8.41%. The TiN 600s sample had a lower weight % than the PANI TiN 600s sample, this confirms the presence of PANI increases the TiN deposition.

Table 2: Measured TiN loading using EDX

Sample name	Potential held static at 0.5V for / s	Titanium loading	
		Weight %	Atomic %
PANI TiN	0	6.87	7.63
PANI TiN 150s	150	6.10	6.79
PANI TiN 300s	300	5.88	6.48
PANI TiN 450s	450	7.11	7.71
PANI TiN 600s	600	8.41	8.94
TiN 600s	600	7.17	7.95

3.2 Interfacial Contact resistance (ICR)

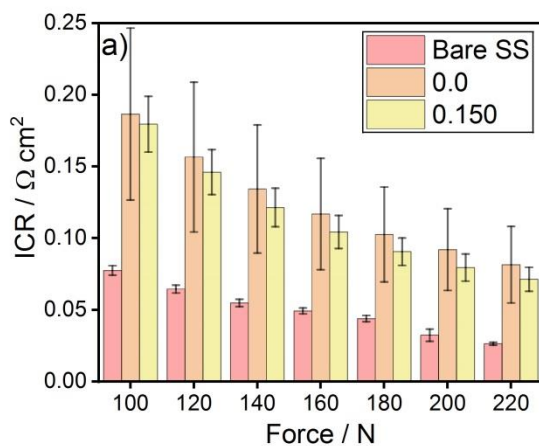
The ICR of the bare stainless steel, PANI and PANI-TiN coated samples were measured as a function of compression force as shown in figure 2. Acid washed bare SS316L had an ICR of $55\text{ m}\Omega\text{cm}^2$ at 140N. This is similar to other reported values for SS316L [20]. Polyaniline although a conducting 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 having 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 [29]. 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 our preliminary optimization work. Previous work found the ICR of 5 cycle polyaniline to be $367\text{ m}\Omega\text{cm}^2$ [29]. This work

produced a polyaniline coating with an ICR of $142 \text{ m}\Omega\text{cm}^2$ (quoted values will be for 140N), which is over 50% lower than previously reported values. This reduction in ICR is a result of the lower temperature forming thinner coatings.

Figure 2a shows the comparison of Bare SS and the two polyaniline coatings, it can be seen that the Bare SS out performs the polyaniline coating even with the reduced thickness of coating. The Bare SS doesn't have a thick passivation layer at this point due to the cleaning process employed and as such has relatively low ICR values.

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. It can be seen in figure 2b 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 600s, 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 2c shows the polyaniline and TiN composite coatings, with samples PANI TiN 150s, PANI TiN 300s, PANI TiN 450s and PANI TiN 600s being the bilayered samples. All bilayer coatings of composite polyaniline TiN with a surface layer of TiN presented lower ICR's than bare, polyaniline and composite layer. Static potentials were held after CV electroplating for 150s, 300s, 450s and 600s seconds. ICR's of the bilayers decreased as follows $150\text{s} > 300\text{s} > 450\text{s} > 600\text{s}$. Interestingly the PANI TiN 150s sample had a higher ICR than the PANI TiN sample whereas the subsequent samples, PANI TiN 300s, PANI TiN 450s and PANI TiN 600s, all showed lower ICR's than the composite layer. PANI TiN 600s 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 [4]. The decrease in ICR as the time of static potential held increases is due to the increase in TiN loading at the surface of the sample. 0.5V was held to plate the surface of the coating with TiN, the longer the potential was held the more TiN electrophoretically deposited on the surface. The improved ICR of TiN over polyaniline results in an overall reduced ICR.



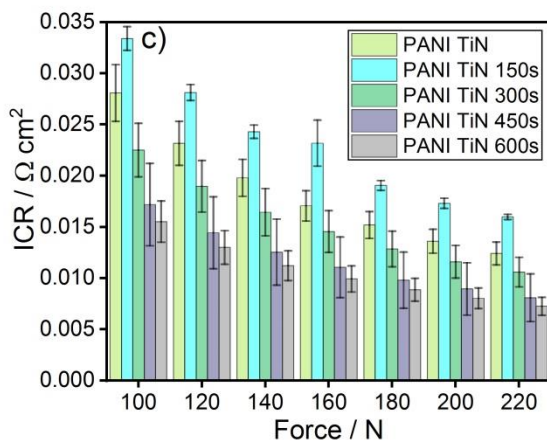
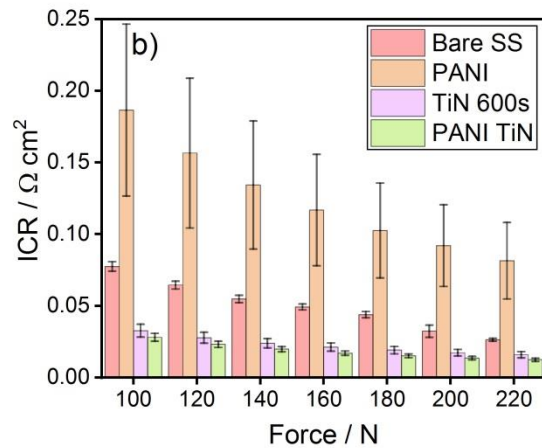


Figure 2: Interfacial contact resistance measurements for before corrosion, a) Comparison between Bare SS samples and PANI coated samples. B) shows how TiN effects the ICR values, comparing PANI TiN and TiN 600s C) shows how increasing the time the potential was held at 0.5V effects the ICR

3.3 Electrochemical corrosion

Figure 3 shows the potentiodynamic curves obtained in a 1mM (pH 3) sulphuric acid solution at 80°C saturated with N₂. The highest corrosion potential measured was that of the bare SS sample with a potential of -0.086 V_{SHE}. The corrosion potentials observed in this work for the PANI coating, -0.126 V_{SHE}, are lower than those observed for other works, where potentials for polyaniline coated samples were in the range of 0.22 V_{SHE} [29]. 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 with the bilayered sample, PANI TiN 600s, having the highest potential of them all. It is proposed that the TiN blocked pores in the PANI structure, preventing the diffusion of corrosive media to the SS surface, with the bilayer further filling the pores.

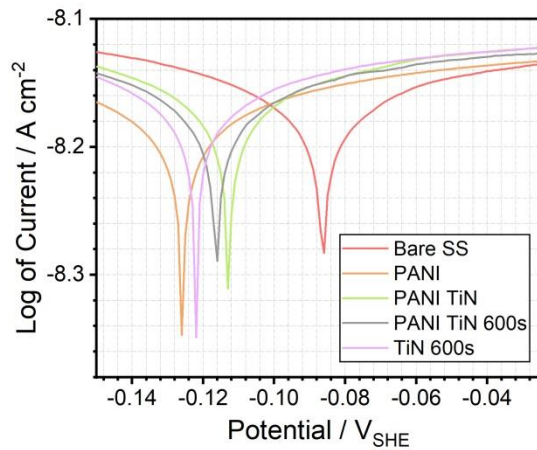


Figure 3: Linear sweep voltamograms of the samples (Conditions: pH3 H₂SO₄ solution, 80 degC and saturated in N₂)

The potentiostatic corrosion values are presented in table 3. The thin polyaniline coatings all achieved DoE targets with corrosion current densities in the range of $\sim 0.02 - 0.06 \mu\text{Acm}^{-2}$. 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, [20], showed a corrosion current density of $1.4 \mu\text{Acm}^{-2}$. It would therefore be expected that TiN doped coatings would outperform the gold doped coatings in long run tests. The improved corrosion resistance relative to other composite polyaniline coatings could be related to the thinner coatings achieved by the reduced electroplating temperature being less porous. The TiN loading is suggested to also increase the density of the coating which could further enhance the corrosion resistance of the substrate. For the composite and bilayered coatings the more time with a static potential after the CV's show a trend of decreasing corrosion current density with increased time. This could be a result of the TiN filling the defects of the polyaniline structure.

Table 3: potentiostatic corrosion current at $0.9V_{\text{SHE}}$

Sample	Corrosion current density / nA cm^{-2}
Bare SS	31.677
PANI	62.116
PANI TiN	48.080
PANI TiN 600s	22.754
TiN 600s	21.802

BPP's 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.

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 [29]. It is possible that the PANI oxidation state was changed during the corrosion test thereby decreasing the contact resistance of the coating.

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 600s increased from $11.2 \text{ m}\Omega\text{cm}^2$ to $39.9 \text{ m}\Omega\text{cm}^2$. The TiN 600s 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.

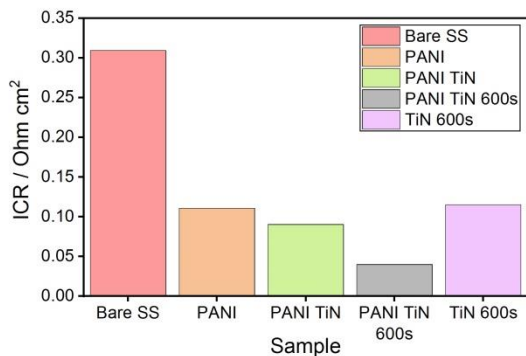


Figure 4: Shows ICR's of samples after corrosion for 24 hours at 80 degC in a pH 3 solution under cathodic conditions (saturated with air, potential 0.9V)

4. Conclusion

A PANI-TiN composite bilayer was developed in a two-step electrochemical process and confirmed by EDX and FTIR studies. It was intended to optimise polyaniline coatings by using: a low temperature for electroplating, by doping of the polyaniline layer with TiN and by the addition of a surface layer of TiN to create a bilayered coating. 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 contact resistance. The doping of the polyaniline layer didn't 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. One of the barriers to metallic BPP has typically been the high cost of the necessary coatings required. The coating in this work was formed from low cost reactants and plated in a simple two-step process. The best coating in this work PANI TiN 600s achieved corrosion current density requirements of DoE and achieved an ICR of $11 \text{ m}\Omega\text{cm}^2$, this doesn't quite achieve the $10 \text{ m}\Omega\text{cm}^2$ target of DoE. With further optimization of the surface layer, it is expected that the DoE targets can be achieved with this coating. Future work will investigate the effect of polishing and other pre-treatment processes on the coating and performance of the substrate. The coating characteristics on a formed bipolar plate should also be investigated and its *In-situ* performance in PEFC must also be tested.

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