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# Local Corrosion of Electronic Materials

Corrosion Mechanisms and Optimisation Strategies  
for ENIG Coatings on Copper Substrates

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MIRSAJJAD MOUSAVI



# **Local Corrosion of Electronic Materials**

**Corrosion Mechanisms and Optimisation Strategies  
for ENIG Coatings on Copper Substrates**

# INVITATION

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It is my pleasure to invite you to the public  
defence of my PhD thesis

## Local Corrosion of Electronic Materials

Corrosion Mechanisms and Optimisation  
Strategies for ENIG Coatings on Copper  
Substrates

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**Thursday, 17 September 2026  
at 10:00**

in the Senaatszaal of the  
Aula Conference Centre  
Delft University of Technology  
Mekelweg 5, 2628 CD Delft

Prior to the defence, at 09:30, I will give a  
brief presentation about my work.

You are cordially invited to the reception  
after the defence.

---

MIRSAJJAD MOUSAVI

An abstract, stylized illustration of a circuit board or microchip layout. It features a dense network of yellow and orange lines, representing traces and connections, set against a dark background with a subtle pattern of small, glowing yellow dots. The lines vary in thickness and form, creating a complex, geometric pattern that resembles a modern electronic design.



# Local Corrosion of Electronic Materials

Corrosion Mechanisms and Optimisation  
Strategies for ENIG Coatings on Copper  
Substrates

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MIRSAJJAD MOUSAVI

PARANYMPHS

Dr. Paria Ettehadi

&

Dr. Virgina Bertolo



# **Local Corrosion of Electronic Materials**

Corrosion Mechanisms and Optimisation Strategies for  
ENIG Coatings on Copper Substrates

## **Dissertation**

for the purpose of obtaining the degree of doctor  
at Delft University of Technology,

by the authority of the Rector Magnificus

Prof.dr.ir. H. Bijl,

chair of the Board for Doctorates,

to be defended publicly on

Thursday, 17 September 2026, 10:00

By

**Mirsajjad MOUSAVI**

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The research described in this thesis was carried out in the Department of Materials Science and Engineering, Delft University of Technology.

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Keywords: Electroless nickel immersion gold, localised, corrosion mechanism, PCBs, SECM, Electroless NiP, SKPFM, electronics integrity, process optimisation

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Human beings are members of a whole,  
In creation of one essence and soul.  
If one member is afflicted with pain,  
Other members uneasy will remain.  
If you've no sympathy for human pain,  
The name of human you cannot retain!

Saadi Shirazi, Iranian poet (c. 1210–1292)

To the brave people of Iran, who in their ancient history laid the foundations of human rights, yet today are deprived of the most fundamental of those rights.

تقدیم به مردم شجاع ایران، که در تاریخ کهن خود بنیان‌های حقوق بشر را پی‌ریزی کردند، اما امروز از ابتدایی‌ترین همان حقوق محروم‌اند.



# Summary

The rapid advancement in electronics, driven by intricate circuit design and manufacturing miniaturisation, has enabled the development of compact devices used in a wide range of applications. To ensure the performance and reliability of these sophisticated devices, it is crucial to study corrosion behaviour and performance at micro- and nanoscale levels. Traditional methods often fall short in addressing these challenges, highlighting the need for advanced localised techniques to understand corrosion mechanisms and develop strategies that ensure the durability of these critical devices in harsh conditions. This thesis investigates the localised aqueous corrosion study of Electroless Nickel Immersion Gold (ENIG) final finishing on copper substrates, which are widely used in printed circuit boards (PCBs) for electronic applications. Through a series of experimental studies, the research explores how micro-defects, phosphorus content, and bath parameters influence the corrosion resistance of ENIG and electroless nickel-phosphorus (NiP) coatings. Utilising advanced electrochemical and surface analysis techniques, the findings provide valuable insights into optimising coating processes to enhance the reliability and longevity of electronic components in harsh environments.

**The first chapter** provides a brief introduction to the research background and motivation, outlines the research aims, and describes the research approach.

**The second chapter** addresses the research question on the effect of micro-defects in the gold layer of ENIG coatings on corrosion initiation and progression. The study employs potentiodynamic polarisation (PDP) to assess corrosion behaviour, scanning electrochemical microscopy (SECM) to map local electrochemical activity, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS) for surface morphology and physicochemical characterisation, atomic force microscopy (AFM) for topographical analysis, and focused ion beam (FIB) microscopy for cross-sectional imaging. The main results reveal that micro-defects in the gold layer are the primary sites for corrosion initiation. These defects expose the underlying nickel layer to an acidic chloride-containing environment, leading to the formation of a galvanic couple between

the gold and nickel layers. The corrosion initiates with localised nickel dissolution, propagating both lateral and perpendicular to the surface. Over time, the direction of metallic dissolution changes during corrosion evolution, depending on the pit geometry and the exposed materials. The high cathode-to-anode ratio in the gold-nickel galvanic couple accelerates nickel dissolution. This finding underscores the importance of minimising micro-defects in the gold layer to enhance the corrosion resistance of ENIG-coated copper systems, thereby improving the reliability of electronic components exposed to corrosive environments.

**The third chapter** investigates how varying phosphorus content in NiP coatings affects their microstructure and corrosion resistance when applied to copper substrates. The study aims to investigate the correlation between phosphorus content, coating crystallinity, and susceptibility to localised corrosion in aqueous chloride-containing environments. Three different NiP coatings with phosphorus contents of 13.2%, 12.9%, and 8.3% are analysed. Methodologies include SEM/EDS and FIB microscopy for microstructural analysis, X-ray diffraction (XRD) for crystallinity analysis, AFM and scanning Kelvin probe force microscopy (SKPFM) for surface topography and potential mapping, and electrochemical techniques like PDP and electrochemical impedance spectroscopy (EIS) to evaluate corrosion behaviour. Key findings indicate that higher phosphorus content yields a more amorphous and uniform coating structure, thereby significantly improving corrosion resistance. In contrast, coatings with lower phosphorus content exhibit a crystalline structure with minor surface defects, especially along nodule boundaries, increasing their susceptibility to localised corrosion due to uneven charge distribution. The chapter concludes that optimising the phosphorus content in NiP coatings is crucial for enhancing their protective performance. High-phosphorus NiP coatings offer superior corrosion protection, making them more suitable for industrial applications where durability is essential.

**The fourth chapter** explores the impact of electroless nickel phosphorus bath parameters—specifically agitation methods and immersion times—on the localised corrosion resistance of ENIG coatings. The research problem aims to optimise bath conditions to produce coatings with enhanced corrosion resistance



for electronic applications. The study compares ultrasonic agitation and mechanical stirring during the coating process. Electrochemical analyses, including PDP and SECM, are used to assess the corrosion resistance of the resulting coatings. Key results demonstrate that ultrasonic agitation increases the phosphorus content in the ENP layer, leading to smoother, more defect-free coatings with improved corrosion resistance. Conversely, mechanical stirring produces thicker coatings with lower phosphorus content and more defects, which reduces corrosion resistance. The chapter concludes that optimising ENP bath parameters, particularly using ultrasonic agitation, significantly enhances the quality and durability of ENIG coatings. This optimisation is vital for electronic devices operating in harsh environments, as it improves the corrosion protection of copper substrates, thereby ensuring the performance and longevity of PCBs.

**Overall**, this research provides a comprehensive analysis of factors affecting the localised corrosion of ENIG and NiP coatings on copper substrates. By identifying micro-defects as primary corrosion initiation sites and studying pit growth behaviour, elucidating the role of phosphorus content on coating microstructure and corrosion behaviour, and demonstrating the benefits of optimising bath parameters, the research offers practical solutions for improving corrosion resistance. These findings have significant implications for the electronics industry, where enhancing the durability and reliability of PCBs is critical for the performance of electronic devices in demanding environments.

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# Samenvatting

De snelle vooruitgang in de elektronica, aangejaagd door geavanceerd circuitontwerp en miniaturisatie in de productie, heeft de ontwikkeling mogelijk gemaakt van compacte apparaten die in een breed scala aan toepassingen worden gebruikt. Om de prestaties en betrouwbaarheid van deze geavanceerde apparaten te waarborgen, is het essentieel om het corrosiegedrag en de prestaties op micro- en nanoschaal te bestuderen. Traditionele methoden schieten vaak tekort bij het aanpakken van deze uitdagingen, wat de behoefte benadrukt aan geavanceerde, lokaal gerichte technieken om corrosiemechanismen te begrijpen en strategieën te ontwikkelen die de duurzaamheid van deze kritische apparaten in zware omstandigheden waarborgen. Dit proefschrift beschrijft de lokale corrosie in een waterige omgeving van de Electroless Nickel Immersion Gold (ENIG) afwerking op kopersubstraten, die veel worden gebruikt in printplaten (PCBs) voor elektronische toepassingen. Door een reeks experimentele studies is onderzocht het onderzoek hoe microdefecten, het fosforgehalte en badparameters de corrosieweerstand van ENIG- en electroless nikkel-fosfor (NiP) coatings beïnvloeden. Met behulp van geavanceerde elektrochemische en microscopische technieken bieden de bevindingen waardevolle inzichten om coatingprocessen te optimaliseren en de betrouwbaarheid en levensduur van elektronische componenten toegepast in corrosieve omstandigheden te verbeteren.

**Het eerste hoofdstuk** geeft een korte introductie van de achtergrond en motivatie van het onderzoek, schetst de onderzoeksdoelen en beschrijft de onderzoeksaanpak.

**Het tweede hoofdstuk** beschrijft hoe microdefecten in de goudlaag van ENIG-coatings bijdragen aan het ontstaan en de voortschrijding van corrosie. De studie maakt gebruik van potentiodynamische polarisatie (PDP) om het corrosiegedrag te beoordelen, scanning electrochemical microscopy (SECM) om lokale elektrochemische activiteit in kaart te brengen, scanning-elektronenmicroscopie met energie-dispersieve röntgenspectroscopie (SEM/EDS) voor

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oppervlaktekarakterisering, atomaire krachtmicroscopie (AFM) voor topografische analyse en focused ion beam (FIB) microscopie voor doorsnedeafbeeldingen. De belangrijkste resultaten tonen aan dat microdefecten in de goudlaag de primaire plaatsen zijn voor het ontstaan van corrosie. Deze defecten stellen de onderliggende nikkellaag bloot aan een zure omgeving met chloride, wat leidt tot de vorming van een galvanisch koppel tussen de goud- en nikkellagen. De corrosie begint met lokale oplossing van nikkel, die zowel lateraal als in de diepte voortschrijdt. In de loop van de tijd verandert de richting van de metaaloplossing tijdens de corrosie-evolutie door de geometrie van de put en de blootgestelde materialen. De hoge kathode-tot-anode-verhouding in het goud-nikkel galvanische koppel versnelt de nikkeloplossing. Deze bevinding onderstreept het belang van het minimaliseren van microdefecten in de goudlaag om de corrosieweerstand van ENIG-gecoate kopersystemen te verbeteren, en zo de betrouwbaarheid van elektronische componenten die aan corrosieve omstandigheden worden blootgesteld te vergroten.

**Het derde hoofdstuk** beschrijft hoe het fosforgehalte in NiP-coatings de microstructuur en corrosieweerstand beïnvloedt wanneer deze op kopersubstraten worden aangebracht. De studie heeft tot doel het verband te onderzoeken tussen het fosforgehalte, de kristalliniteit van de coating en de gevoeligheid voor lokale corrosie in waterige omgevingen met chloride. Drie verschillende NiP-coatings met fosforgehalten van 13,2%, 12,9% en 8,3% worden geanalyseerd. Methodologieën omvatten SEM/EDS en FIB-microscopie voor microstructurele analyse, röntgendiffractie (XRD) voor de bepaling van de kristalstructuur, AFM en scanning Kelvin probe force microscopy (SKPFM) voor oppervlaktopografie en potentiaalmapping, en elektrochemische technieken zoals PDP en elektrochemische impedantiespectroscopie (EIS) om het corrosiegedrag te evalueren. Belangrijke bevindingen geven aan dat een hoger fosforgehalte resulteert in een meer amorphe en uniforme coatingstructuur, wat de corrosieweerstand aanzienlijk verbetert. Coatings met een lager fosforgehalte vertonen daarentegen een kristallijne structuur met kleine defecten, vooral langs de grens van nodules, wat hun gevoeligheid voor lokale corrosie vergroot door een ongelijke ladingsverdeling. Het hoofdstuk concludeert dat het optimaliseren

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van het fosforgehalte in NiP-coatings cruciaal is voor het verbeteren van hun beschermende prestaties. NiP-coatings met een hoog fosforgehalte bieden superieure corrosiebescherming en zijn daardoor beter geschikt voor industriële toepassingen waar duurzaamheid essentieel is.

**Het vierde hoofdstuk** onderzoekt de invloed van electroless nikkel-fosfor badparameters met name agitatie en dompeltijden op de lokale corrosieweerstand van ENIG-coatings. Het onderzoeksprobleem richt zich op het optimaliseren van badomstandigheden om coatings te produceren met verbeterde corrosieweerstand voor elektronische toepassingen. De studie vergelijkt ultrasone agitatie en mechanisch roeren tijdens het coatingproces. Elektrochemische analyses, waaronder (PDP) en SECM, worden gebruikt om de corrosieweerstand van de resulterende coatings te beoordelen. De resultaten tonen aan dat ultrasone agitatie het fosforgehalte in de ENP-laag verhoogt, wat leidt tot gladdere, defectvrije coatings met verbeterde corrosieweerstand. Mechanisch roeren daarentegen levert dikkere coatings op met een lager fosforgehalte en meer defecten, wat de corrosieweerstand vermindert. Het hoofdstuk concludeert dat het optimaliseren van ENP-badparameters, met name het gebruik van ultrasone agitatie, de kwaliteit en duurzaamheid van ENIG-coatings aanzienlijk verbetert. Deze optimalisatie is van cruciaal belang voor elektronische apparaten die in zware omgevingen werken, omdat het de corrosiebescherming van kopersubstraten verbetert en zo de prestaties en levensduur van printplaten waarborgt.

Samenvattend biedt dit onderzoek een grondige analyse van de factoren die van invloed zijn op de lokale corrosie van ENIG- en NiP-coatings op kopersubstraten. Door microdefecten te identificeren als primaire initiatieplaatsen voor corrosie en het gedrag van lokale corrosie te onderzoeken, de rol van het fosforgehalte op de microstructuur en corrosie-eigenschappen van de coating te verduidelijken, en de voordelen aan te tonen van het optimaliseren van badparameters, biedt het onderzoek praktische oplossingen om de corrosiebestendigheid te verbeteren. Deze bevindingen hebben belangrijke implicaties voor de elektronica-industrie, waar het verbeteren van de duurzaamheid en

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betrouwbaarheid van printplaten (PCB's) cruciaal is voor de prestaties van elektronische apparaten in veeleisende omgevingen.



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# Chapter 1. Introduction

1.1 Introduction and Motivation

In the contemporary era of highly sophisticated electronic and communication technology, electronic devices have influenced nearly every aspect of our daily lives. From smartphones and laptops to medical equipment and industrial control systems, these devices are integral to modern society's functioning and advancement [1]. In recent years, the COVID-19 pandemic also highlighted their important role by creating an unexpected surge in demand for consumer electronics due to remote work and digital connectivity needs, while also causing major disruptions in the semiconductor industry's supply chain [2]. As illustrated in Figure 1.1, global production in the electronics and information technology industries has shown a steady upward trajectory over the past decade, with a marked increase during the pandemic years. This pandemic-driven acceleration underscores the high importance of electronics in sustaining social and economic activity under disruptive conditions [3].

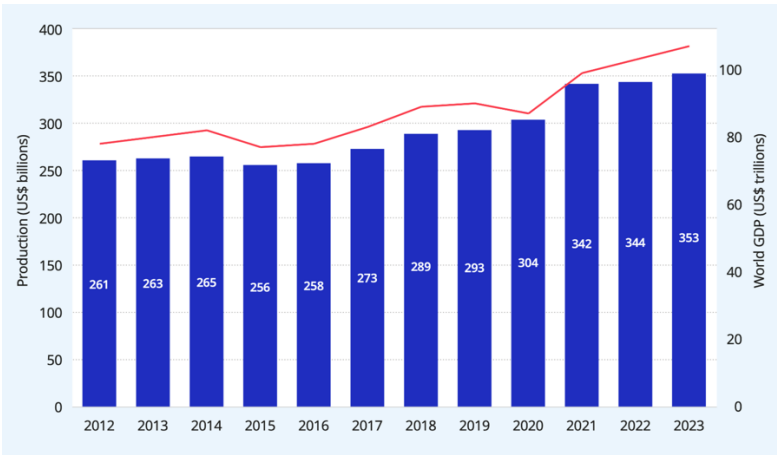
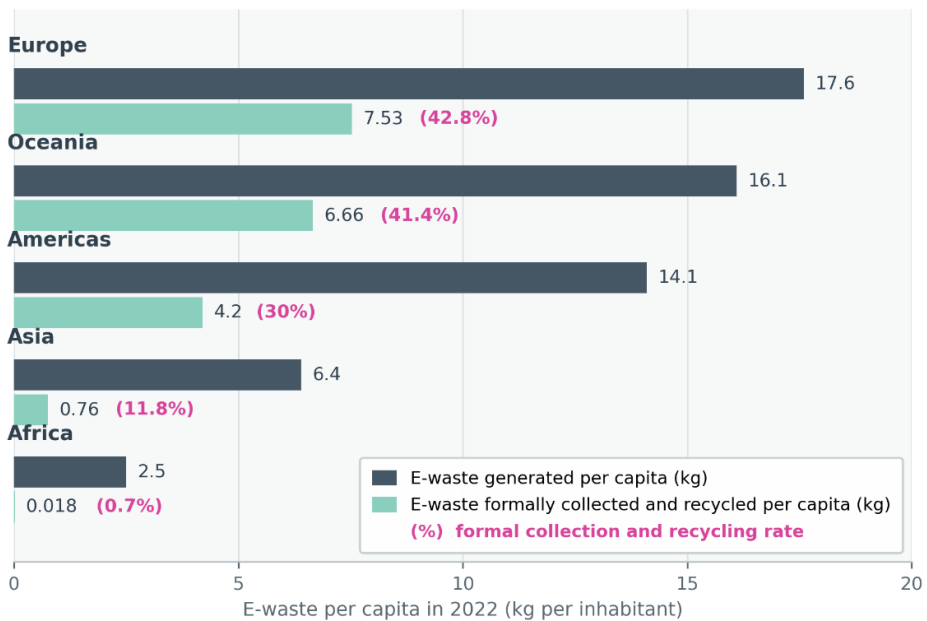


Figure 1.1. Global output of electronics and information technology industries, 2012–2023, measured in billions of US dollars [3].

As our reliance on electronic systems intensifies, ensuring their reliability and longevity becomes increasingly critical, particularly given their frequent exposure to harsh environmental conditions that can compromise performance [4, 5]. One of the primary challenges affecting the durability and functionality of electronic devices is corrosion, especially in the metallic components that are vital for signal

processing and transmission. Corrosion can diminish the conductivity of these parts, leading to performance loss or complete device failure [6]. The year 2022 marked a significant milestone in global environmental metrics, with electronic waste (e-waste) reaching an unprecedented 62 billion kilograms. This output is equivalent to an annual average of 7.8 kilograms per capita. Critically, data presented in Figure 1.2 indicate that the formal collection and environmentally sustainable recycling rate for this e-waste was merely 22.3% [7].



*Figure 1.2. E-waste generated and formally collected and recycled per capita by world region in 2022, together with the corresponding formal collection and recycling rate (%). Annual average formal collection and recycling rate in 2022 [7].*

The transition to lead-free electronics, driven by European directives and market pressures, is essential to avoid global market losses [8, 9]. This shift demands significant changes in materials, processes, and testing methods, including requalifying assembly and rework procedures. Therefore, various lead-free surface finishes have been developed to protect electronic components from corrosion, including Organic Solderability Preservatives (OSP) [10], Immersion Tin [11], Immersion Silver [12], and Electroless Nickel Immersion Gold (ENIG) [13]. Among these, ENIG coatings are widely adopted due to their excellent

solderability, uniform thickness, and compatibility with fine-pitch components [14]. However, despite their widespread use, fundamental knowledge about the corrosion behaviour of ENIG finishes remains limited. Most academic work on ENIG finishes has focused on improving the coating itself by altering its composition, adding intermediate layers, or changing the overall stacking sequence. Although these studies have improved surface properties, they offer little insight into how corrosion actually begins and develops in ENIG systems. In particular, the sequence from the first moments of attack at a micro-defect through the growth of a localised pit to coating failure is not well understood. Most published studies rely on the narrow set of experimental techniques that have been used so far. Methods such as scanning electrochemical microscopy (SECM), cross-sectional FIB analysis, and sequential corrosion-progression studies have rarely been applied to ENIG coatings. SKPFM has not been used to evaluate how the phosphorus content of the nickel layer affects local electrochemical behaviour. Traditional electrochemical measurements average the response across the entire surface, masking the very localised processes that dominate ENIG degradation. Because corrosion usually initiates at microscopic defects or pores in the thin gold layer, techniques capable of resolving activity at the micrometre and nanometre scale are essential. SECM can track local anodic or cathodic reactions as they develop; SKPFM can reveal micro-galvanic potential differences linked to Ni–P chemistry; and FIB-SEM provides direct visual access to subsurface attack and the geometry of hidden defects [15-18]. As an example of an electronic device, Figure 1.3 presents a schematic illustration of an SD memory card with an ENIG finish, along with a cross-sectional view showing a water droplet containing corrosion-inducing contaminants, such as chloride ions and acidic species, that may initiate localised corrosion on the surface. The schematic also highlights the studied system moving from the macroscopic device level to the microscopic features where corrosion processes begin.

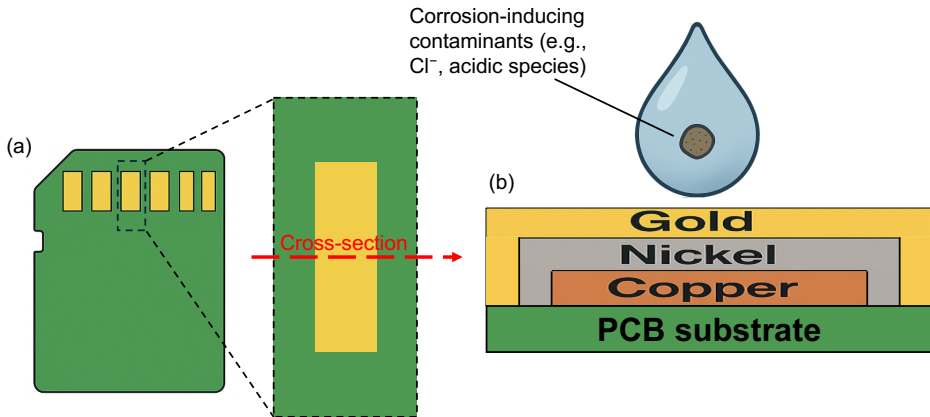


Figure 1.3. Schematic illustration showing (a) the ENIG-coated PCB substrate and (b) a cross-sectional view of the ENIG coating with a water droplet containing corrosion-inducing contaminants, such as chloride ions and acidic species, that may initiate localised corrosion.

Understanding these mechanisms at a micro-level is crucial for identifying the initiation sites of corrosion—such as micro-defects in the gold layer—and for developing strategies to mitigate them [19, 20]. By addressing this gap, it becomes possible to optimise production processes not just by changing material compositions but by fundamentally enhancing corrosion resistance through a better understanding of the underlying processes. Previous work by Yi *et al.* [13] investigated the failure mechanisms of ENIG-coated PCBs primarily through post-corrosion failure analysis, focusing on the characterisation of corrosion products and their influence on the subsequent corrosion behaviour of the PCB surface. While this study provided valuable insight into the nature of corrosion products and final degradation states, it did not address the underlying mechanisms governing corrosion initiation or the evolution of corrosion from its earliest stages.

Addressing these knowledge gaps is even more pressing given the environmental and economic implications associated with electronic waste (e-waste). In 2019, an estimated 53.6 million tonnes of e-waste were generated globally, making it one of the fastest-growing waste streams worldwide, with a projected increase to 74 million tonnes by 2030. Alarmingly, only about 17.4% of this e-waste, equivalent to 9.3 million tonnes, was documented as formally

collected and recycled, while the vast majority ended up in landfills or was processed informally, leading to environmental pollution and the loss of valuable materials. While recycling remains a critical component of e-waste management, extending the lifespan of electronic devices offers a proactive approach to mitigating this issue [21, 22]. By preventing corrosion and its resulting performance degradation, we can reduce the frequency with which devices become obsolete and are discarded. Enhancing the durability of electronics not only lessens the environmental burden but also offers economic benefits by reducing replacement costs for consumers and production costs for manufacturers. Moreover, maintaining the performance integrity of electronic devices is essential in critical applications where failure is not an option, such as in healthcare, aerospace, and defence systems [23]. Furthermore, corrosion often reduces electronic performance by impairing the conductivity of metallic components, thereby hindering signal processing and transmission. This degradation can have far-reaching consequences, impacting the efficiency and reliability of communication networks, data processing systems, and control mechanisms in various industries [24].

Although the examples above are drawn from consumer electronics, the reliability challenges addressed in this thesis apply to industrial electronics too, including power electronics, automotive and transport systems, telecommunications infrastructure and process-control equipment [5]. In these applications, devices operate in considerably harsher service environments, with elevated humidity, temperature cycling, condensation and aggressive gaseous or particulate contamination [25], and ENIG is a widely used surface finish for connectors and contact pads [29]. Power electronic modules and automotive connectors, in particular, have been shown to fail through corrosion and fretting-corrosion mechanisms under such conditions [26-28]. A further consideration, central to this thesis, is economic. Since gold is costly, the Au top-layer of an ENIG finish is deliberately kept as thin as possible, typically around of one hundred nanometres or less for immersion gold processing. The porosity of a gold layer increases as its thickness decreases, and a certain level of through-layer porosity is therefore difficult to avoid in industrial practice. This cost-driven trade-off between the

thickness and the porosity of the Au top-layer is what makes the localised corrosion initiating at defects in the Au layer, the central subject of Chapters 2 to 4, a persistent problem in practice.

Field experience and systematic investigations into ENIG finishes reveal that, although ENIG is widely used for its solderability, a range of reliability issues have been observed in both production and deployed PCBs. The most widely recognised failure mode is the so-called 'black pad', associated with excessive corrosion of the electroless nickel layer during the immersion gold process, which leads to weak, brittle solder joints that can fail under mechanical or thermal stress. In addition to black pad, structural defects such as insufficient gold thickness, gold porosity, nickel migration, high phosphorus content in the Ni layer, poor plating quality, and excessive coating stress have been reported; these defects degrade solderability and the integrity of the metal finish itself. When ENIG-related problems occur, they often affect entire product batches and are only detected after assembly or in field service, resulting in elevated failure rates, costly reworks, and degraded reliability metrics for the affected electronic assemblies [30].

Motivated by these challenges, this research aims to provide fundamental understanding of the corrosion mechanisms affecting ENIG coatings on copper substrates. By employing localised electrochemical and microscopic techniques, this thesis seeks to uncover the initiation and progression of corrosion at the micro-defect level—an area that has not been extensively explored in current literature. This approach differs from previous studies that primarily focus on using inhibitors, adding an extra layer on ENIG, or modifying the layer configurations of ENIG finishes [16-18]. Instead, this research emphasises understanding the corrosion behaviour from a fundamental perspective without altering any component of the ENIG system to improve the performance but purely understanding the corrosion mechanism, which is essential for developing more effective corrosion prevention strategies. Additionally, the study explores how varying phosphorus content in electroless nickel-phosphorus (NiP) coatings and optimising bath parameters during the coating process can influence corrosion resistance. By investigating these factors, the research aims to identify

methods to enhance the protective qualities of ENIG coatings without relying solely on compositional changes or additional layers.

### 1.2 Research aim

The aim of this thesis is to understand localised corrosion mechanisms of Electroless Nickel Immersion Gold (ENIG) and Electroless Nickel-Phosphorus (NiP) coatings on copper substrates, which are crucial in electronic applications such as printed circuit boards (PCBs).

The research addresses three key areas: (1) the role of micro-defects in the gold layer of ENIG coatings in initiating and propagating corrosion; (2) the influence of phosphorus content on the microstructure and corrosion resistance of NiP coatings; and (3) the impact of electroless nickel bath parameters, specifically agitation methods and immersion times, on the corrosion behaviour of ENIG coatings.

To achieve these aims, this study employs an integrated research approach that combines advanced materials characterisation with localised electrochemical analysis. The microstructural, compositional, and topographical properties of the coatings are investigated using a suite of techniques, including Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy (SEM/EDS), Focused Ion Beam (FIB) microscopy for cross-sectional analysis, Atomic Force Microscopy (AFM), and X-ray Diffraction (XRD). The corrosion behaviour is evaluated through both conventional electrochemical methods, such as potentiodynamic polarisation, and advanced localised techniques, including Scanning Kelvin Probe Force Microscopy (SKPFM) and Scanning Electrochemical Microscopy (SECM), to map electrochemical activity at the microscale.

This multi-faceted approach provides a comprehensive insight into how micro-defects and coating parameters affect localised corrosion mechanisms. Results show that gold-layer defects expose the nickel layer, creating galvanic coupling and accelerating localised corrosion. Higher phosphorus content in NiP coatings yields more amorphous and uniform structures with improved corrosion

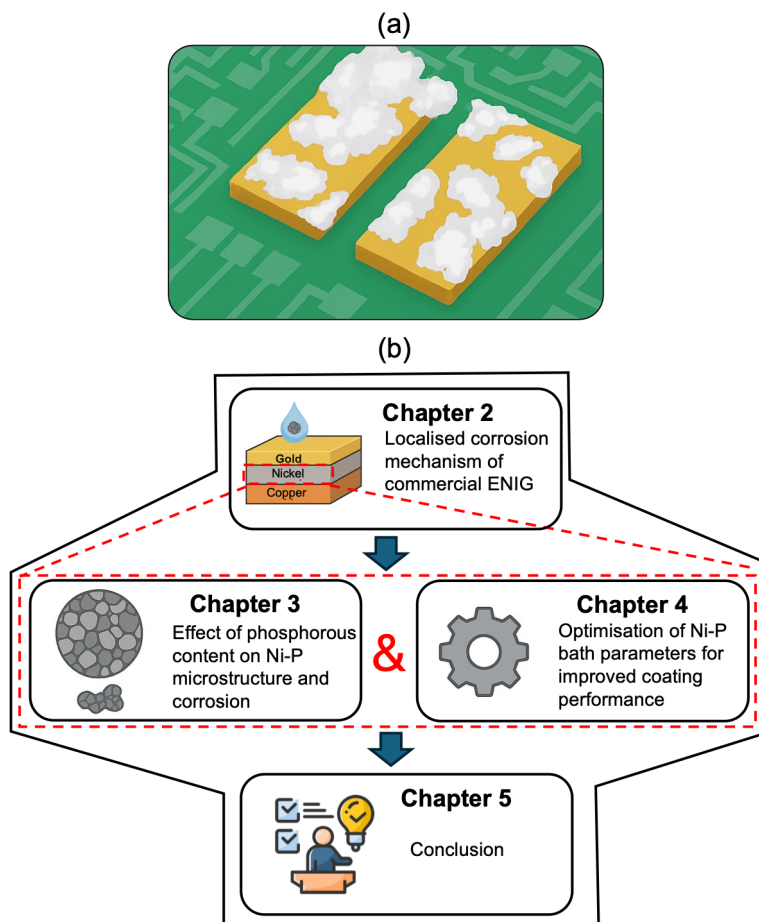


resistance, while lower-phosphorus coatings are more prone to localised attack. Finally, ultrasonic agitation during ENP deposition enhances phosphorus incorporation and coating quality, offering superior protection compared to mechanically stirred processes. Collectively, these findings underscore the significance of microstructural control and process optimisation in enhancing the reliability of coated copper systems in harsh environments.

### 1.3 Thesis outline

This thesis begins by establishing the research motivation, providing a comprehensive background, and clearly defining the research aims and methodological approach. Figure 1.4 presents a schematic overview illustrating the corrosion of the ENIG-coated copper system investigated in this thesis. **Chapter 2** investigates the localised corrosion mechanisms of commercial Electroless Nickel Immersion Gold (ENIG) coatings. By stopping the corrosion process at various stages and conducting detailed post-corrosion surface analyses, the study offers a precise understanding of how corrosion initiates, progresses, and ultimately leads to failure. The mechanisms identified are crucial to understanding the degradation behaviour of ENIG coatings. **Chapter 3** examines the influence of phosphorus content in the intermediate electroless nickel-phosphorus (NiP) layer on microstructural properties and corrosion resistance when applied to copper substrates. By analysing NiP coatings with varying phosphorus concentrations, the chapter reveals how phosphorus content affects surface characteristics and corrosion behaviour. Detailed microstructural and electrochemical analyses establish clear links between phosphorus levels, coating crystallinity, and corrosion performance. **Chapter 4** shifts focus to the impact of NiP bath parameters, including agitation methods and immersion times, on the overall quality and effectiveness of ENIG coatings. The study compares ultrasonic agitation with mechanical stirring to determine their influence on phosphorus content, coating thickness, and structural integrity. Applying a gold layer to different NiP coatings produces ENIG samples, which are then evaluated for localised corrosion resistance. This analysis highlights the importance of optimising bath parameters to achieve durable and high-quality coatings.

**Chapter 5** concludes the thesis by summarising key findings and offering recommendations for future research, with proposed strategies aimed at enhancing the corrosion resistance of ENIG coatings in various electronic applications.



*Figure 1.4. Schematic overview of the corrosion of the ENIG-coated copper system studied in this thesis (a) and the logical relationship among Chapters 2–5 (b). Chapter 2 investigates the localised corrosion mechanisms of ENIG coatings, while Chapters 3 and 4 focus on the influence of Ni–P composition and processing parameters, respectively, leading to the concluding insights on corrosion resistance optimisation.*

## 1.4 References

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## Chapter 2. Localised aqueous corrosion of electroless nickel immersion gold-coated copper

### **Abstract:**

Electroless nickel (Ni) immersion gold (Au), commonly referred to as ENIG, is the most common protective coating applied to the exposed copper (Cu) traces of printed circuit boards (PCBs). A comprehensive understanding of the complex local corrosion mechanism of the ENIG-Cu system will facilitate microstructure control strategies, enhancing the system's long-term reliability and integrity. In this work, we elucidate the local corrosion mechanism of the ENIG-Cu system using spatial high-resolution microscopic, surface analysis, and electrochemical techniques. The corrosion initiation and propagation of the ENIG-Cu system in aqueous corrosive media were investigated by combining electrochemical and surface characterisations. Corrosion initiation is highly localised and associated with pores or microdefects in the Au layer. Corrosion initiates with the dissolution of the underlying Ni layer, which is less noble than Au. The dissolution propagates laterally and perpendicular to the surface in an elliptical pattern. With time, the direction of corrosion propagation changes to a predominantly lateral attack of the Ni layer. The corrosion process is governed by the cathode/anode ratio of the Au/Ni galvanic couple.

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### 2.1 Introduction

In an era of highly sophisticated electronic and communication technology, electronic devices have become an integral part of all aspects of our daily lives. As non-volatile data storage device, Secure Digital (SD) memory cards increase the storage capacity of electronic devices, including smartphones, digital cameras, and tablets. The central part of every SD memory card consists of a PCB that includes metallic pins [1, 2]. Considering the electronic application of every single PCB in an integrated system, a specific number of circuits are mounted on a plastic backbone. Electronic PCB components, such as resistors, capacitors, and inductors, are connected via Cu traces that carry electrical current. However, as they are used in many potentially corrosive service environments, the oxidation of non-embedded Cu without protective coating is highly probable [3-5]. Moreover, the functional integrity of electronics is not only affected by the corrosion of Cu in itself, but also by electrochemical migration and redeposition of dissolved Cu ions on a neighbouring Cu electrode, due to oxidation of Cu and the presence of an electric field potentially jeopardising the reliability of electronics in service [6-9].

Preserving the electronic performance of SD memory cards from corrosion attacks is of great importance. The corrosion rate of metallic pins in SD memory cards is determined by their final finishing and service environment. Electroless nickel immersion gold (ENIG) is the leading surface finish used in the electronic industry, along with other final finishes such as hot air solder levelling, organic solderability preservatives, immersion tin, and immersion silver. ENIG consists of a bi-layered metallic coating of Ni and Au to protect the Cu traces [10, 11]. ENIG is characterised by high resistance to corrosion and whisker growth, excellent electrical conductivity, and solderability, and represents a lead-free, environmentally friendly fabrication process [1, 12-14].

The intermediate Ni layer between the Cu and Au acts as a barrier against the interdiffusion of Au and Cu. Interdiffusion of Au and Cu causes problems such as loss of solderability, bonding strength and conductivity [15-17]. Moreover, the Ni layer provides the wear resistance of the ENIG double-layer system [18]. The Au

top-layer provides good corrosion resistance to oxidation of the Ni and excellent electrical conductivity for self-standing PCBs such as SD cards [19]. Although the ENIG-Cu system provides a compatible surface for a broad range of component assemblies and high corrosion protection, microstructural heterogeneity or porosity in the Au top layer may initiate local corrosion during the final finishing [5, 17]. Due to the relatively expensive nature of Au, the thickness of the top-layer Au in the ENIG-Cu system is always aimed to be as thin as possible, even down to 0.25  $\mu\text{m}$  [5]. However, the porosity level is inversely correlated to the thickness of the Au top layer. Au coatings at a thickness of 2  $\mu\text{m}$  are reported as pore-free, but an Au coating with a thickness of 0.8  $\mu\text{m}$  is indicated as porous [5, 19-21]. A porous structure across the thickness of the Au layer in the ENIG-Cu system provides channels for corrosive media to reach the intermediate Ni layer. Consequently, extensive local corrosion attacks may initiate, also galvanically enhanced by a relatively high cathode-to-anode surface ratio, being Au-to-Ni in this case [22, 23]. To decrease the porosity of the Au top-layer and improve the corrosion performance of the ENIG-Cu system, Bahramian *et al.* [22] showed the effect of pore sealing by electrodepositing poly(methyl methacrylate), which resulted in an overall decrease in corrosion current density of about ten times after 10 cycles of electropolymerisation.

To clarify the corrosion mechanism of the ENIG-Cu system, research has focused on post-corrosion microscopic studies, including after long-term exposure to harsh natural environments [3, 24] and harsh artificial environments [5, 17, 25-29]. Xiao *et al.* [3] investigated the corrosion behaviour of microporous ENIG-plated PCBs by exposing samples in the Turpan area of China for 24 months, which has a harsh corrosive environment. By the post-corrosion analysis of the intermittently selected samples, they concluded that galvanic corrosion through the microporous surface of Au occurred through the following steps, (a) water condensation and dust sedimentation in the vicinity of the pores, (b) formation of corrosion product induced by galvanic coupling, and (c) piling up of corrosion products reaching the surface. The proposed corrosion mechanism for the ENIG-Cu system exposed to the Turpan area is based on the high surface ratio of cathode-to-anode in which the cathodic reactions occurred at the Au surface (Eq.

1). The underlying layers of Ni and Cu act as an anode. The anodic reactions occur inside the micropores (Eq. 2 and Eq. 3).



Subsequently, corrosion products can form by chemical reaction with dissolved polyatomic anions such as  $OH^-$ ,  $HCO_3^-$ , and  $SO_4^{2-}$  (Eq. 4, Eq. 5, Eq. 6, Eq. 7).



Salahinejad *et al.* [25] proposed a galvanic corrosion mechanism of the ENIG-Cu system in a sulphur-containing corrosive atmosphere. Au acts as a cathode and both Ni and Cu anodes. They observed that corrosion propagation occurred in the Cu rather than in the Ni when the sulphur-containing solution reached the Ni/Cu interface. They claimed that Cu is more susceptible to sulphur-containing solutions than Ni, even though Cu is listed as more noble than Ni in the electromotive force series.

Murugan *et al.* [17] exposed a set of different stack configurations of Ni, Ni-P, and Au coatings with identical thicknesses to harsh artificial environments to investigate the corrosion mechanism for the ENIG-Cu system. They showed that multi-layered stack configurations, such as Ni-P/Ni/Au, Ni/Ni-P/Au, and Ni-P/Ni/Ni-P/Au, expedite corrosion due to having multiple interfaces enhancing galvanic corrosion as compared to that in the presence of a single layer of intermediate Ni-based materials, such as Ni/Au and Ni-P/Au. On the other hand, Collins *et al.* [5] showed that multi-layered stack designs of electrical connector coatings, such as Ni/Ni-P/Au and Ni/Ni-Pd/Au, displayed better corrosion

performance than Ni/Au and Ni-P/Au. They reported that the enhanced corrosion performance of the multi-layered stack design was attributed to the thickness of the multi-layered coating system, compactness of the Au layer with fewer defects, and reduction in the electrochemical potential difference between layers which alleviated the effect on local galvanic corrosion. In the research mentioned above, a post-mortem analysis approach was used to elucidate the corrosion mechanism in ENIG-Cu samples.

Although many studies have focused on the post-corrosion analysis of the ENIG-Cu system after long-term exposure to harsh corrosive media, to the authors' knowledge, no prior research has adopted a step-by-step approach in terms of visualizing the corrosion phenomenon to elucidate the corrosion initiation and propagation mechanisms. To understand the corrosion process at the local level, local electrochemical techniques give a thorough insight into the spatial distribution of local anodic and cathodic reactions [30]. Scanning electrochemical microscopy (SECM) is a versatile local electrochemical technique that provides resolved electrochemical data from a confined region of interest of an immersed substrate surface. By operating the SECM in feedback mode, a steady-state redox current can be measured in the region of the bulk solution. The measured steady-state current by hemispherical diffusion of the redox mediator is perturbed while approaching the scanning probe, called microelectrode, to the proximity of the substrate. Negative feedback indicates a less electrochemical active area while positive feedback indicates the opposite. The resulting local current map obtained while operating at feedback mode provides insight into the spatially resolved local electrochemical activity of the surface [31-33].

In this research, we provide a fundamental understanding of the local corrosion behaviour of the ENIG-Cu system on metallic pins of SD memory cards in an acidic chloride-containing aqueous environment. The microstructural, compositional, electrochemical, and topographical characterisation of as-received samples were performed using Scanning Electron Microscopy / Energy-dispersive X-ray (SEM/EDS) spectroscopy, X-Ray diffraction (XRD), Atomic Force Microscopy (AFM) and Open Circuit Potential (OCP) measurements. Focused Ion Beam (FIB), Potentiodynamic Polarisation (PDP), and SECM

experiments provided quantitative and qualitative insight into the corrosion behaviour of the ENIG-Cu system. The FIB milling technique complemented the PDP information to study the corrosion attack morphology at various stages of the anodic polarisation. The local electrochemical activity of the ENIG surface after each polarisation step was investigated by the SECM operating in feedback mode.

## 2.2 Experimental procedure

### 2.2.1 Material

The commercial SD memory cards were purchased from Coolblue company (Dutch electronic commerce). The plastic holder of the SD card was removed to gain access to the inside PCB. The Cu pins inside PCB are coated with an ENIG final finishing. The dimensions of each pin are 2 mm × 4 mm. The schematic cross-sectional configuration of the ENIG system on a Cu substrate which is plated on a plastic backbone of the SD memory card is shown in Figure 2.1a.

### 2.2.2 Microstructural and compositional analysis

#### 2.2.2.1 *Scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDS) analyses*

To study morphology and elemental composition of the as-received and post-corroded samples, a SEM equipped with EDS detector (Jeol JSM-IT100) was used. The top-view SEM/EDS data were collected at an accelerated voltage of 20 keV in collecting emitted secondary electrons (SE) mode. For cross-sectional imaging of the entire thickness of the ENIG-Cu system, an as-received sample was embedded in an epoxy resin and subsequently ground to 4000 grit with SiC sanding paper. Afterward, the sample was polished with a fine diamond suspension (Struers DiaDua-2) with particle sizes of 3 and 1 µm. The sample was cleaned for 10 min immersed in isopropanol (IPA) using an ultrasonic bath (Emag Emmi 20HC) and dried with compressed air.

#### 2.2.2.2 *X-ray diffraction (XRD) analyses*

To study the crystallinity of the underneath Ni layer, XRD measurements were carried out. The Au top-layer of the as-received samples was ground with 4000 grit of SiC sanding paper to expose the underneath Ni layer. An X-ray

diffractometer (Bruker D8 Advance) with Bragg-Brentano geometry and Lynxeye position-sensitive detector was used. Cu/K $\alpha$  radiation and Ni filter were applied. The XRD measurement was carried out in the scan range ( $2\theta$ ) of 20 to 100°, with a step size of 0.03° and a dwell time of 1s.

### 2.2.2.3 Atomic force microscopy (AFM) analyses

The surface topography of the as-received sample was characterized using AFM. The AFM measurements were performed in tapping mode using a Bruker Dimension Edge<sup>TM</sup> instrument with Nanodrive v8.05 software. Antimony (n) doped silicon cantilevers were used. AFM maps of 25  $\mu\text{m}$   $\times$  25  $\mu\text{m}$  (XY plane) were performed at a scan rate of 0.4 Hz and a resolution of 256  $\times$  256 points. To ensure the data were statistically significant, four map measurements were taken at random locations. The raw data were analysed using the open-source software Gwyddion v2.50.

### 2.2.2.4 Plasma-focused ion beam (PFIB)

PFIB was used to investigate the cross-section of the as-received and post-corroded samples. A Thermo Scientific<sup>TM</sup> Helios<sup>TM</sup> UXe DualBeam G4 PFIB microscope was used. An accelerated voltage of 5 keV was set for surface imaging and 20 keV for the EDS measurements. Both are in high-resolution SE mode. The blind mode for FIB sectioning was selected to preserve the surface and the ion-beam was used for the milling [34].

## 2.2.3 Electrochemical analysis

### 2.2.3.1 Open circuit potential and potentiodynamic polarisation measurements (OCP and PDP)

OCP and PDP measurements were used to determine the surface integrity of as-received samples and corrosion performance of the ENIG-Cu system in different pHs. The measurements were performed with a Biologic SP 300 multichannel potentiostat. A typical three-electrode cell consisted of Ag/AgCl electrode (sat. KCl) as a reference electrode, platinum wire as an auxiliary electrode, and the ENIG-Cu system as a working electrode. To prevent crevice corrosion from the edges of the backbone plastic, the ENIG-Cu sample (metallic pins) were masked with an adhesive sealing tape, and each pin's central part was exposed to the

aqueous electrolyte. The exposed surface area was calculated before the experiments by using the ImageJ software.

OCP measurements of Au, Ni, and Cu were performed in an aerated 3.5 wt.% NaCl solution at pH 2. To measure the OCP of Au, a commercially pure Au flake was used and for the Cu and the intermediate Ni layer, a tilted abrasion of the ENIG-Cu sample was performed by SiC 2000 grit sanding paper to partly remove the Au layer and expose the Cu and the Ni as shown in Figure 2.1b. The OCP measurements were recorded during the 600s.

OCP and PDP measurements of the ENIG-Cu samples were performed in an aerated 3.5 wt.% NaCl at different pHs (2, 3, 4, 5 and 10). The pH adjustments of the solution were carried out using concentrated hydrochloric acid (HCl) for acidic solutions and concentrated NaOH for alkaline solutions, with Milli-Q® ultrapure water at room temperature. Before the electrochemical measurements, the ENIG-Cu samples were cleaned in an ultrasonic bath (Emag Emmi 20HC) for 10 min in isopropanol, then dried with compressed air. OCP values were stabilized to a steady-state response for 25 min. Then, PDP measurements were performed over the potential range from -0.15 V to 0.80 V (vs. OCP) at a scan rate of 1 mV/s. To estimate the corrosion potential ( $E_{\text{corr}}$ ) and the corrosion current density ( $i_{\text{corr}}$ ), Tafel extrapolation was applied using EC-Lab V11.33 software. At least three repetitions were carried out to assess the reproducibility of the experiments. Sample preparation for SEM/EDS analysis of the different stages of corrosion evolution was performed by terminating anodic polarisation measurements at seven anodic potentials: +40, +80, +130, +200, +320, +680, and +800 mV vs OCP. Then, the post-corroded samples after each stage of anodic polarisation were rinsed with Milli-Q® ultrapure water and dried with compressed clean air.

### 2.2.3.2 Scanning Electrochemical Microscopy (SECM)

The post-corroded samples obtained after each step of the anodic PDP measurements were embedded in epoxy. An SECM instrument SCV370 model (Princeton Applied Research, AMETEK Inc.) was used. Scanning experiments operating in feedback mode were carried out using 3.5 wt.% NaCl + 2mM ferrocenemethanol (FcMeOH) as a redox mediator. The SECM electrochemical



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cell consisted of a disk-shaped Pt-microelectrode of 10  $\mu\text{m}$  diameter (by Sensolytics Inc.) as a working electrode, a platinum plate as an auxiliary electrode, and an Ag/AgCl, KCl (sat.) electrode as a reference electrode. During the experiments, the microelectrode was polarised at 0.5 V (vs. Ag/AgCl) to oxidise the mediator from Fe (II) to Fe (III). The sample remained at OCP conditions.

To establish the distance between the microelectrode and the ENIG-Cu surface before scanning, an approach curve of the SECM tip was measured. The tip-sample distance was fixed at 15  $\mu\text{m}$ , and a scan rate of 20  $\mu\text{m/s}$  was used. SECM scans were initiated after a 5-minute resting period following immersion, prior to each scan.

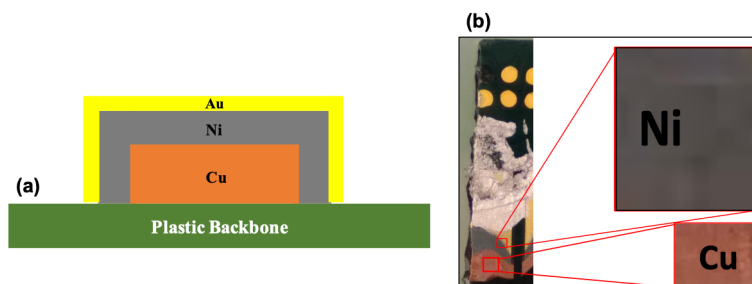


Figure 2.1(a) The schematic cross-sectional illustration of the ENIG-Cu system in the SD card (The width of each pin is approx. 2 mm; the thickness of each layer is not to scale for representative purposes), (b) sample preparation by fine abrasion of the ENIG-Cu sample.

## 2.3 Results and discussion

### 2.3.1 Microstructural and compositional characterisation of as-received ENIG-Cu samples

In Figure 2.2, microstructural, topography, and compositional analysis of the ENIG-Cu system are shown. The top-view SEM image of the metallic pin of the as-received SD memory card with the ENIG-Cu system (Figure 2.2a). It shows a heterogeneous topology with local defects. In addition, the topographic map of the top layer is presented in Figure 2.2b. From the analysis of the topography map, the maximum valley depth ( $S_v$ ) and root mean square roughness ( $S_q$ ) values of the surface were  $251 \pm 38$  nm and  $72 \pm 2$  nm, respectively. Line 1 is a selected topography line scan from the topography map having the highest pit height

(Figure 2.2b). The depth profile of Line 1 shows a sudden drop of the height, 151 nm, over a micro-defect, illustrated in the red dashed box in Figure 2.2c. To gain more insight into the Au layer thickness at the trough of the selected micro-defect and the Au/Ni interface quality, FIB milling was performed on the same spot. In Figure 2.2a, the red dashed line in the top-view SEM image of the selected micro-defect shows the plane of interest for FIB milling. The cross-sectional FIB-SEM image at the plane of interest is shown in Figure 2.2d. A Pt layer was deposited to protect the Au layer from Xe damage while milling. The uneven topography of the Au layer shown in Figure 2.2b by AFM was corroborated by the cross-sectional FIB-SEM image (Figure 2.2d). The inset shows a magnified view of the Au/Ni interface at the bottom of the microdefect.

Furthermore, to perform a compositional study of each layer, a cross-sectional SEM image of the whole ENIG-Cu system is shown in Figure 2.2e. Point EDS analyses provided the element compositions of each layer from top to bottom. The spectra are presented in Figure 2.2f, g, and h. Also, the thickness of the entire metallic pin attached to the plastic board is  $27.0 \pm 1.4 \mu\text{m}$ . The thickness of the ENIG-Cu layers is  $15.7 \pm 0.9 \mu\text{m}$  of Cu,  $10.5 \pm 0.5 \mu\text{m}$  of Ni, and  $408 \pm 127 \text{ nm}$  of top-layer Au. Finally, XRD measurements were carried out on the intermediate Ni layer. The XRD pattern is shown in Figure 2.2i. The results demonstrate that the intermediate layer consisted of pure Ni with a nanocrystalline structure. By considering the thickness and the  $S_v$  values of the Au top-layer, the micro-defects can be regarded as superficial, and they do not reach the underlying Ni layer.

A cross-sectional FIB-SEM image of the selected micro-defect showed that a thin layer of the protective Au layer, with a thickness of  $186 \pm 27 \text{ nm}$ , is present on the intermediate Ni layer. Also, the flat Au/Ni interface shows that the uneven surface of the top-layer is not due to the surface quality of the Ni layer. Therefore, the bottom of the deepest micro-defect, where the thinnest thickness of the Au layer covers the Ni substrate, might be a location of high porosity. The relative amount of "empty" volume or that of exposed substrate area is considered the porosity of a layer. The porosity level of the Au top-layer is inversely correlated with its thickness [35].

## Localised corrosion of electroless nickel immersion gold-coated copper

The spectrum for the Au top-layer (Figure 2.2f) shows Au-peaks as the dominant element and a minor peak corresponding to the Ni. The detection of Ni may be explained by the thin layer of the Au layer and the significant interaction volume of the incident electron beam [36]. The spectrum corresponding to the intermediate layer showed mainly peaks attributed to Ni (Figure 2.2g). A phosphorus signal around 2 keV energy [37] was not detected. This element is typically a constituent of the electroless Ni layer. In Figure 2.2h, the spectrum of the substrate layer is shown. The main element detected is Cu, as expected. Minor peaks corresponding to C are found in all spectra (Figure 2.2f, g, and h), which can be attributed to organic contamination.

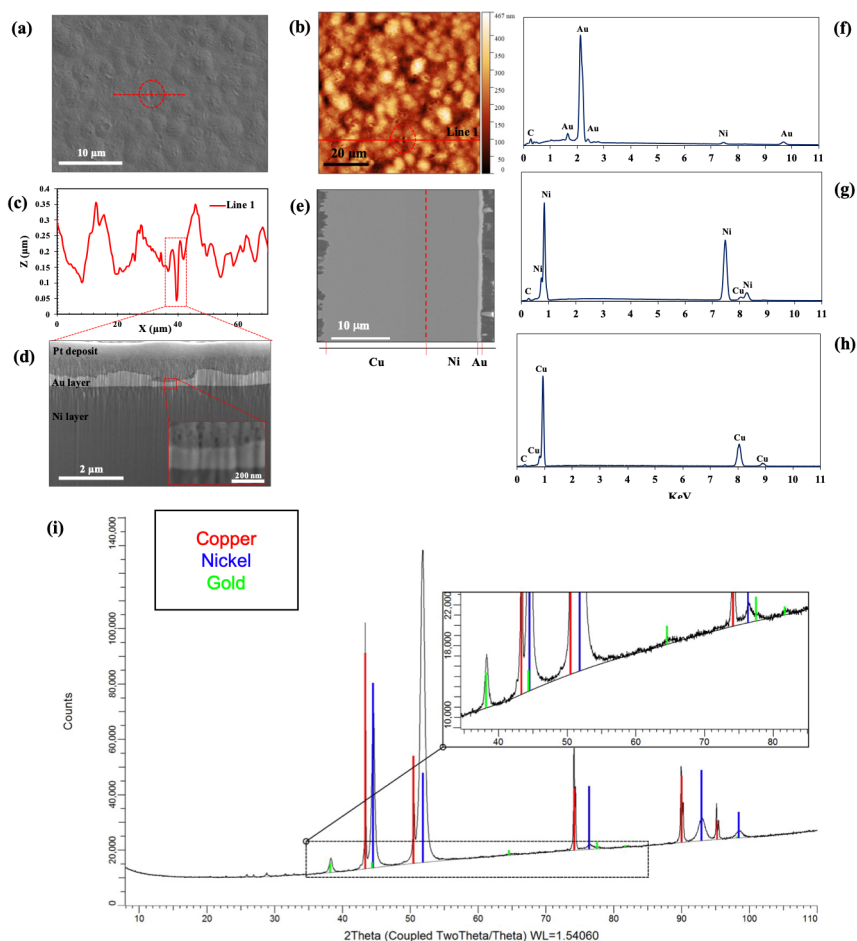


Figure 2.2. Microstructural, topography, and compositional analysis of the ENIG-Cu system. (a) Top-view SEM image of the ENIG-Cu system surface with a dashed line for

the micro-defect indication, (b) AFM topography map of the ENIG-Cu system surface with a line for the micro-defect indication, (c) the line depth profile on the micro-defect (d) the cross-sectional FIB-SEM image of the micro-defect, low and high magnification. (e) the polished cross-section of the sample for compositional analysis of each layer. EDS points analysis of (f) Au top-layer, (g) intermediate Ni layer, (h) the Cu substrate, and (i) the XRD pattern from the abraded ENIG surface showing the nano-crystalline structure of the nickel layer.

### 2.3.2 Electrochemical study of as-received samples

The corrosion properties of the ENIG-Cu sample were studied by potentiodynamic polarisation experiments. The behaviour of the sample was studied in 3.5% NaCl solutions at different pHs ranging from 2 to 10. Representative curves at each pH are shown in Figure 2.3a. The cathodic process is under activation polarisation control. The anodic branches show relatively high anodic activity even at low overpotentials. At acidic pHs, higher overpotentials result in a stable, relatively high anodic current density, indicating the absence of passivation behaviour [38]. At pH 2, the polarisation curve reaches a limiting current density of  $9.59 \pm 1.40 \text{ mA/cm}^2$ . On the other hand, active/passive behaviour in the anodic curve of the ENIG-Cu system at an alkaline pH of 10 is shown. The intact surface of the ENIG-Cu system at a basic pH of 10 after anodic polarisation is shown in Figure 2.3b.

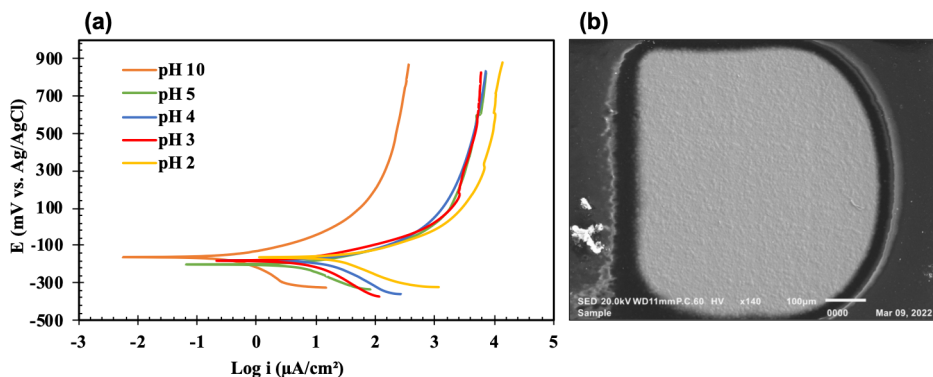


Figure 2.3(a) Potentiodynamic polarisation curves for ENIG-Cu sample in 3.5% NaCl solution at different pHs, (b) SEM image of the surface of the ENIG-Cu system at basic pH of 10 after anodic polarisation until + 800 mV (vs. OCP).

In Figure 2.4a and Figure 2.4b, the average values of corrosion current density and corrosion potential extrapolated from the polarisation curves are presented, respectively. The corrosion current densities at acidic pHs are higher than at pH

10. For pH 10 and based on the Pourbaix diagram [39], passivity of the Ni and Cu is expected, with the presence of stable (hydr)oxides such as  $\text{Ni(OH)}_2$ , and  $\text{Ni}_3\text{O}_4$ . Nevertheless, the high concentration of chloride species and the presence of porosity limit their stability, leading to localised activity at both high anodic potentials and low overpotentials, as observed in the polarisation curves. The corrosion potential values do not differ significantly, as shown in Figure 2.4b. The highest corrosion potential is  $-175 \pm 20$  mV for pH 3 and the lowest corrosion potential is  $-216 \pm 19$  mV for pH 5.

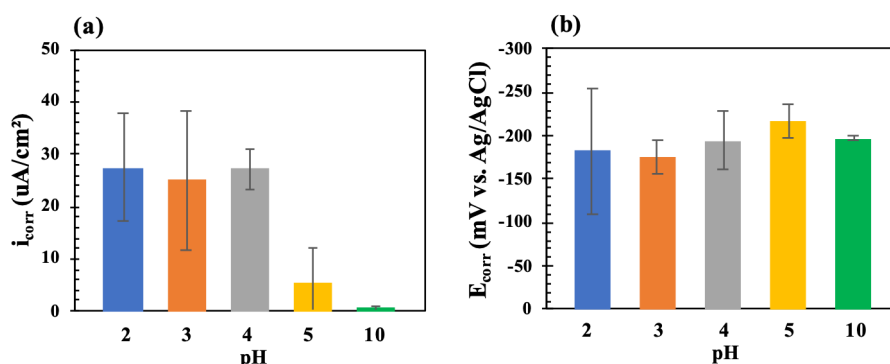


Figure 2.4 The effect of solution pH on corrosion behaviour of the ENIG-Cu system: (a) corrosion current density vs. pH, (b) corrosion potential vs. pH.

To further analyse the corrosion mechanism of the ENIG-Cu sample, additional studies were conducted in an acidic solution at pH 2. From the SEM/FIB and AFM analysis in Figure 2.2, the presence of micro-defects facilitating the exposure of the underlying Ni through possible porosities was hinted. To confirm the presence of defects in the outer Au layer exposing the Ni underneath, OCP measurements were carried out for three different sample types: pure Au flake, intermediate Ni layer, and as-received ENIG-Cu sample.

OCP measurements in 3.5 wt.% NaCl at pH 2 are shown in Figure 2.5. During the measurements, the potential values of the Au flake and Ni layer remained relatively stable with minor changes. The potentials of Au and Ni were  $304 \pm 20$  mV and  $-142 \pm 37$  mV at time zero, respectively. The initial OCP value of  $162 \text{ mV} \pm 43$  mV of the as-received sample laid between the potentials of the Au and Ni

layers. After a short time, the OCP value of the sample decreased to  $-147 \text{ mV} \pm 49 \text{ mV}$  and approached the potential values of the Ni layer. This might indicate that Ni was exposed from the early stages of exposure in the as-received sample. However, the defects on the Au layer conducting the corrosive solution to the underneath Ni were not detected by cross-sectional FIB milling in Figure 2.2d. The presence of imperfections in the Au top-layer, which exposes bare Ni to air, is typically attributed to flaws during the fabrication process. For instance, Monlevade *et al.* [28] showed that evaporation of trapped impurities during the immersion gold process leaves behind a cavity in the top-layer of the ENIG-Cu system.

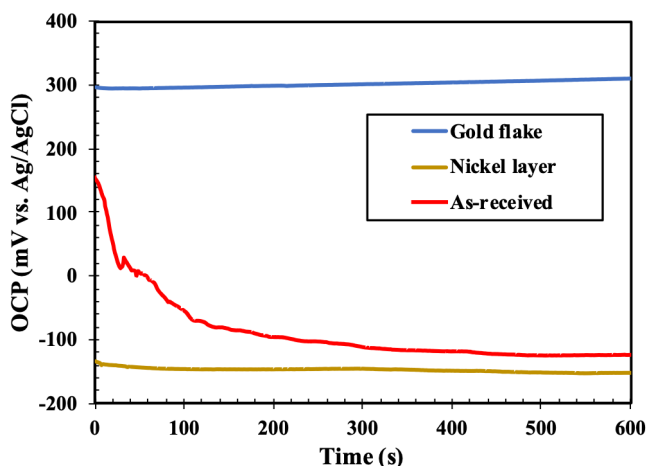


Figure 2.5 The OCP values of Au flake, Ni layer, and as-received ENIG sample in 3.5 wt.% NaCl at pH 2.

### 2.3.3 Microstructural and electrochemical characterisation of post-corroded ENIG samples

To comprehensively elucidate the ENIG surface's corrosion mechanism in the aqueous acidic media, potentiodynamic polarisation measurements for the ENIG surface in 3.5 wt.% NaCl solution at pH 2 were terminated at different anodic potentials: +40, +80, +130, +200, +320, +680, and +800 mV vs OCP. The surface of the sample was analysed by SEM/EDS after each applied potential.

In Figure 2.6, the top-view SEM/EDS pit analysis of ENIG samples at the different stages of the anodic polarisation is shown (+40, +80, +130, +200, +320, +680,

and +800 mV vs OCP). Here, the results of the selected three potentials (+80, +200, and +800 mV vs OCP) have been interpreted. After anodic polarisation to 80 mV, one circular pit formed, and the rest of the surface remained intact. As shown in Figure 2.6a, only Ni is detected in the circular pit by EDS mapping analysis. Figure 2.6d shows the SEM/EDS images of the surface after anodic polarisation until 200 mV (vs OCP). Five circular pits were formed in the overall exposed sample, leaving the rest of the surface intact. The pit mouth diameter was not significantly different from the sample polarised to +80 mV (Figure 2.6a). Pits now reached the underneath Cu layer as well. The presence of Ni inside the pit is reduced. The final stage, anodic polarisation until 800 mV, is shown in Figure 2.6g. Seven circular pits were formed in the overall exposed sample surface and the rest of the surface was intact. Two major circular pits with a larger mouth diameter and five minor pits. The localised attacks are now significantly more extensive, and the intermediate Ni layer is completely gone.

After anodic polarisation until 80 mV (vs OCP), the lack of Cu signal inside the pit shows that the localised corrosion was confined to the Ni. At the beginning of the anodic polarisation, the local corrosion of the Ni is assumed to initiate from an existing breach. With the elliptical dissolution of the Ni, whenever a sufficient amount of the Ni is depleted, the loose lid of the undercut top-layer Au would be detached to leave a circular shape of the pit mouth. The autocatalytic nature of pitting growth, coupled with the surface imperfections, provides a high ratio of cathode-to-anode surface to propagate the pitting process. Pits do not form simultaneously; some form earlier than others, depending on local electrolyte and surface (defect) conditions [17]. After anodic polarisation until 800 mV (vs OCP), the high potential polarisation resulted in the intensive dissolution of the Ni layer, not only reaching the underlying Cu substrate but also propagating in the near-surface area.

The surface morphology analysis shows that a loose circular Au layer is removed from the surface and dissolved into the solution after extensive dissolution of the underlying Ni. Since the removal of the loose lid of the Au top-layer is also dependent on the mechanical strength of the Au layer at that specific region, the detachment can happen already in the early stages of polarisation. In Figure 2.7a,

due to the dissolution of the underlying metallic layer, a circular dent forms a loose lid of the top-layer Au, with a void beneath, after anodic polarisation to +320 mV (vs OCP). A mechanical force was applied to remove the loose lid by manually peeling off the plastic tape from the surface. In Figure 2.7b, the detachment of the open circular lid of the Au top-layer due to applied mechanical force from the same pit is shown. The SEM images of the overall surface of post-corroded samples after the termination of the potentiodynamic polarisation measurements at the selected three potentials are shown in Figure 2.8.

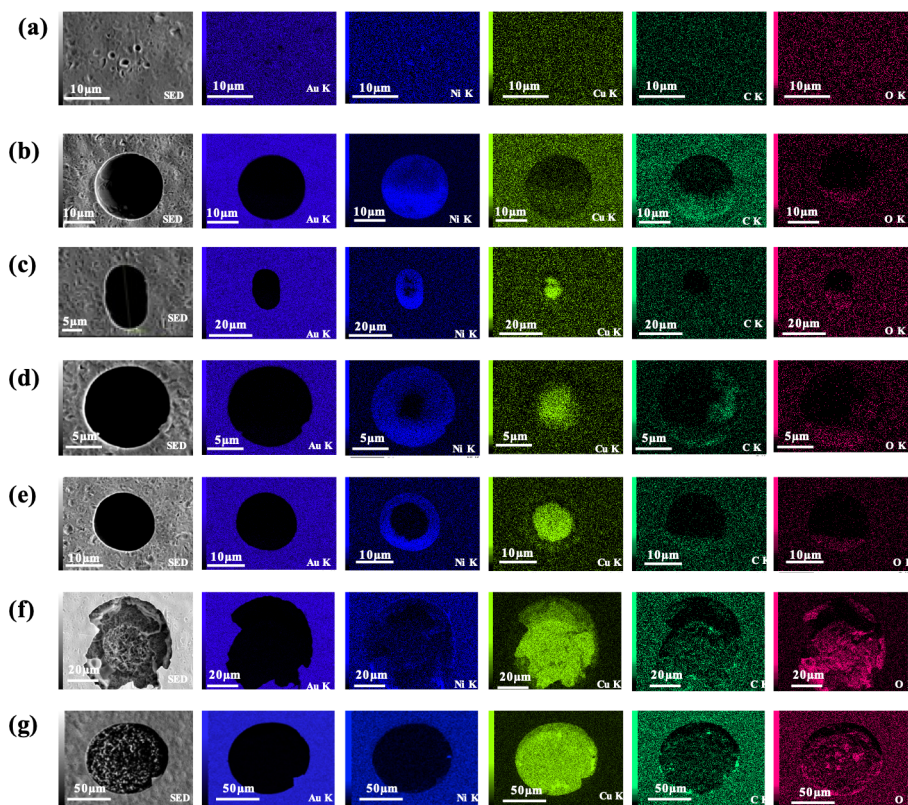


Figure 2.6 The top-view SEM image and EDS elemental maps for pit analysis of ENIG samples in 3.5% NaCl - pH2, after anodically scan polarisation until the following potentials: (a) 40mV, (b) 80mV, (c) 130mV, (d) 200mV, (e) 320mV, (f) 680mV, and (g) 800mV.



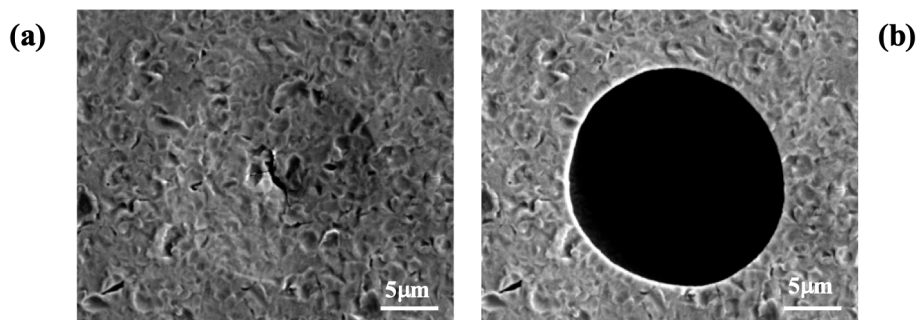


Figure 2.7 (a) The loose circular lid of top-layer Au with a void underneath, before applying the mechanical force of tape peel-off after anodic polarisation until 320 mV (vs OCP), (b) the same pit after the tape peel-off.

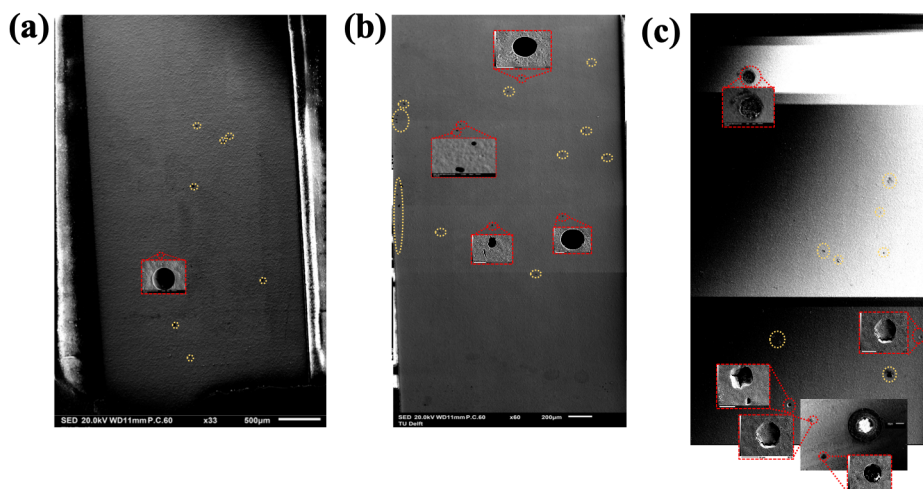


Figure 2.8 The top-view overall SEM of post-corroded ENIG-Cu samples: (a) after 80mV anodic PDP, (b) after 200mV anodic PDP, and (c) after 800mV anodic PDP, red dashed lines and yellow dashed lines show localised corroded and carbon contamination regions, respectively. Due to electrostatic charging at low magnifications, it was not possible to achieve optimal contrast and brightness in a single image acquisition. The overall post-corroded surface was shown by piling up the discrete SEM images.

Cross-sectional and top-view FIB-SEM analyses of the pits detected at the different potentials are shown in Figure 2.9. The cross-section analysis for the sample polarised to 80 mV (Figure 2.9a) shows an elliptical shape of the pit growth, confirming that the general dissolution direction of Ni was a combination of lateral and in-depth. However, the bottom of the pit does not reach the Ni/Cu interface. In Figure 2.9b, the cross-section of the pit of the sample polarised to

200 mV as the middle stage is shown. The ternary system of Au/Ni/Cu was exposed to the corrosive solution, and a large undercutting region, compared to the initial stage, was formed in the Cu layer. Although the direction of the localised corrosion is a combination of lateral and in-depth propagation, the lateral propagation contributes slightly more than the in-depth propagation. The elliptical growth pattern of the undercutting region in the Cu layer leaves a spiky surface for the Cu layer. The morphology of a major pit on the post-corroded ENIG surface after the final stage of the anodic polarisation, i.e., after 800mV anodic polarisation, is shown in Figure 2.9c<sub>1</sub>, c<sub>2</sub>, and c<sub>3</sub>. The dominant lateral corrosion propagation direction led to the formation of a significantly larger circular pit with an average diameter of  $154.0 \pm 70.1 \mu\text{m}$ , showing a wide variation in pit mouth size distribution. In Figure 2.9c<sub>2</sub>, the shallow dent in the centre of the pit shows the Cu dissolution. The in-depth progression of corrosion in the Cu layer was limited, as lateral corrosion in the Ni resulted in a large pit mouth diameter. The Ni/Cu interface at the edge of the pit shown in Figure 2.9c<sub>3</sub> demonstrates the lateral corrosion growth.

In the initial stage, the galvanic coupling of the Ni as an anode with a small surface area and the Au as a cathode with a large surface area led to the fast dissolution of the Ni. The high ratio of cathode-to-anode surface provides a high galvanic driving force for the localised corrosion of the Ni with a high local anodic current [16]. The anodic reaction for Ni dissolution is expected to follow Eq. 2 [3, 26]. Due to the nano-crystalline structure of the Ni, the exposed Ni in the pit contains a high concentration of grain boundaries that may act as structural discontinuity. These microstructural heterogeneities might contribute to the inferior corrosion performance of the Ni [5]. Due to the acidity of the solution, the possible reduction reaction on the Au surface is expected to occur according to Eq. 8.



Eq. 8

In Figure 2.9b, owing to the expected high acidity and high concentration of chloride ions of the solution at the bottom of a pit [40-42], imperfect undercutting is occurring at the bottom of the pit. Due to solution chemistry, copper purity, and the configuration of the intermediate Ni layer, the shape and severity of Cu

undercutting beneath the Ni layer can be influenced. For instance, Collins *et al.* [5] showed different severities of Cu undercutting in Ni/Au, Ni-P/Au, Ni/Ni-P/Au, and Ni/Ni-Pd/Au coating systems after exposing them for 10 days to a harsh artificial environment. In the current ternary system, Cu dissolution in the undercutting region became more favorable as the acidic, highly Cl<sup>-</sup>-concentrated solution at the bottom of the pit became harsher than the bulk solution [43, 44]. In Figure 2.9c<sub>2</sub>, the shallow dent in the centre of the pit is attributed to the growth of the undercutting region mentioned in Figure 2.9b. Based on the current set of results, the corrosion mechanism for the current ENIG system in an acidic solution is proposed as follows: the small oxygen-depleted area at the bottom of the micro-defect which exposes the bare Ni, being thermodynamically less stable, acting as the anode and the large surface area of the surrounding Au, having access to the oxygen in the acidic bulk solution, acts as the cathode [26]. The high surface ratio of cathode-to-anode and the relatively high electrochemical potential difference between Ni and Au ( $516 \pm 47$  mV) enhance local corrosion. As the ternary system of Au/Ni/Cu is exposed to the corrosive media, preferential dissolution of the Ni will occur as the less noble element. However, in the first moments of the ternary system exposure, local Cu dissolution may temporarily occur at aggressive pit bottom conditions. The localised corrosion growth direction at the beginning was a combination of lateral and in-depth growth; however, after exposure to the ternary system of Au/Ni/Cu, the corrosion growth direction shifted to lateral growth preferentially [17]. Local variations of solution chemistry, including local acidity and metallic ion, chloride, and oxygen concentrations, may affect the local (galvanically driven) pitting corrosion conditions.

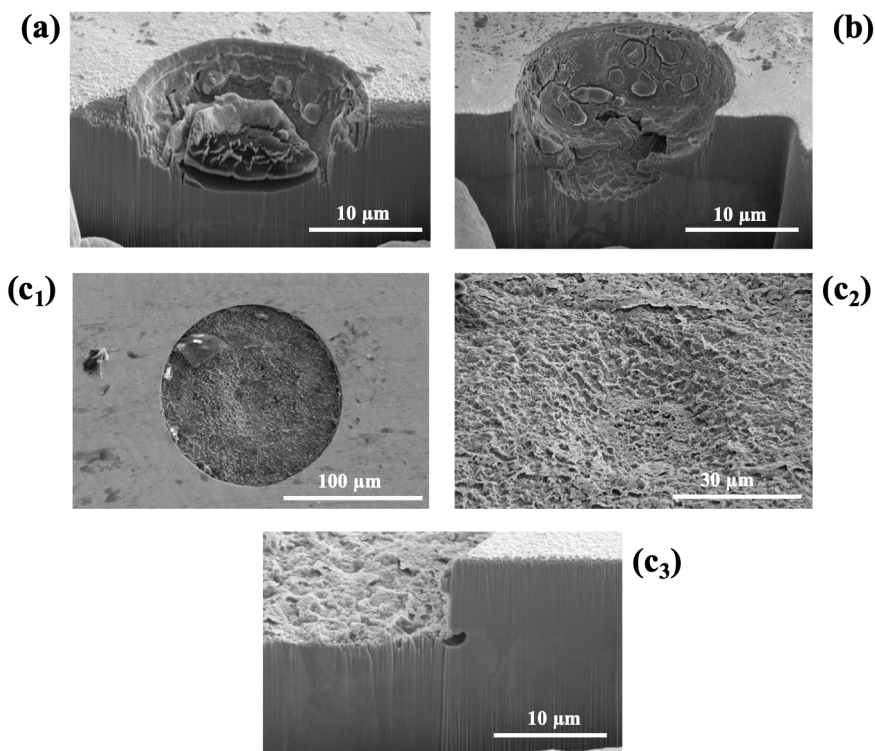
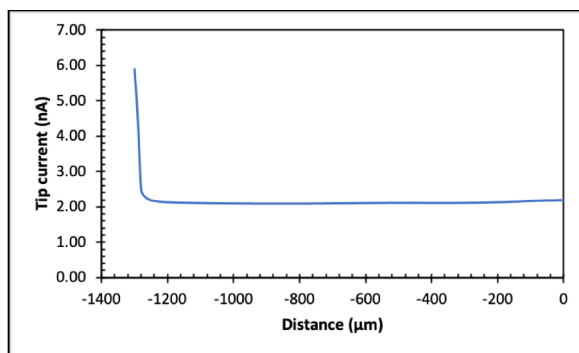


Figure 2.9 The cross-sectional and top view FIB-SEM/EDS pit analysis of ENIG samples in 3.5% NaCl at pH2 after: (a) 80mV anodic PDP, (b) 200mV anodic PDP. (c<sub>1</sub>) top-view SEM image after 800mV anodically PDP, (c<sub>2</sub>) tilted top-view SEM image from inside the pit after 800mV polarisation, and (c<sub>3</sub>) cross-sectional view of the pit edge after 800mV polarisation.

### 2.3.4 Local electrochemical study of post-corroded samples by SECM

To study the local electrochemical activity of the post-corroded ENIG surface after the initial, middle, and final stages of anodic polarisation, SECM measurements in feedback mode were performed. Because of the conductive nature of the Au top-layer, a positive feedback approach curve was obtained when the microelectrode was approaching the ENIG surface, as shown in Figure 2.10. In the positive feedback approach curve, due to the active electrochemical behaviour of the substrate in terms of regenerating the redox species, the tip current increases dramatically as the tip approaches the surface in close vicinity to the substrate. The SECM normalised (normalised current =  $i/i_{\text{limit}}$ ) maps in the positive feedback mode are shown in Figure 2.11. Due to the small diameter of pit mouths in the initial and the middle stages, scan areas of  $400\text{ }\mu\text{m} \times 400\text{ }\mu\text{m}$

were mapped, Figure 2.11a, b; however, for the final stage of the anodic polarisation, a relatively large scan area of  $800\text{ }\mu\text{m} \times 800\text{ }\mu\text{m}$ , Figure 2.11c, was chosen to cover the whole area of the pit mouth. The normalised current on the pit from the initial stage of anodic polarisation to the final stage was diminished. In Figure 2.11a, the SECM normalised current map of the post-corroded surface of ENIG after 80mV of anodic polarisation showed the active site with an intense peak at the pit location. During the middle stage of the anodic polarisation, the pit mouth remains almost the same as the initial stage but the in-depth growth of the pit leads to exposing the Cu layer to the solution. Therefore, due to the greater distance between the surface at the bottom of the pit and the SECM tip, the peak intensity at the active sites in the middle stage is reduced, as shown in the SECM normalised current map (Figure 2.11b). At the final stage of polarisation, as shown in Figure 2.11c, the size of the pit mouth was enlarged, and the pit was deeper due to the complete dissolution of the intermediate Ni layer. In Figure 2.11c, the size of the active site corresponds to the large pit mouth and the low intensity of the normalised peak is due to the high distance of the gap between the surface at the bottom of the pit and the SECM tip.



*Figure 2.10 SECM approaching curve showing positive feedback response. Measurements carried out in 3.5 NaCl + 2mM FcMeOH solution.*

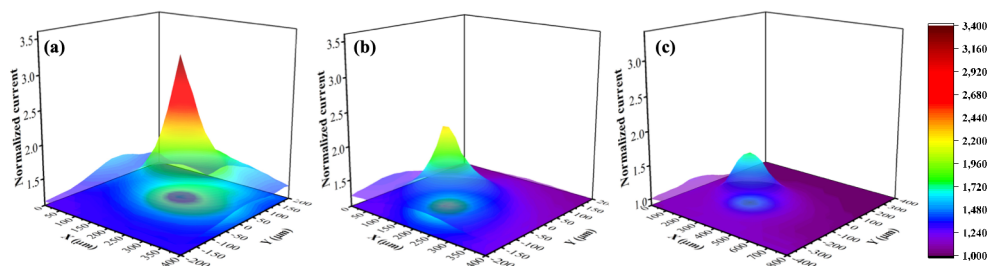


Figure 2.11 The SECM pit analysis of ENIG-Cu samples in 2mM FcMeOH, 3.5% NaCl at pH 2 after the anodic polarisation until (a) 80mV (b) 200mV, (c), and 800mV.

### 2.3.5 Corrosion mechanism of ENIG samples with micro-defects

The results from the morphological and electrochemical experiments have shown that the as-received ENIG-Cu system contains some micro-defects that exposed the bare Ni to corrosive media. The imperfections in the Au top layer provide a preferred location for the initiation of a localised corrosion attack. A schematic cross-sectional sketch of the first step of localised corrosion attack from a pre-existing micro-defect as the corrosion initiation location is shown in Figure 2.12a. To initiate the localised corrosion attack, the micro-defects provided a high cathode-to-anode surface area ratio. In the next step of the anodic polarisation, the elliptical dissolution of the Ni indicates that the dissolution proceeds with a combination of lateral and in-depth pit growth. By progressive elliptical dissolution of the Ni, the Au top-layer is undercut and the thin Au layer shows a dented morphology from a top-view, Figure 2.12b. With further undercutting of the Au top-layer, the loose Au cap is detached to open the pit, Figure 2.12c. It is worth noting that detachment of the loose lid may occur at either earlier or later steps due to the Au layer's mechanical properties, which are influenced by the top-layer surface texture. As shown in Figure 2.12a, b, and c, until reaching the Ni/Cu interface, the direction of the Ni dissolution is governed by an elliptical dissolution morphology which results in an increasingly widening and deepening of the pit. As shown in Figure 2.12d, as soon as the Cu is exposed to the corrosive media, the limited elliptical dissolution of the Cu occurs due to the acidic and highly Cl<sup>-</sup> concentrated solution at the bottom of the pit. Subsequently, the rate for Cu dissolution remains limited, and the corrosion attack direction tends to show

lateral growth in the Ni layer, Figure 2.12e. Eventually, in Figure 2.12f, the post-corroded surface of the ENIG-Cu system after the final stage of the anodic polarisation leaves a large hole with a small dent in the middle of the hole, at which the Cu was slightly corroded.

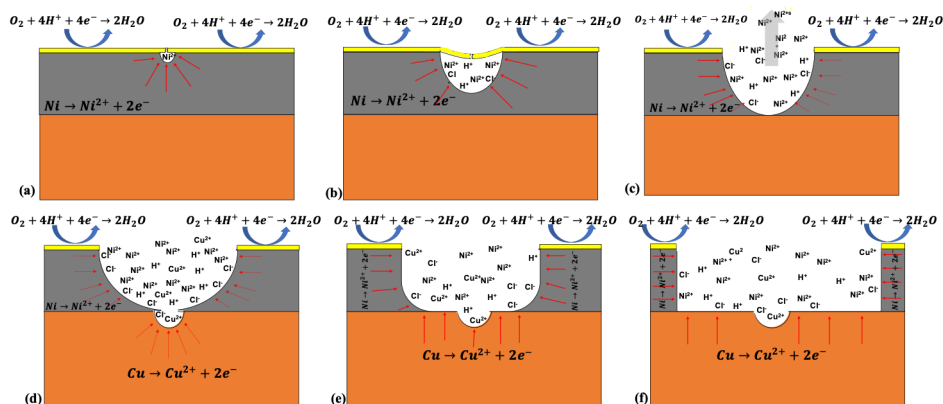


Figure 2.12 Schematic illustration of step-by-step localised corrosion of ENIG-Cu samples in 3.5% NaCl at pH 2 by potentiodynamic polarisation, (a, b, c) showing progressive dissolution of the Ni involving both lateral and vertical directions within the galvanic couple of Au//Ni, (d, e, f) depict the progressive dissolution of the Ni in a lateral direction and marginal dissolution of the Cu in an in-depth direction, the ternary system of Au/Ni/Cu. (The thickness of each layer was exaggerated for representation purposes)

## 2.4 Conclusions

This study aims to show a fundamental understanding of the localised corrosion mechanism of an as-received ENIG-Cu system of an SD memory card in an acidic chloride-containing aqueous environment. The applied step-by-step methodology, in terms of visualization of the gradually progressing corrosion phenomena, based on a combination of microscopic, analytical, and electrochemical measurements, enabled the illustration of the localised corrosion evolution. It was revealed that some micro-defects were present in the Au top-layer as imperfections. Exposing the Ni layer through these micro-defects led to local galvanic corrosion of the ENIG-Cu system which was governed by the high ratio of Au-to-Ni, cathode-to-anode, and surface area. The high driving force for galvanic corrosion of the Au/Ni couple led to rapid, sustained dissolution of Ni. The elliptical dissolution of the Ni, a combination of lateral and in-depth pit growth, continued to reach Ni/Cu interface. Then, the Ni dissolution direction changed to

lateral growth after a relatively limited elliptical dissolution of the Cu. In the ternary system of Au/Ni/Cu, the corrosion rate of Ni was considerably higher than that of Cu. It was concluded that the direction of metallic dissolution changed during corrosion evolution due to changes in pit geometry and the exposed materials over time.



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## 2.6 Addendum

Two aspects of the discussion presented in this chapter deserve further consideration.

The first concerns the cathodic reaction governing corrosion in this study. In the corrosion mechanism proposed in this chapter, the cathodic reaction was considered to be the reduction of dissolved oxygen (Equation (8)). Owing to the acidity of the solution at pH 2, proton reduction ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ) is also thermodynamically feasible and may proceed in parallel with oxygen reduction, both on the Au surface and on the Ni exposed at the bottom of the pits, where local acidification further favours it. The proposed mechanism, i.e. the localised dissolution of the Ni layer driven by the galvanic couple with a high cathode-to-anode (Au-to-Ni) surface area ratio, holds for either cathodic pathway, since both reactions sustain the galvanic couple. Separating the two cathodic contributions, for instance by comparative measurements in aerated and deaerated electrolytes, is suggested as a direction for future work.

The second concerns the deposition method for the Ni and Au layers of the commercial SD-card samples. The manufacturer was contacted in an attempt to confirm the fabrication route for these layers, but the requested information on the deposition method was not disclosed. In the absence of this confirmation, the designation ENIG is used throughout this chapter in the sense in which it is commonly applied to this type of surface finish in the electronics industry, rather than as a verified process specification. Some indication of the deposition method for the Au top-layer can be inferred from its measured thickness of  $408 \pm 127$  nm

(Section 2.3.1). This value is thicker and considerably more variable than typically reported for immersion gold, which is more consistent with an Au layer obtained by another method, such as electroplating, than with a conventional immersion-gold layer. However, the local Au thickness at the studied micro-defect, where corrosion was observed to initiate, was considerably thinner than the bulk average, at  $186 \pm 27$  nm (Section 2.3.1), closer to, although still somewhat above, the thickness range typically associated with immersion gold. This suggests that the porosity-driven initiation mechanism proposed in this chapter may remain locally applicable in such thinner regions of the coating, irrespective of the bulk deposition method, although the likelihood and spatial distribution of these thin, defect-prone regions would be expected to differ between a genuinely thin, uniformly deposited immersion-gold layer and a thicker layer, such as one obtained by electroplating, in which only isolated regions happen to be locally thin. The corrosion mechanism established in this chapter does not, in either case, rest on a specific assumption about the bulk deposition method. The exposure of the underlying Ni was demonstrated experimentally: the OCP of the as-received samples approached the potential of the bare Ni layer within minutes of immersion (Figure 2.5), and micro-defects with a locally thinned Au layer were documented by AFM and cross-sectional FIB-SEM analyses (Figure 2.2). The galvanic corrosion mechanism follows from this demonstrated exposure, irrespective of whether the through-layer defects originate from the intrinsic porosity of a thin immersion-gold layer or from isolated thin regions in a layer deposited by another method.







## Chapter 3. The effect of phosphorus content on the microstructure and localised corrosion of electroless nickel-coated copper

### Abstract

A detailed microstructural and electrochemical analysis of electroless nickel phosphorus (NiP) coatings with P contents of  $13.2 \pm 1.2$  wt.%,  $12.9 \pm 0.7$  wt.%, and  $8.3 \pm 0.8$  wt.% on a copper substrate was performed to study the corrosion behaviour of electroless NiP/Cu systems. The P content of the electroless NiP coatings plays an essential role in the microstructure of the coatings in terms of crystallinity. The crystallinity variations, representing the extent of crystalline and amorphous phases within the material, with P content, affect the local electrochemical characteristics and, hence, the corrosion protection behaviour of electroless NiP coatings. The coatings with the highest P content showed the best corrosion performance in a 3.5 wt.% NaCl solution. In contrast, the surface of electroless NiP coatings with low P content is more susceptible to corrosion due to heterogeneous electronic properties that initiate localised corrosion. Microgalvanic interactions with a high cathode-to-anode surface ratio govern the localised corrosion kinetics of the low P-content samples. A high concentration of nodule boundaries and/or other existing structural defects on the surface serves as anodic sites, whereas the remainder of the surface serves as cathodic sites.

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### 3.1 Introduction

Metallic coatings are of significant practical and technological importance in our daily lives as functional or protective surface coverage concepts [1]. As a widely used metallic coating, electroless nickel (EN) is a chemical or autocatalytic plating process that deposits a layer of nickel onto the surface of a substrate, typically a metal or plastic component [2]. EN coatings offer several advantages, including uniform and controlled deposition [3], good wear and corrosion performance, high hardness, improved electrical conductivity, and good solderability [4, 5]. The versatility and ease of application of EN coatings have made them extensively used in several industrial sectors, including renewable energy applications [6-8], automotive [9], aerospace [10, 11], biomedical [12], oil and gas [13, 14], and electronics industries [15-20].

The use of EN coatings on copper substrates for electronic applications has become increasingly prevalent due to their ability to address the specific, stringent requirements of the electronic industry, such as safety measures and high-performance reliability. This is particularly crucial given copper's high susceptibility to oxidation. EN coatings are utilised in the electronic industry as an intermediate coating between the copper substrate and gold top layer in the electroless nickel immersion gold (ENIG) coating system for printed circuit boards (PCBs). PCBs with EN coatings are ideal for high-wear applications like connectors and switches and can withstand exposure to harsh environments. Additionally, EN coatings exhibit good solderability, which is important for PCB assembly [21, 22]. The intermediate EN coating in PCBs prevents copper and gold interdiffusion [17]. However, the performance of EN coatings can be significantly affected by factors such as composition, electronic properties, microstructure, and deposition conditions.

The presence of P, as the predominant alloying element in electroless NiP coatings, notably influences the microstructure of the coatings in terms of crystallinity level. Depending on the P content, the microstructure of electroless NiP coatings has been found to be either amorphous, crystalline, or both. Crystalline ( $\beta$ ), mixed amorphous crystalline ( $\beta$  and  $\gamma$  coexist), and amorphous ( $\gamma$ )

phases have been reported for coatings with low (3–5 wt.%), medium (6–10 wt.%), and high (11–18 wt.%) P contents, respectively [23, 24]. Electroless NiP coatings are less porous, have a more uniform thickness, and are harder than the corresponding P-less electroplated nickel coating [24–26]. Moreover, the P content in the EN coating significantly affects the coating's corrosion protection performance. In addition to their passive nature, the mentioned unique properties of electroless NiP coatings make them excellent at resisting corrosion in various environments, such as neutral and acidic conditions, where a higher P content (above 10 wt.%) is advantageous, as well as in strong alkaline media, where coatings with lower phosphorus content are more effective [4]. Electroless Ni coatings with a high P concentration provide superior corrosion protection, whereas those with a moderate or low P content perform poorly in neutral or acidic corrosive environments. Because grains and grain boundaries, which are often sites of corrosion attack in crystalline materials, are absent, amorphous alloys exhibit superior corrosion resistance compared to equivalent polycrystalline materials [27, 28]. This is not the only mechanism reported in the literature for the enhanced corrosion protection provided by high-phosphorus content coatings. As mentioned in Pedrizzetti *et al.*'s work [25], preferential Ni dissolution enriches the surface with phosphorus, promoting the formation of stable  $\text{Ni}_3\text{P}$  and  $\text{Ni}_x\text{P}_y$  compounds. These compounds create a pseudo-passive barrier layer on the surface, thereby hindering further corrosion.

Microstructural and electrochemical studies on various substrates, including mild steel, twinning-induced plasticity (TWIP) steel, AZ31 Mg alloy, and aluminium alloy 2024-T3, have been conducted to investigate the impact of P content on the corrosion protection of electroless NiP coatings [10, 24, 29–32]. Shibli *et al.* [30] investigated the microstructural and morphological effects of P content and  $\text{TiO}_2$ -reinforcement on electroless NiP coatings for hydrogen evolution reactions on mild steel. In terms of microstructure, they concluded that the electroless NiP-coated surface with low P content exhibits Ni (111) and Ni (200) lattice structures, as evidenced by X-ray diffraction (XRD), revealing its crystalline nature. On the other hand, in the case of medium P content, they detected more blurry and diffused diffraction peaks. Most notably, no diffraction peaks were observed for

the electroless NiP plates with high P content due to their amorphous structure. The disordered lattice caused by an increase in the P content of the plates may have resulted in a transition from a crystalline to an amorphous texture. Regarding the morphological integrity of electroless NiP surfaces, coatings with high P content showed a defect-free top-surface morphology, while those with medium content showed distinguished nodules. Medium P content coatings also displayed porous surfaces. Coatings with low P content exhibited porous surfaces, non-uniform nodular sizes, irregular nodular boundaries, and minor defects.

Numerous studies have demonstrated that the addition of phosphorus to electroless nickel coatings enhances their corrosion performance in neutral or acidic conditions by increasing the tendency for passivation and forming stable intermediate compounds ( $\text{Ni}_x\text{P}_y$ ) [4, 23, 24, 28, 30, 33-36]. Bai *et al.* [33] investigated the corrosion behaviour of electroless Ni-P coatings with supersaturated P contents of 20, 24, and 28 at. % in chlorine-containing corrosive media by accelerated electrochemical techniques and a brine-fog method. They concluded that the P content has a substantial impact on the corrosion rate in brine media. They demonstrated that an increased P content results in a positive shift in the corrosion potential and a reduction in the corrosion current density. In addition, they demonstrated that the corrosion rate of the coatings depends significantly on the annealing temperature. Bonin *et al.* [35] studied the corrosion behaviour of electroless nickel-boron-phosphorus duplex coatings on mild steel in different corrosion media. They demonstrated that a hypophosphite layer is generated during anodic polarisation in a 3.5 wt.% NaCl solution at a pH of 5.9. Ni hydration is impeded by the formation of a hypophosphite layer, which prevents the electrolyte from reaching the Ni electrode surface and interacting with it.

Furthermore, there are many studies in the recent literature about enhancing the corrosion resistance of electroless NiP-coated substrates by introducing novel composite coatings such as Ni-P-ZnO [37], NiP- $\text{C}_3\text{N}_4$ /ZnO [38], NiP-TiO<sub>2</sub>-ZrO<sub>2</sub> [39], Ni-P-NiTi [40], NiMoP [41], Ni-WP [42], etc. For instance, Chintada *et al.* [37] investigated the impact of heat treatment temperature, the quantity of ZnO nanoparticles on microhardness, and the corrosion behaviour of electroless NiP

coatings on mild steel. They found that when ZnO nanoparticles were added to the electroless bath up to an amount of 2 g/L, the pores in the Ni-P lattice were filled, and the electrochemically active area of the composite coatings was reduced, leading to improved corrosion performance.

To the best of the authors' knowledge, no prior research has thoroughly explored the impact of P content on the corrosion behaviour of electroless NiP coatings. This study introduces a novel approach that integrates surface analysis, local surface potential measurements, and combined AC/DC electrochemical methods to comprehensively investigate this aspect. Rather than solely optimising coating performance and deposition parameters, the focus is on unravelling local corrosion mechanisms under varying P contents and microstructural variations. Through this combined methodology, insights into localised corrosion processes are revealed, shedding light on the driving forces behind corrosion initiation on metallic surfaces. This integration not only elucidates the spatial distribution of anodic and cathodic reactions but also identifies potential sites of corrosion initiation, providing invaluable insights into how local microstructural variations affect local corrosion susceptibility [43]. The obtained data can aid in comprehending micrometre-to-nanometre micrometre-to-nanometre-scale localised corrosion and galvanic activity. In scanning Kelvin probe force microscopy (SKPFM) studies of corrosion behaviour, differences in work function across microstructural features of the studied surface result in distinct lateral variations in Volta potential. These variations potentially offer valuable insights into the electrochemical characteristics of the materials, particularly in distinguishing anodic and cathodic behaviours. Benaïoun *et al.* [44] employed the SKPFM technique to directly measure the difference in work function values between the sample surface and the tip. This allowed for detailed chemical analysis at a microscopic level. Their use of SKPFM yielded critical insights into the development of passive films, revealing a uniform surface potential across the analysed surfaces.

This study provides a fundamental insight into the local corrosion behaviour of electroless NiP coatings with P contents of  $13.2 \pm 1.2$  wt.%,  $12.9 \pm 0.7$  wt.%, and  $8.3 \pm 0.8$  wt.% on copper substrates in an aqueous chloride-containing

environment. Using scanning electron microscopy/energy-dispersive X-ray (SEM/EDS) spectroscopy, focused ion beam (FIB), X-ray diffraction (XRD), atomic force microscopy (AFM), and SKPFM measurements, the as-received samples were characterised in terms of their microstructural, compositional and topographical properties, and their local Volta potential difference distribution. For corrosion performance testing under immersed conditions, potentiodynamic polarisation (PDP) measurements were performed. Also, open-circuit potential (OCP), linear polarisation resistance (LPR), and electrochemical impedance spectroscopy (EIS) measurements were performed over a prolonged period of immersion to study their temporally resolved behaviour.

### 3.2 Experimental procedures

#### 3.2.1 Materials and sample preparation

A commercially operated bath based on nickel hypophosphite was used to deposit electroless NiP coatings of varying P contents onto commercially pure copper sheet (purity > 99.9 wt.%). The dimensions of each copper plate were approximately 0.1 cm × 30 cm × 30 cm. The three electroless NiP samples used in this study were named as NP-a, NP-b, and NP-c, corresponding to their P content of  $13.2 \pm 1.2$  wt.%,  $12.9 \pm 0.7$  wt.%, and  $8.3 \pm 0.8$  wt.%, respectively.

#### 3.2.2 Microstructural and compositional analysis

##### 3.2.2.1 *Scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDS) analyses*

SEM with an EDS detector (Jeol JSM-IT100) was used to analyse the morphology and chemical composition of both the as-received and post-corroded samples. Secondary electron imaging (SEI) was used to map the top-view morphology. The accelerating voltage was 20 keV. An ultrasonic bath (Emag Emmi 20HC) was used to clean the samples by immersing them in isopropanol (IPA) for 10 minutes before drying them with compressed air.

##### 3.2.2.2 *Plasma-focused ion beam (PFIB)*

Using PFIB microscopy, the cross-section of the as-received electroless NiP coatings was examined. Utilising a Thermo Scientific™ Helios™ UXe DualBeam G4 PFIB microscope. The surface imaging voltage was set at 5 keV, whereas the

EDS measurement voltage was 20 keV. Each is operating in high-resolution SE mode. To protect the surface, the blind mode for FIB sectioning was chosen and ion-beam milling was performed.

### 3.2.2.3 X-ray diffraction (XRD) analysis

The crystallinity of the coatings was investigated by XRD analysis. Bragg-Brentano geometry was employed using Cu/K $\alpha$  radiation and an X-ray diffractometer (Bruker D8 Advance) equipped with a graphite monochromator and a Vantec position-sensitive detector. Divergence slit Var12, scatter screen height 5 mm, 45 kV 35 mA. The XRD analysis was performed using a scan range (2 $\theta$ ) of 20 to 120°, a step size of 0.050°, and a dwell time of 0.5s. The Full Width at Half Maximum (FWHM) values were used to determine the grain sizes using the Scherrer equation [45]:

$$D = \frac{0.94 \lambda}{\beta \cos \theta} \quad \text{Eq. 1}$$

D represents the average size of the crystallites,  $\beta$  is the width of the diffraction peak at half its maximum intensity,  $\theta$  denotes the Bragg angle, and  $\lambda$  is the wavelength of the X-ray used.

### 3.2.2.4 Scanning Kelvin probe force microscopy (SKPFM) analyses

The SKPFM technique has a high spatial resolution and enables mapping the Volta potential distribution over a heterogeneous surface microstructure. The SKPFM technique measures Volta potential difference (VPD) values between a conductive tip and the sample surface. The Volta potential values of a conductive sample surface are due to the diverse work function energies of the studied sample and the measuring tip, as explained by the following equation:

$$\Delta V_{(sample/tip)} = \frac{(\phi_{tip} - \phi_{sample})}{-e} \quad \text{Eq. 2}$$

Where  $\phi_{tip}$  and  $\phi_{sample}$  are the Work Functions Energies (WFE) of the tip and sample, and  $e$  is the electronic charge.

The VPD distribution of a metallic coating surface is reported to be a potential indicator of places prone to the formation of localised corrosion and micro-

galvanic couples due to surface heterogeneity and diverse surface features; however, a direct correlation between VPD distribution and micro-galvanic couple formation is not straightforward [46]. To have an insight into the corrosion behaviour of electroless NiP coatings, the electronic properties of the electroless NiP surface in terms of charge distribution and volta potential mapping at the nanoscale level SKPFM measurements were carried out. The SKPFM device used in this study was a Bruker Dimension Edge with an n-type doped silicon pyramid single-crystal tip, coated with PtIr5 (SCM-Pit probe). The VPD maps were captured using the dual-scan mode. In the first scan, surface topography data were obtained using tapping mode. Topography and VPD maps were performed in the air at 21 ° C with an approximate relative humidity of 24%, a pixel resolution of  $512 \times 512$ , a zero-bias voltage, and a scan frequency rate of 0.3 Hz. The amplitude of the AC voltage applied to the tip was 6 V. To mitigate the possibility of inaccurate measurements caused by the sensitivity of the technique, this study used the identical measuring tip throughout the whole set of measurements on the same day. For the top-view AFM/SKPFM measurements of as-received electroless NiP coatings, the same cleaning procedure of SEM/EDS measurements was applied. For cross-sectional AFM/SKPFM measurements of the thickness of the electroless NiP coatings, the as-received samples were embedded in an epoxy resin and ground to 4000 grit with SiC sanding paper. Afterwards, the samples were polished with a fine diamond suspension (Struers DiaDua-2) with particle sizes of 3 and 1  $\mu\text{m}$ . The cross-sectional AFM/SKPFM measurements of the electroless NiP coatings were performed in the electroless NiP/Cu interface region. Therefore, a histogram analysis based on multimodal Gaussian distributions was employed to provide a more detailed interpretation of the VPD values at the electroless NiP/Cu interface.

### 3.2.3 Electrochemical analysis

A Biologic SP 300 multichannel potentiostat was used for all electrochemical measurements hereafter. A typical three-electrode cell consists of an Ag/AgCl electrode (saturated KCl) as the reference electrode, a platinum mesh as the auxiliary electrode, and electroless NiP samples as the working electrode. A circular area of the electroless NiP surface with a diameter of 10 mm was exposed



to the corrosive media. PDP, OCP, LPR, and EIS measurements were performed in an aqueous electrolyte solution of 3.5 wt.% NaCl. The electroless NiP coatings were cleaned in an ultrasonic bath (Emag Emmi 20HC) for 10 minutes during immersion in isopropanol and then dried with compressed air prior to all measurements.

### 3.2.3.1 *Potentiodynamic polarisation measurements (PDP)*

PDP tests were performed after an OCP stabilisation time of 25 min. PDP measurements were conducted in the potential range of -0.25 V to 0.50 V (vs. OCP) at a scan rate of 1 mV/s. The EC-Lab V11.33 software was utilised to extrapolate the Tafel curves. The reproducibility of the results was evaluated by performing the tests in triplicate.

### 3.2.3.2 *Open circuit potential (OCP) and linear polarisation resistance (LPR)*

OCP and LPR measurements were used to determine the temporally resolved corrosion behaviour of the as-received electroless NiP coatings over 72 hours of immersion in a 3.5 wt.% NaCl solution. In a potential range of  $\pm 10$  mV around the open circuit potential, LPR measurements were performed intermittently, i.e., every hour for the initial 12 hours and subsequently every 3 hours until the experiment reached the 72-hour immersion mark. The scan rate was 0.167 mV/s. The samples were rinsed with Milli-Q® ultrapure water and dried with compressed clean air following 72 hours of immersion in a 3.5 wt.% NaCl solution for morphological and compositional analysis of post-corroded samples. The lower LPR scan rate compared to PDP is due to the focus on accurate, stable measurements of corrosion resistance within a limited potential range, thereby minimising system perturbation. The scan rate for LPR was chosen relatively low to ensure precise measurements of polarisation resistance, while for PDP tests, a faster scan rate was employed to capture dynamic corrosion processes across a wider potential range, facilitating the identification of critical thresholds and kinetic characteristics of the coating.

### 3.2.3.3 *Electrochemical impedance spectroscopy (EIS)*

As an additional non-destructive electrochemical characterisation technique, EIS measurements were utilised to assess the corrosion performance of electroless NiP coatings temporally. An AC signal of 10 mV amplitude was applied to the

working electrode at the  $E_{OCP}$  to determine the electrochemical impedance. The impedance measurements were performed intermittently during the OCP and LPR measurements over 72 hours of immersion time in a 3.5 wt.% NaCl solution. The frequency range for EIS measurements was 100 kHz to 0.01 Hz, with data acquisition at 6 points per decade. Nyquist and Bode plots are used to represent the EIS data graphically. The evolution of the polarisation resistance ( $R_p$ ) of the samples is characterised by the impedance modulus value  $|Z|$  at 0.01 Hz ( $\Omega \cdot \text{cm}^2$ ) [47, 48].

### 3.3 Results and discussion

#### 3.3.1 Microstructural and compositional characterisation of as-received electroless NiP coatings

To study the morphology and chemical composition of the NiP/Cu coatings in top-view and cross-section, SEM/EDS analyses on differently prepared samples were performed. In Figure 3.1, top-view and cross-sectional microstructural and compositional analyses of as-received electroless NiP coatings with varying P contents are shown. The EDS spectra of the cross-sectional area of the NP-a, NP-b, and NP-c samples are shown in Figure 3.1a<sub>1</sub>, 1a<sub>2</sub>, and 1a<sub>3</sub>. The thickness, P content values, average nodules diameter, and length of nodular boundaries presented in this study for each sample of the NiP coatings are determined from triplicate cross-sectional EDS line scans, ensuring the reliability and reproducibility of the measurements, as detailed in Table 3.1. The EDS line scan showed a uniform elemental distribution of Ni and P across the thickness, as depicted in Figure 3.2.

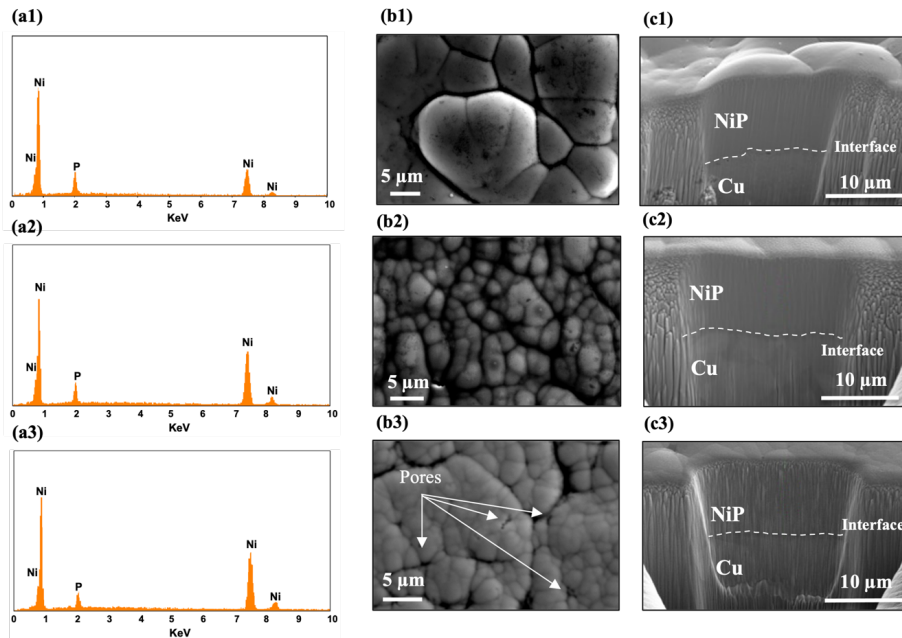
*Table 3.1 Thickness values, P content, and nodular dimensions of NP-a, NP-b, and NP-c samples*

| Electroless NiP coatings | Thickness ( $\mu\text{m}$ ) | P content (wt.%) | Average diameter of the nodules ( $\mu\text{m}$ ) | length of nodular boundaries per unit area ( $\mu\text{m}/\mu\text{m}^2$ ) |
|--------------------------|-----------------------------|------------------|---------------------------------------------------|----------------------------------------------------------------------------|
| <b>NP-a</b>              | $10.8 \pm 0.2$              | $13.2 \pm 1.2$   | $14.7 \pm 5.1$                                    | $0.15 \pm 0.01$                                                            |
| <b>NP-b</b>              | $9.5 \pm 0.1$               | $12.9 \pm 0.7$   | $3.8 \pm 2.3$                                     | $0.53 \pm 0.01$                                                            |
| <b>NP-c</b>              | $10.0 \pm 0.1$              | $8.3 \pm 0.8$    | $1.9 \pm 0.8$                                     | $0.78 \pm 0.02$                                                            |

The SEM/EDS analysis included both a top-view and a cross-sectional perspective. Figure 3.1b<sub>1</sub>, 1b<sub>2</sub>, and 1b<sub>3</sub> show the top-view SEM images of NiP samples with varying P contents. The top-view SEM images show NiP samples with surface nodules of different sizes, as depicted in Figure 3.1b<sub>1</sub>-1b<sub>3</sub>. As indicated in Table 3.1, the order of nodule dimensions, based on the average diameter, is NP-a > NP-b > NP-c. Consequently, the length of nodular boundaries per unit area was calculated in the reverse order of nodular size. Comparing the nodule sizes of the samples reveals that large individual nodules are present for the NP-a sample, resulting in a relatively low nodule boundary density at the surface. With decreasing nodule sizes for the NP-b and NP-c samples, the nodule boundary density increases, respectively. Wang *et al.* [49] and Dadvand *et al.* [50] also showed surface morphological changes in NiP alloys as the P content increased, with more compact nodules observed in the higher P content specimen. Although the nodule size decreases from NP-a to NP-b samples, the distribution and arrangement of nodules are relatively uniform. In Figure 3.1b<sub>3</sub>, the NP-c surface exhibits numerous pores/voids, as indicated by the white arrows. These features can be regarded as irregularities along the nodular boundaries, as reported by Shibli *et al.* [30]. The formation of voids can be attributed to varying plating times, which cause hydrogen bubbles to adsorb on the catalytic surface. These bubbles hinder the growth of new nickel crystals, leading to defects like small pores [51]. They observed that variations in P content within the NiP coatings affect the surface quality. The study by Shibli *et al.* [30] revealed that variations in P content within NiP coatings influence surface quality. High P content leads to a uniform, smooth, and amorphous surface; medium phosphorus content results in porous surfaces with distinct grains. Low P content produces porous surfaces with unevenly sized grains and minor flaws such as segregation and voids.

FIB milling was performed to acquire higher-resolution information on the NiP layer thicknesses and the NiP/Cu interface structure. Cross-sectional FIB milling of NiP samples (NP-a, NP-b, and NP-c) are shown in Figure 3.1c<sub>1</sub>, 1c<sub>2</sub>, and 1c<sub>3</sub>. As a generic characteristic of electroless NiP coatings, all cross-sectional images of the samples show a compact structure. Also, they show a flawless interface

between the Cu and NiP layers independent of the P content. Variation in the surface morphology of the NiP samples regarding nodule size reveals a distinct correlation between their P content and the nodule size. As is typical of amorphous substances, the NP-a surface exhibits cauliflower-like nodules [34, 49, 50, 52].



*Figure 3.1 Microstructural and compositional analysis of the electroless NiP coatings. (a1, a2, a3) Representative EDS spectra acquired from the cross-sectional regions of NP-a, NP-b, and NP-c samples, (b1, b2, b3) top-view SEM images of NP-a, NP-b, and NP-c, and (c1, c2, c3) the cross-sectional FIB-SEM images of NP-a, NP-b, and NP-c with the dashed lines indicating the NiP/Cu interface.*

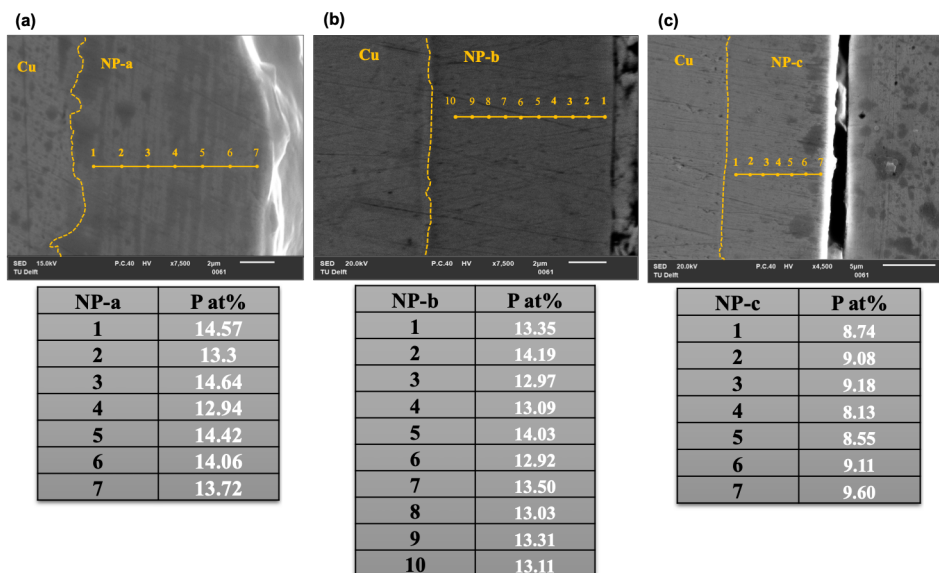


Figure 3.2 Cross-sectional EDS line scan showing phosphorus (P) content for samples (a) NP-a, (b) NP-b, and (c) NP-c, with corresponding values listed in the tables below each image. (The P content reported for each sample in the manuscript reflects an average value).

XRD measurements were performed to investigate the effect of P content within the NiP coatings on the crystallographic texture of the samples. The P content is a critical factor in determining the microstructure, influencing whether the coating exhibits a crystalline, amorphous, or mixed structure (30). In Figure 3.3, the XRD spectra of the as-plated samples are shown. At sites corresponding to the Ni (111) plane, there was a single large diffraction peak for all samples at a position of 30 to 50 degrees. In the NP-a sample, the corresponding peak to the Ni (111) shows a broad peak profile; however, in the NP-b and NP-c samples, the peak becomes sharper. In the diffraction patterns for the NP-b and NP-c samples, the less intensive peaks corresponding to Ni (200), Ni (311), and Ni (220) are shown; in the NP-a sample, the mentioned peaks are difficult to recognize. The sharp peaks marked by the star sign in the plot indicate the Cu substrate. The grain sizes for the samples NP-a, NP-b, and NP-c have been calculated using the Scherrer equation. The grain size values are approximately 20 Å for NP-a, 23 Å for NP-b, and 46 Å for NP-c, respectively. These results are consistent with the study by Choi *et al.* [53], with observed variations attributable to differences in phosphorus content, deposition parameters, and substrate materials. The P

content directly impacts the electrical properties and corrosion resistance performance of the coatings [54, 55]. The presence of a broad profile associated with the Ni (111) peak within the range of 30 to 50 degrees, alongside the discernible peaks corresponding to Ni (200), Ni (220), and Ni (311) in all three examined samples, collectively suggests a coexistence of amorphous and nanocrystalline phase structures within the coatings [30, 56]. The highly diffused characteristics of the Ni (200), Ni (220), and Ni (311) peaks in the NP-a sample may be attributed to a higher concentration of the Ni amorphous phase as opposed to the nanocrystalline phase structure. Furthermore, the broadening observed in the Ni (111) peak of the NP-a sample provides additional evidence of a greater proportion of the amorphous phase. Conversely, the discernible peaks related to Ni (200), Ni (220), and Ni (311) in samples NP-b and NP-c can be attributed to the prevalence of a higher proportion of Ni nanocrystalline phase structure relative to the amorphous phase. An increase in phosphorus content increases lattice strain, which in turn decreases grain size and leads to an amorphous or highly nanocrystalline microstructure [57]. Based on the XRD measurements depicted in Figure 3.3 and the grain size calculations conducted on the samples under study, it is inferred that NP-a exhibits a predominantly amorphous ( $\gamma$ ) structure, while NP-b and NP-c exhibit a combination of

nanocrystalline and amorphous phases (presence of  $\beta$  and  $\gamma$ ), with the proportion of nanocrystalline phase increasing from NP-a to NP-b and further to NP-c.

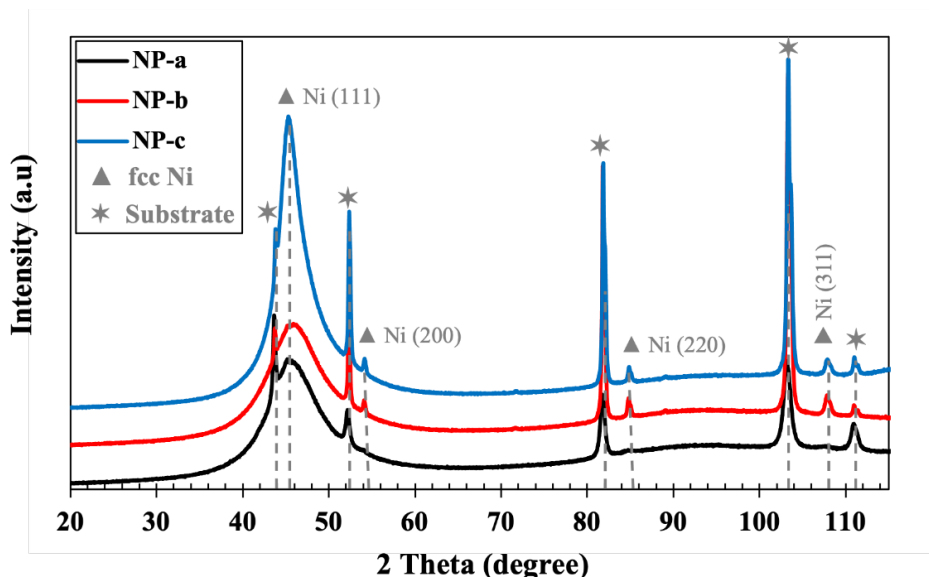


Figure 3.3 The XRD patterns from the top surface of samples NP-a, NP-b, and NP-c.

### 3.3.2 Volta potential characterisation of electroless NiP coatings

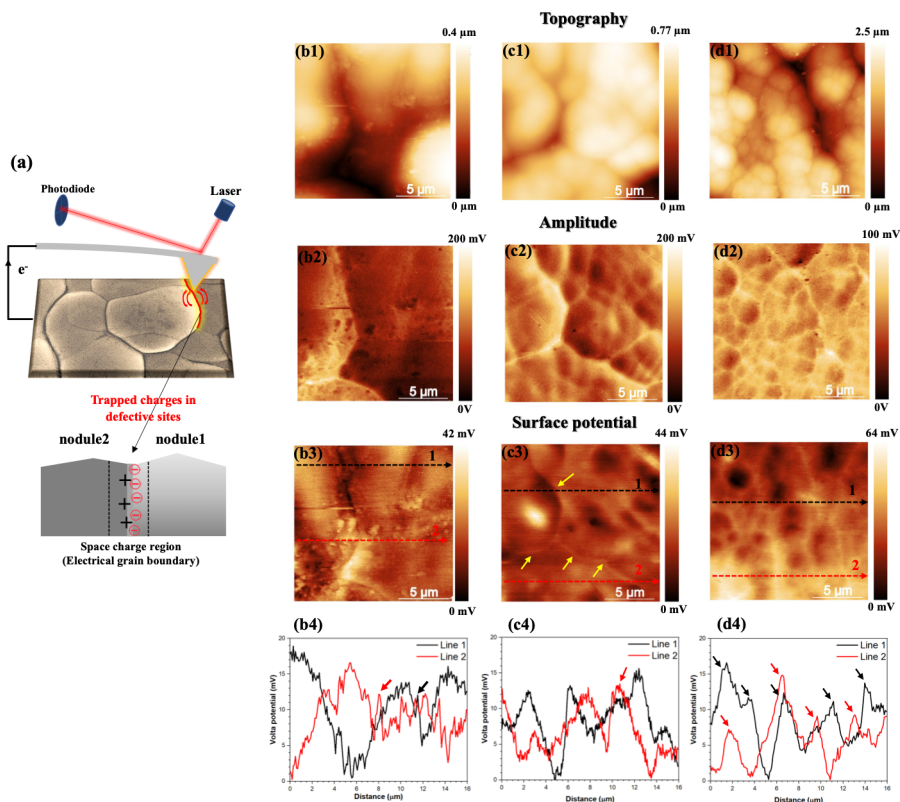
The P content in NiP coatings not only affects the crystallinity of the coatings but also can alter the electronic structure of Ni–P alloys as has been reported before [58]. Volta potential characterisation of electroless NiP coatings was carried out to comprehend the impact of phosphorus content. Figure 3.4 illustrates the surface topography, amplitude, and VPD mappings of the three samples. The topography and amplitude mappings clearly show the nodules and the distribution of grain boundaries on the surfaces of NiP coatings. The root-mean-square ( $S_q$ ) roughness values obtained from the topographic maps are presented in Table 3.2. There are significant differences in roughness between the samples. The differences in surface roughness and nodular size between the samples can be attributed to variations in nodular growth rate and in the number and uniform distribution of nucleation sites, both influenced by the local chemical environment during deposition [59].

Figure 3.4b3, 4c3, and 4d3 depict the corresponding VPD maps. For the NP-a sample, there is a correlation between potential variations and the large nodules observed in the topography. The highest VPD values are located at both the highest hills of the nodules and the vicinity of nodule boundaries in NP-a and not at the nodule boundaries. However, NP-b exhibits the appearance of higher VPD values at certain nodule boundaries (presented by yellow arrows in Figure 3.4c3). The VPD is more pronounced in the NP-c sample than in NP-a and NP-b, demonstrating a consistently high VPD at all nodule boundaries and their surroundings. This dominant high VPD can be attributed to the smaller nodules and lower roughness in NP-c, which have influenced the distribution of surface Volta potential. According to the literature [60, 61], localised charges at grain boundaries can create defect states, leading to a bending of energy levels, establishing a contact potential difference (CPD) in the area of nodular boundaries. It is worth noting that the surface potential map of the nodular boundary, detected by the SKPFM probe, represents an electrical grain boundary with a space-charge region involving a mixture of surface potential and surface charge, rather than a crystallographic grain boundary. This is due to the size of the AFM tip-apex (20 nm), which is larger than the actual grain boundaries. Figures 3.4b4, 4c4, and 4d4 illustrate the statistical VPD variations along the dashed lines. The lowest VPD values are set to zero to eliminate the possibility of misinterpreting VPD maps due to varying measurement conditions across samples.

The VPD distribution for NP-a is challenging to interpret due to the sample's rough topography. However, in the case of the NP-b sample (with lower roughness values, which allows us to measure VPD values), slightly higher VPD values observed along the nodular boundaries indicate a higher density of accumulated negative charges in these regions, as schematically shown in Figure 3.4a. This suggests a potential vulnerability to corrosion initiation at the nodule boundaries, requiring additional confirmation through electrochemical measurements. It is important to highlight that the difference in VPD values between nodule boundaries and nodules in the NP-b sample is not statistically significant. In contrast, the high VPD values along the nodule boundaries of the NP-c sample



may suggest a high density of agglomerated negative charges. When exposed to corrosive media, this can lead to a higher sensitivity to corrosion attack.



*Figure 3.4 Analysis of surface topography, amplitude, and Volta potential analysis of the electroless NiP coatings. (a) Schematic showing internodular SKPFM measurements (b1, c1, and d1) AFM topography maps of the top surface of NP-a, NP-b, and NP-c, (b2, c2, and d2) amplitude maps of NP-a, NP-b, and NP-c top surface, (b3, c3, and d3) SKPFM maps of NP-a, NP-b, and NP-c top surface, (b4, c4, and d4) variations of VPD values along the dashed lines.*

Cross-sectional analysis of the Cu/NiP system not only reveals the coating's composition and morphology but also provides insights into the electronic properties of both NiP and Cu. The electrical connection between layers equilibrates the Fermi levels, causing electrons to migrate from the metal with the lower work function to the metal with the higher work function. Consequently, cross-sectional VPD measurements in this study might indirectly indicate the intrinsic nobility of the layers [46, 62]. The cross-sectional topography and VPD mappings of the NP-a, NP-b, and NP-c samples are depicted in Figure 3.5. The

topographical maps show the cross-section with some light scratches related to polishing. The dashed white lines in the topography maps show the Cu/NiP interface.

Figures 3.5b, 5d, and 5f depict the VPD mappings revealing two well-distinct areas attributed to the Cu and NiP layers. NP-a and NP-b samples show almost identical VPD images, and there are no significant differences in potential values between the NP-a and NP-b layers. This is more clearly depicted in the histogram shown in Figure 3.5g, with the Cu substrate as the reference material. In the case of the NP-c layer, the VPD value is much higher than that of the NP-a and NP-b layers. In summary, low P-containing samples present a larger Volta potential difference with the substrate. This can have significant implications for the substrate's corrosion rate when defects expose the Cu underneath. The VPD values for the Cu and NiP layers are shown in Table 3.2.

It is worth noting that, in correlating corrosion studies with SKPFM studies, variations in work function among microstructural features lead to noticeable differences in Volta potential across the surface, potentially providing insights into their electrochemical characteristics by characterising anodic and cathodic behaviours. The terms "anodic" and "cathodic" are commonly used in reference to Volta potentials, indicating the intrinsic nobility of metals. However, the direct correlation between these potentials and the electrochemical behaviour in actual corrosion scenarios is not always simple. Factors such as environmental conditions, alloy composition, and impurities can introduce complexity into the corrosion process. Despite the intrinsically valuable insights offered by theoretical and experimentally measured Volta potentials under atmospheric conditions, their direct correlation with purported corrosion behaviour without scrutinising the experimental conditions can be intricate or even misleading [46, 54, 63].

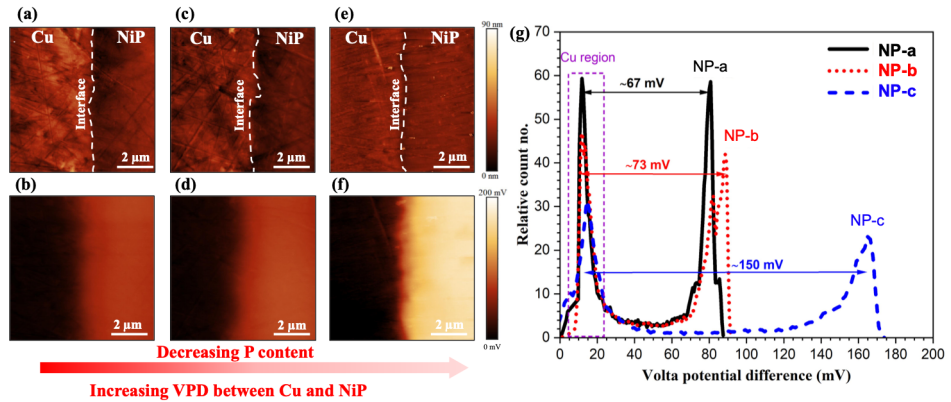


Figure 3.5 Cross-sectional AFM morphology and SKPFM potential maps, (a, b) NP-a, (c, d) NP-b, and (e, f) NP-c. (g) histogram distribution of Volta potential difference values in the cross-sectional region of NP-a, NP-b, and NP-c.

Table 3.2 The VPD difference values (between Cu and NiP coatings) and surface roughness of NP-a, NP-b, and NP-c samples

| Electroless NiP coatings | VPD difference (mV) | Sq (nm)       |
|--------------------------|---------------------|---------------|
| NP-a                     | $67 \pm 2$          | $409 \pm 200$ |
| NP-b                     | $73 \pm 2$          | $111 \pm 38$  |
| NP-c                     | $150 \pm 3$         | $60 \pm 15$   |

### 3.3.3 Electrochemical study of electroless NiP coatings

A combination of destructive and non-destructive electrochemical methods has been employed to investigate the behaviour of NiP coatings. The PDP experiments were conducted in a 3.5 wt.% NaCl solution to evaluate the corrosion behaviour of the samples. In addition, OCP, LPR, and EIS measurements were carried out intermittently to assess the corrosion properties with exposure time. Figure 3.6 shows representative PDP curves for the NP-a, NP-b, and NP-c samples. All cathodic branches exhibit similar behaviour, and the cathodic process is controlled by activation polarisation. Samples NP-a and NP-b showed similar corrosion behaviour in their anodic branches. However, not only does the anodic branch for the NP-a sample show a lower anodic current compared to the NP-b sample, but NP-a also has a steeper anodic slope, indicating that NP-a might exhibit less significant changes in current density values in response to applied anodic polarisation. The distinct increase in current density at higher

potentials for NP-b suggests that its passive film is unstable and prone to breakdown under anodic polarisation, potentially due to microstructural characteristics such as roughness and nodular boundary density, which facilitate localised film breakdown and transpassive dissolution [64]. On the other hand, the anodic branch of NP-c shows a higher anodic current density and a lower slope compared to NP-a and NP-b. The lower open-circuit potential (OCP) values observed in the NP-c sample compared to NP-a and NP-b can be attributed to differences in passive film characteristics and their surface stability. In electroless NiP coatings, a more negative OCP does not necessarily indicate inferior corrosion resistance but rather reflects the electrochemical stability of the surface film. The NP-a sample, characterised by higher phosphorus content, forms a predominantly amorphous structure that promotes the formation of a uniform and protective passive film. This film stabilizes at a more negative potential due to its favorable electrochemical properties. In contrast, NP-c, with lower phosphorus content, exhibits a higher density of nodular boundaries and more pronounced surface Volta potential differences, leading to an uneven charge distribution and reduced corrosion resistance, as evidenced by its lower OCP values. The values for corrosion current density ( $i_{\text{corr}}$ ), anodic Tafel plot slope ( $\beta_a$ ), and the  $E_{\text{corr}}$  estimated from Tafel extrapolation are shown in Table 3.3. The corrosion rate (indicated by the corrosion current density) for the studied samples follows the order: NP-a < NP-b < NP-c.

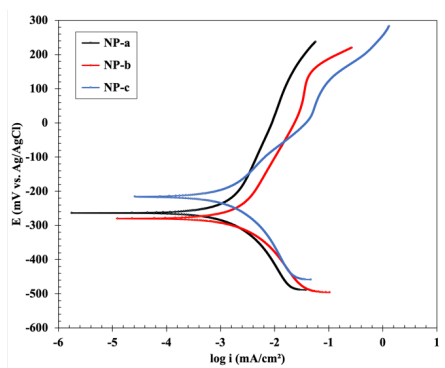


Figure 3.6 Potentiodynamic polarisation curves in 3.5 wt.% NaCl solution for the NP-a, NP-b, and NP-c samples.

Table 3.3. Potentiodynamic polarisation parameter values by Tafel extrapolation for the NP-a, NP-b, and NP-c samples in 3.5 wt.% NaCl solution

| Electroless NiP coatings | $i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ ) | $\beta_a$ (mV/decade) | $E_{\text{corr}}$ (mV vs. Ag/AgCl) |
|--------------------------|-------------------------------------------------|-----------------------|------------------------------------|
| <b>NP-a</b>              | $1.89 \pm 0.08$                                 | $309 \pm 85$          | $-261 \pm 54$                      |
| <b>NP-b</b>              | $2.19 \pm 0.18$                                 | $277 \pm 74$          | $-274 \pm 63$                      |
| <b>NP-c</b>              | $2.45 \pm 0.49$                                 | $125 \pm 26$          | $-218 \pm 10$                      |

In Figure 3.7, the OCP and LPR values for the samples after 72 hours of immersion in a 3.5 wt.% NaCl solution are shown. The OCP values are intermittently measured to allow for LPR and EIS measurements. The LPR values are reported at various times of exposure under OCP conditions. As shown in Figure 3.7a, although the OCP values for NP-a are higher than those for NP-b (particularly in the first 28 hours), NP-a and NP-b OCP values display comparable high or low potential OCP values. On the other hand, the OCP values for NP-c during the 72 hours of immersion in 3.5 wt.% NaCl solution consist of three changes in OCP values, i)  $\sim -40$  mV (0-10 hours), ii)  $\sim +25$  mV (10-30 hours), and iii)  $-35$  mV (30-72 hours). The inset shows a magnified view of the OCP values over the first 10 hours of measurement for the samples, indicating that after 4 hours of immersion, the NP-c sample had the lowest OCP values compared to the NP-a and NP-b samples. The following equation describes the polarisation resistance ( $R_p$ ) as the primary parameter derived from this method:

$$R_p = \left( \frac{\Delta E}{\Delta i} \right)_{\Delta E \rightarrow 0} \quad \text{Eq. 3}$$

Where  $\Delta E$  is the polarisation potential and  $\Delta i$  is the polarisation current.

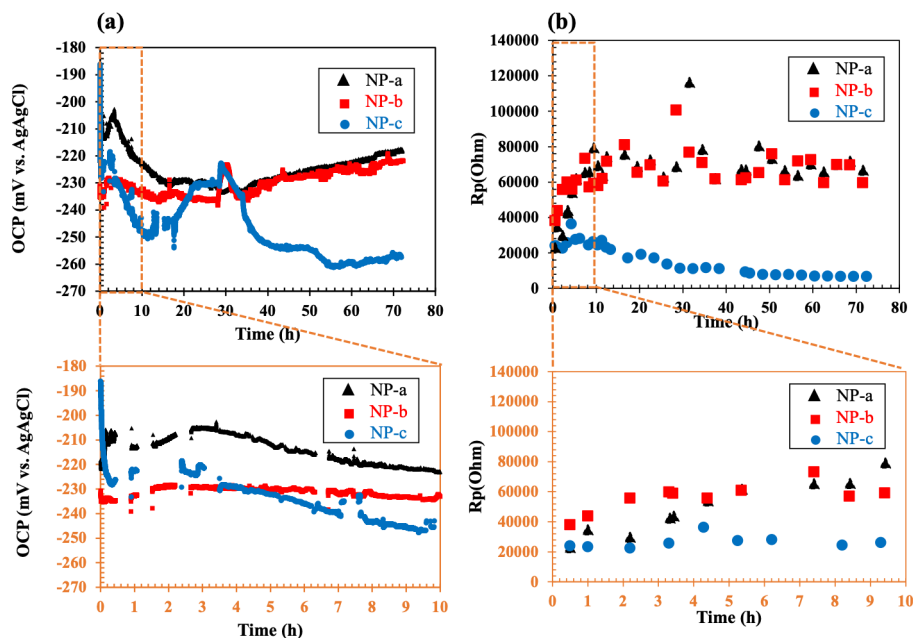


Figure 3.7 Electrochemical analysis for NP-a, NP-b, and NP-c samples in 3.5 wt.% NaCl solution over 72 hours of immersion (a) OCP, and (b) LPR.

Figure 3.8 shows the Nyquist and Bode plots of NP- samples exposed to a 3.5 wt.% NaCl solution for 72 hours at various exposure times. Nyquist and Bode plots for NP-a and NP-b are shown in Figure 3.8 (a, b) and Figure 3.8 (c, d) respectively. The Nyquist plots show similar behaviour at the same time intervals for the different samples, a single well-defined depressed semicircle. The EIS spectra for the NP-a and NP-b samples indicate that after 2 hours of immersion, the polarisation resistance ( $R_p$ ), represented by the impedance modulus  $|Z|$  at 0.01 Hz, increases and subsequently stabilises, with minor fluctuations over time. Figure 3.8 (e, f) shows the Nyquist plots in NP-c. After 0.5, 1, and 2 hours of immersion in a 3.5 wt.% NaCl solution, they exhibit a well-defined depressed semicircle. After 6 and 24 hours of exposure to the corrosive media, the plots show depressed semicircles with ill-defined tails. They show a single well-defined depressed semicircle again after 48 and 72 hours of immersion in 3.5 wt.% NaCl solution with a low  $R_p$ . Figure 3.9 shows the variation of  $|Z|$  values at 0.01 Hz for the samples as a function of exposure time.

In NP-a and NP-b, the rise in polarisation resistance may be attributed to the higher intrinsic corrosion resistance of the natural oxide of the Ni-layer. The elevated resistance of NP-a and NP-b samples could be associated with a uniformly distributed surface charge, as revealed by SKPFM measurements in Figure 3.4, thereby promoting the formation of a more protective oxide layer. The nearly identical shapes of well-defined semicircles with the same polarisation resistance values in NP-a and NP-b suggest that the corrosion mechanisms are identical, validating the LPR values in Figure 3.7b. On the other hand, after two hours of immersion in a 3.5 wt.% NaCl solution, NP-c exhibited a decreasing trend in polarisation resistance. More than one time constant in the Nyquist plots suggests a different corrosion mechanism than uniform corrosion [65]. In addition, the decreasing trend in the polarisation resistance of the NP-c sample validates the LPR values shown in Figure 3.7b. The lower resistivity observed in NP-c samples may be attributed to an uneven surface Volta potential and/or charge distribution, with higher charge density concentrated in nodular boundaries and lower density in nodular regions, as demonstrated by the SKPFM measurements in Figure 3.4. This non-uniform Volta potential and/or charge distribution could render the nodular boundaries more susceptible to corrosion attacks. The corrosion performance of the electroless NiP alloys shows a direct correlation with the P content and nanostructure of the coatings. Therefore, reducing the P content in the nickel electroless process results in smaller nodule sizes or elevated nodule boundaries, characterised by a high level of surface Volta potential heterogeneity and significant charge accumulation at nodule boundaries. This observation further confirms the NP-c sample's susceptibility to localised corrosion. Additionally, this finding aligns with the polarisation resistance observed in LPR and EIS, where electrochemical signals at the solid/solution interface with the lowest polarisation resistance or resistivity to charge transfer (resulting in the highest  $i_{\text{corr}}$ ) are evident in the NP-c sample.

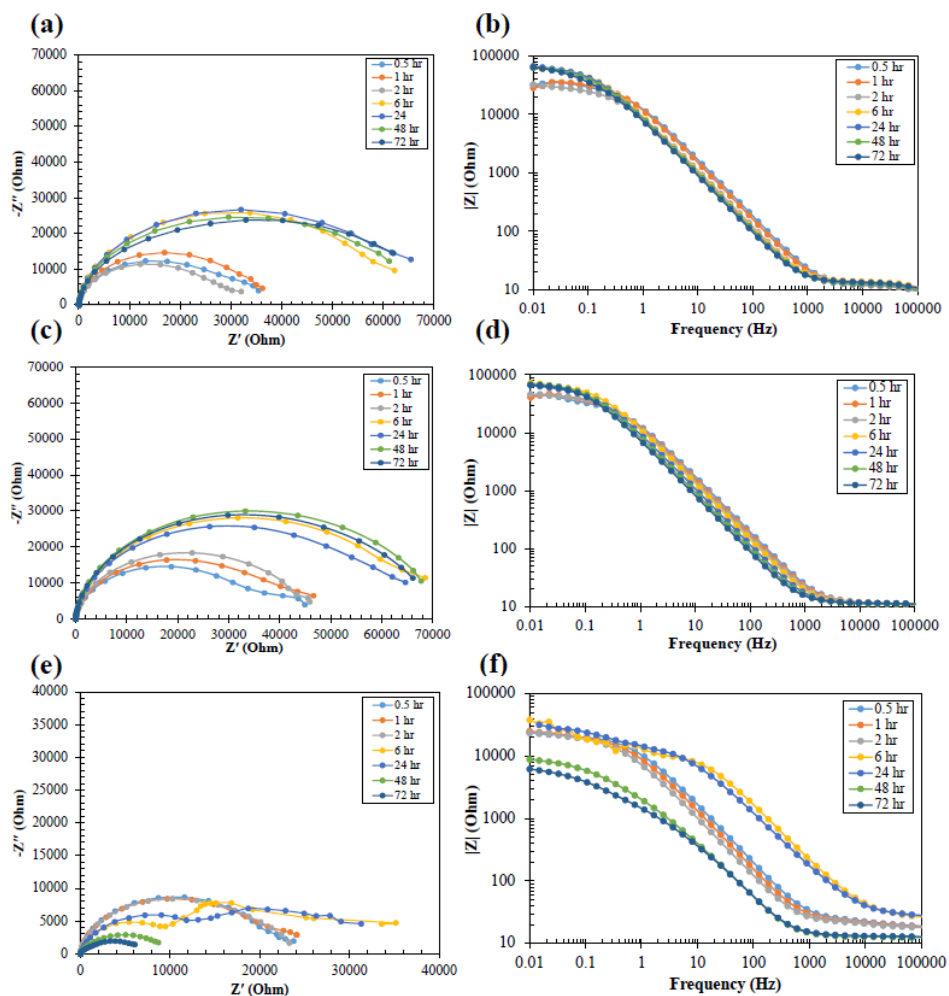


Figure 3.8. EIS analysis in 3.5 wt.% NaCl solution over 72 hours of immersion: Nyquist and Bode plots (a, b) NP-a, (c, d) NP-b, and (e, f) NP-c.



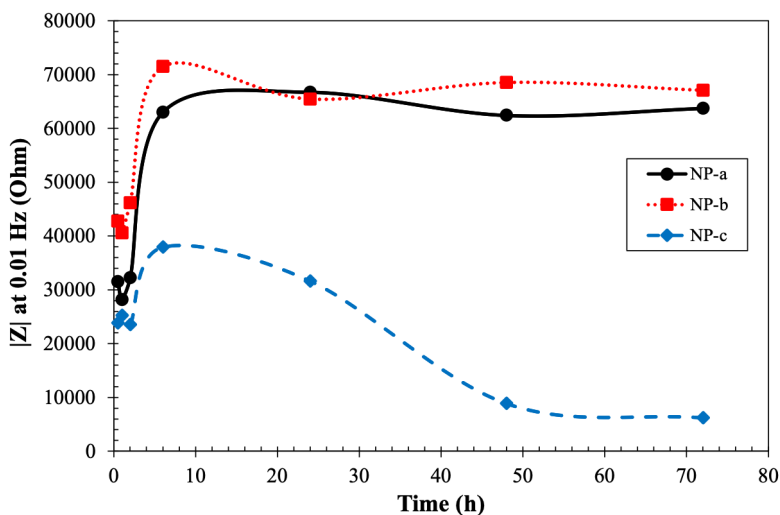


Figure 3.9 Electrochemical impedance magnitudes at 0.01 Hz vs. immersion time in 3.5 wt.% NaCl solution over 72 hours of immersion.

### 3.3.4 Microstructural and compositional characterisation of post-corroded electroless NiP coatings

Figure 3.10 shows the top-view SEM/EDS analysis of the samples after 72 hours of immersion in the 3.5 wt.% NaCl solution. The low-magnification SEM images of the post-corroded samples after 72 hours of immersion are shown in Figure 3.11. Figure 3.10a and Figure 3.10b show the top-view SEM and EDS mapping analyses of the post-corroded surface of the NP-a and NP-b samples. The post-corroded surfaces of NP-a and NP-b samples show a relatively intact surface. However, Figure 3.10c shows a localised corrosion attack for the NP-c sample. The localised corrosion attack in the NP-c sample consists of two types of pits, distinguished by pit-mouth size. The average diameter value for the big pit mouth size is  $2.12 \pm 0.70 \mu\text{m}$ , and the pits were formed at the nodule boundaries, and most of the big pits reached the Cu substrate layer. Large pits are indicated by red dashed circles in Figure 3.10c. On the other hand, many relatively small pits are distributed primarily on the nodules, with an average diameter of  $0.43 \pm 0.10 \mu\text{m}$ .

The mostly undamaged post-corroded surfaces of NP-a and NP-b samples indicate that the coatings' corrosion resistance has increased with P content. Due

to the coatings' predominantly amorphous structure and uniform charge density distribution, a protective oxide layer may form during the initial immersion. Figure 3.6 illustrates wider passive regions for the NP-a and NP-b samples. In contrast, the NP-c sample exhibits poor corrosion behaviour, as evidenced by pit formation attributed to microstructural heterogeneity and a high negative charge density along the nodular boundaries of the coating with a lower P content [17].

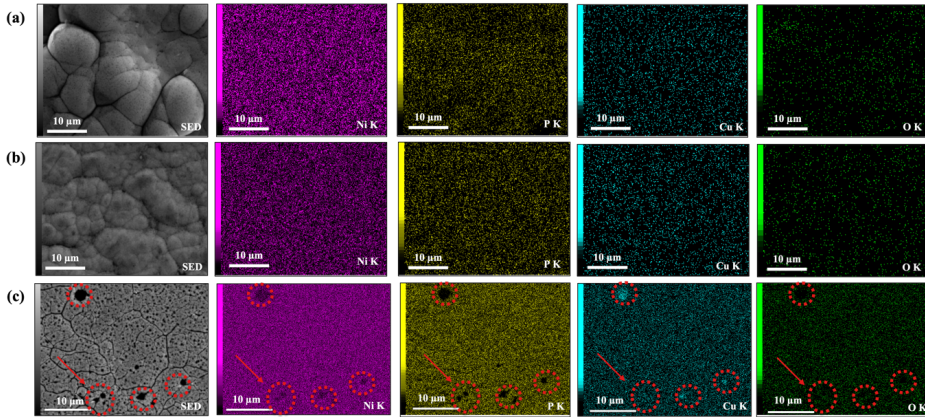


Figure 3.10 Top-view SEM image and EDS elemental maps for the post-corroded samples in 3.5 wt.% NaCl, after 72 hours of immersion: (a) NP-a, (b) NP-b, and (c) NP-c.

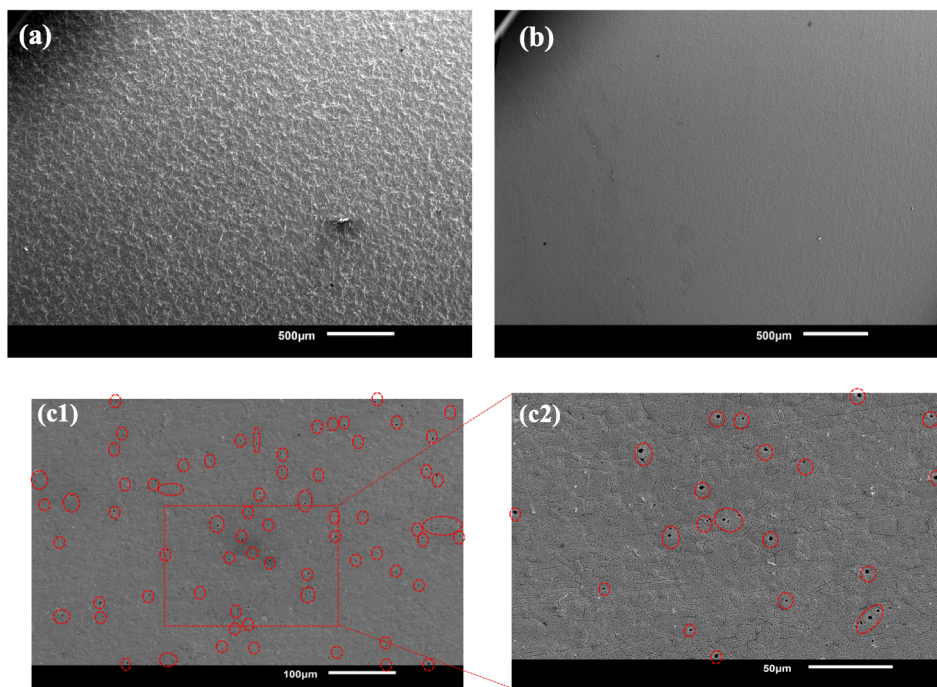


Figure 3.11 The top-view SEM image for the post-corroded samples in 3.5 wt.% NaCl, after 72 hours of immersion: (a) NP-a, (b) NP-b, and (c1 and c2) NP-c.

### 3.3.5 Corrosion mechanism of electroless NiP coatings

The microstructural, morphological, Volta potential, and electrochemical analyses reveal that varying P contents significantly influence the corrosion performance of electroless NiP coatings. In NP-a and NP-b samples, high P content induces a shift in the coating microstructure towards a more amorphous phase, reduces the density of nodular boundaries, provides a sound top surface, and alters the surface electronic properties, thereby offering robust corrosion resistance. Nevertheless, in the NP-c samples, the lower P content of the NiP coating leads to increased crystalline phases, a higher density of nodular boundaries, a defective top surface with holes, and an uneven distribution of Volta potential and/or charge distribution on the surface. These factors could potentially result in a less corrosion-resistant performance of the NiP coating in corrosive environments. In Figure 3.12, the schematic illustration of the microstructure of all three samples reveals a mixture of amorphous and crystalline phases; however, the ratio of amorphous-to-crystalline order is NP-a > NP-b > NP-c. The

microstructural transformation from an amorphous to a crystalline phase by decreasing the P content in NiP layers is shown in Figure 3.12. The dark grey disordered atomic arrangement represents the amorphous part, while the light grey ordered lattice structure signifies the crystalline phase. Regarding the morphological characteristics of the top surface of NiP samples, the density of nodular boundaries increases as the P content decreases. Grey lines depict the density of nodular boundaries on the top surface of each sample. Furthermore, NP-a and NP-b exhibit no surface defects, whereas NP-c shows imperfections, including holes. In terms of the Volta potential properties of the top surface of the three samples, an even negative charge density distribution is evident along the nodular boundaries for the NP-a and NP-b samples, as illustrated in Figures 3.12a and b. Conversely, an uneven negative charge density distribution along the nodular boundaries of the NP-c sample is observed in Figure 3.12c<sub>1</sub>. The uneven negative charge density distribution along the nodular boundaries in NP-c is derived from SKPFM measurements, revealing bright signals in that area. Hence, this high magnitude of surface Volta potential and/or charge distribution in nodule boundaries compared to adjacent nodules may result in a stronger driving force for localised corrosion attack. This can promote rapid corrosion propagation by accelerating the anodic dissolution of the NP-c sample, leading to contact with the Cu substrate. However, it is noteworthy that Volta potential difference values along the nodular boundaries in NP-a and NP-b were not significantly different from those in the nodules. To schematically illustrate the corrosion phenomena, NP-a and NP-b samples remained undamaged throughout the immersion period, as depicted in Figure 3.12a and Figure 3.12b; however, Figures 3.12c<sub>1</sub>, 12c<sub>2</sub>, and 12c<sub>3</sub> reveal pit formation in the NP-c sample after 72 hours of immersion in a 3.5 wt.% NaCl solution. In Figure 3.12c<sub>1</sub>, pre-existing surface defects are located at the nodule boundaries, as the black arrows indicate. Additionally, the red line marks the positions of the pores to illustrate the cross-sectional view of the pits in Figure 3.12c<sub>2</sub>. A thin, weak natural oxide layer might allow corrosive solutions to breach the underlying NiP coating at susceptible areas along the nodular boundaries in the NP-c sample. Consequently, this breach reaches the copper substrate through localised corrosion attack. Furthermore, the SKPFM cross-sectional study demonstrated

that the Volta potential difference values for low P content samples are approximately twice as high as those for high P content samples, likely contributing to a significant galvanic driving force in low P content samples. The possible cathodic reaction (likely on the natural protective layer of the NiP layer) and anodic reactions take place as indicated in Equations (4, 5, and 6).



The presence of imperfections and flaws arising from the low P content allows corrosive solutions to breach the NiP coating, leading to a high cathode-to-anode surface area ratio and promoting pit formation. Pitting occurs rapidly due to this high cathode-to-anode surface ratio, driven by the autocatalytic nature of pitting growth and the flaws within the passive layer. Notably, not all pits emerge simultaneously due to variations in electrolyte and surface conditions in different regions [66]. As the P content in NiP alloys decreases, not only does the nanostructure change from a high amorphous/nanocrystalline ratio to a low ratio of amorphous/nanocrystalline regions, but also a change in the surface morphology from big to small nodule size. Therefore, the poor corrosion performance of low P-content alloys might be correlated with coatings' nanostructure, surface defects, and the abundance of nodule boundaries with high negative charge density, which are susceptible locations for corrosion initiation. The nanostructural coatings have relatively low corrosion resistance by producing a larger number of micro-galvanic cells between the nodule boundaries and the matrix. On the contrary, an amorphous structure should have intrinsic high corrosion performance owing to its structural homogeneity and the absence of preferential corrosion initiation sites, such as nodule boundaries and other structural flaws [67].

The shape of pit growth in the NP-c sample may differ from the narrow shape suggested in Figure 3.12c<sub>2</sub> and could manifest as subsurface, horizontal, or vertical growth. In a prior study, we demonstrated that the direction of electroless

Ni dissolution is influenced by system conditions, such as the exposure of microgalvanic couples, the polarisation state, and the acidity and chloride ion ( $\text{Cl}^-$ ) concentration of the solution within the pit [17].

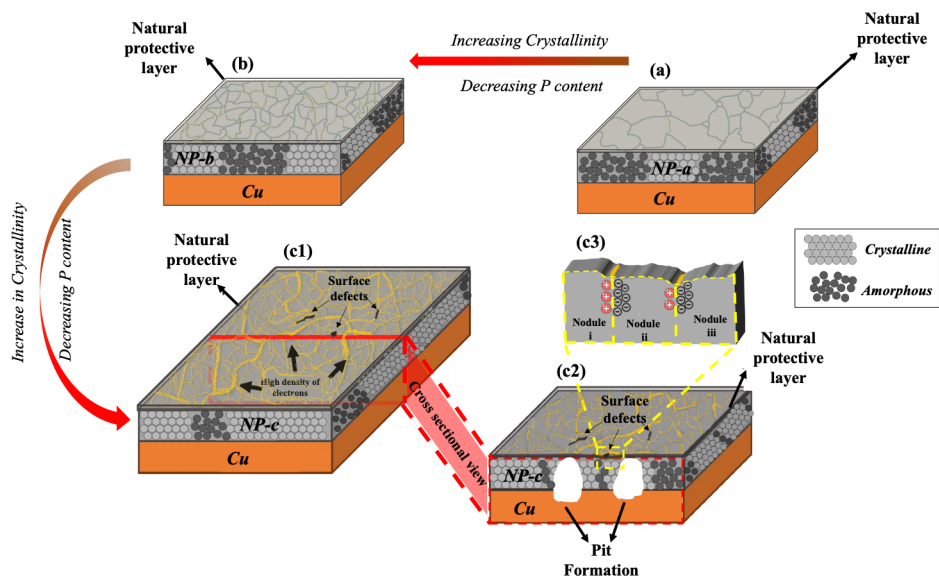


Figure 3.12. Schematic illustration of the corrosion phenomenon of NP- samples after 72 hours of immersion in a 3.5 wt.% NaCl solution (a) NP-a sample, (b) NP-b sample (c1) NP-c sample. (c2) cross-sectional view on red dashed surface area, and (c3) magnified view of the cross-sectional area of NP-c coating showing uneven negative charge density distribution at nodular boundaries.

### 3.3.6 Conclusions

This research aims to provide a fundamental understanding of the effect of three phosphorus contents on the corrosion protection of electroless NiP coatings on a copper substrate in an aqueous chloride-containing environment, specifically focusing on high and low phosphorus levels. Interestingly, samples NiP-a and NiP-b, despite having similar P content, exhibited distinct differences in their microstructural properties, particularly in terms of crystallinity. A combination of microstructural, compositional, topographical, local Volta potential distribution and electrochemical studies of as-received electroless NiP coatings allowed for the detailed explanation of localised corrosion phenomena in electroless nickel coatings with varying P content.

Decreasing the P content in electroless nickel coatings resulted in minor surface flaws, particularly along the nodular boundaries, associated with a high density of nodular boundaries and a high concentration of negative charge densities. Additionally, it was shown that the Volta potential differences of low P content samples are approximately twice those of high P content samples, which likely accounts for the larger galvanic driving force of low P content samples. The high driving force of low P samples, together with minor surface flaws, resulted in a predominantly localised corrosion attack.

The corrosion resistance was found to be in the order of NP-a > NP-b > NP-c for the analysed samples, indicating that increasing P content results in a higher corrosion resistance. The difference in corrosion resistance for the NiP coatings with relatively high but similar P content stresses the importance of not only the P content itself, but also its effect on the microstructure of NiP coatings and the consequent local corrosion properties.

### 3.4 References

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### 3.5 Addendum

The corrosion current densities reported in Table 3.3 were obtained by Tafel extrapolation of polarisation curves recorded in aerated 3.5 wt.% NaCl at pH 5.9. In this near-neutral aerated electrolyte, the cathodic partial reaction, i.e. the reduction of dissolved oxygen, is expected to be partially mass-transport controlled. Therefore, the assumption of activation control underlying the Tafel extrapolation is not strictly valid, and the absolute  $i_{\text{corr}}$  values in Table 3.3 carry a corresponding systematic uncertainty. The comparative conclusions of this chapter are not affected by this limitation. The three coatings were measured under identical hydrodynamic and aeration conditions, and the ranking NP-a < NP-b < NP-c therefore remains a valid relative comparison. Moreover, the inferior corrosion resistance of the low-phosphorus NP-c coating is independently confirmed by the LPR and EIS measurements over 72 hours of immersion (Figures 3.7-3.9), which do not rely on the Tafel assumption.







## **Chapter 4. Optimisation of electroless nickel-phosphorus bath parameters for enhanced corrosion resistance of ENIG coating on copper substrates**

### **Abstract**

Electroless Nickel Immersion Gold (ENIG) coatings are widely used in printed circuit board (PCB) fabrication, providing essential protection and enhancing solderability of copper substrates. This study investigates the influence of the agitation method and immersion time in the electroless nickel-phosphorus (ENP) bath on the localised corrosion performance of ENIG coatings on copper substrates. We elucidated the relationship between ENP bath parameters and the resultant coating properties through detailed microstructural and electrochemical analyses. The findings indicate that ultrasonic agitation enhances coating phosphorus content, improving corrosion resistance, while mechanical stirring results in thicker coatings with lower phosphorus content and increased defects. Scanning electrochemical microscopy (SECM) measurements confirmed the superior localised corrosion performance of coatings subjected to ultrasonic agitation. This study provides comprehensive insights into optimising ENP bath parameters to achieve high-performance ENIG coatings for electronic applications.

### 4.1 Introduction

In the era of rapid technological advancements, the widespread presence of electronic devices across diverse sectors, from telecommunications to medical diagnostics, emphasises their indispensable role in advancing high-tech innovations that aim to enhance comfort, sustainability, efficiency, and safety in our daily lives [1, 2]. Electronic devices commonly experience failure mechanisms such as fatigue, electromigration, stress-induced voiding, corrosion, conduction filament formation, and time-dependent dielectric breakdown. Among these failure mechanisms, corrosion is critical for ensuring the long lifespan of electronic devices. Specifically, it involves the oxidation of copper, which is a primary metallic component in PCBs used to transmit electrical signals between electronic components [3-6]. Although copper is chosen as a conductor due to its superior electrical conductivity, its susceptibility to corrosion requires the implementation of protective measures to maintain its integrity and functionality over time [7, 8]. As the leading surface finish used in electronic industries, the utilisation of ENIG coatings represents a significant advancement in this domain. ENIG coatings offer a dual-layer protective coating system of Ni-based alloy and Au that not only shields the copper substrate from corrosive elements but also significantly enhances its solderability. ENIG is additionally known for its excellent resistance to whisker growth and serves as a lead-free, environmentally friendly fabrication method [9-12].

The intermediate electroless Ni-based alloy layer in the ENIG coating system serves as a barrier against the interdiffusion of Au and Cu. This interdiffusion poses significant challenges, including diminished solderability and conductivity [13]. The Ni-based alloys in the ENIG double-layer system also contribute to its excellent wear resistance [14, 15], particularly in applications where frequent plugging and unplugging, such as in sockets and switches, require durability against wear. Electroless Nickel (EN) plating is an autocatalytic process that deposits metal without an external power supply, using a reducing agent in a complex solution containing nickel cations, complexing agents, and various additives, such as wetting agents, stabilizers, buffers, and accelerators. The careful selection and optimisation of these components under specific

experimental conditions significantly influence the quality and properties of the nickel coatings, enabling efficient applications across various industries [16-23]. In addition to the electrolyte components, achieving high-quality electroless Ni-P coatings relies on optimising the operational conditions of the plating bath such as temperature, pH, solution age, and rate/type of agitation [20, 24].

Bulasara *et al.* showed that agitating the solution by stirring in the electroless Ni-P plating process not only enhances the Ni deposition rate by 20–56% compared to conditions without stirring but also plays a crucial role in controlling the particle incorporation into the coating, thereby affecting the surface roughness of the as-deposited samples [25, 26]. This process ensures even heat distribution and effective solution mixing, which, in turn, improves the uniformity of the coating. By preventing the formation and attachment of hydrogen bubbles, agitation leads to a smoother, brighter coating with enhanced durability. Furthermore, solution agitation can significantly affect the coating's characteristics, including its morphology, hardness, surface roughness, phosphorus content, and corrosion resistance [27, 28]. The corrosion performance of the ENIG coating system is influenced by the corrosion behaviour of the intermediate EN layer [29], which in turn is significantly affected by the agitation and immersion time of the EN plating process. These factors, crucial for achieving higher deposition rates, uniform coatings, and ideal phosphorus content (EN deposits are typically classified into three categories: low (1–5 wt.%), medium (5–8 wt.%), and high (9 wt.% and above) P content [24], collectively contribute to the enhanced corrosion resistance of electronic components protected by ENIG. Our previous study investigated the influence of phosphorus content electroless NiP coatings on the microstructure and electrochemical properties. The results revealed that a reduction in phosphorus content from  $13.2 \pm 1.2$  wt.% to  $8.3 \pm 0.8$  wt.% led to minor surface flaws, particularly along the nodular boundaries. These defects were linked to a high density of nodular boundaries and an increased concentration of negative charge densities, measured by scanning Kelvin probe force microscopy (SKPFM) [30].

Systematic studies of corrosion protective coatings are crucial for enhancing the reliability and extending the lifetime of substrates. Extensive literature

emphasises the significant impact of agitation methods within electroplating baths on the corrosion behaviour of the resultant coatings [24, 31-39]. Ma *et al.* [34], used the ultrasonic-assisted electrodeposition technique, to investigate the fabrication of nickel-alumina (Ni-Al<sub>2</sub>O<sub>3</sub>) nanocomposites on A3 steel. Their findings show that an optimal ultrasonic power of 300 W not only refines nickel grains but also ensures uniform dispersion of Al<sub>2</sub>O<sub>3</sub> nanoparticles, resulting in a nanocomposite with a smooth surface morphology and higher corrosion resistance. In addition, Ridošić *et al.* [33] explored the impact of ultrasonic agitation on the electrodeposition of Zn-Co alloy coatings on mild steel substrates. Their research indicated that ultrasound, compared to conventional stirring methods, significantly enhances the morphological and corrosion-resistant properties of the coatings, attributed to improved uniformity, decreased porosity, and the achievement of a homogenous alloy structure. Complementing these findings, Camargo *et al.* [35] shed light on the influence of ultrasound intensity on the electrodeposition of zinc (Zn) and zinc-titanium dioxide (Zn-TiO<sub>2</sub>) coatings on low-carbon steel substrates. They observed that ultrasonic agitation promotes a more uniform grain structure, which correlates with increased corrosion resistance, due to the effective removal of hydrogen bubbles and the establishment of a denser oxide layer that impedes corrosive attack. Despite these advancements, to the authors' knowledge, there is a notable gap in the literature regarding the combined effect of agitation method and immersion time in the electroless ENP plating bath on the corrosion performance of ENIG coatings. This study would encompass complementary surface analysis, pit analysis, and localised electrochemical characterisation techniques. Moreover, there appears to be a lack of comprehensive research on the initiation and progression of localised corrosion as a function of immersion time in corrosive environments, which is necessary to understand the pit-formation process.

The application of both localised and traditional electrochemical characterisation methods, in conjunction with surface morphology analyses, facilitates the elucidation of the local distribution of cathodic and anodic sites. Among these methods, SECM is a versatile and powerful technique that provides high-resolution electrochemical data from a specific area of interest on the surface of

a substrate immersed in an aqueous environment. The high spatial resolution of the SECM technique makes it particularly valuable in studying localised corrosion phenomena, such as those initiated at micro-discontinuities within multilayer coatings such as nickel-chromium coatings. SECM can effectively map the electrochemical activity over time, revealing changes in chemical species such as oxygen consumption or hydrogen ion concentration, which are directly linked to corrosion reactions. This time-resolved data offers deep insights into how multilayer systems degrade over prolonged exposure to aggressive environments, such as chloride-based electrolytes [13, 40]. Ganborena *et al.* [41] used redox competition and surface generation/tip collection SECM modes to study the influence of cupric ions on the corrosion mechanisms of multilayer coatings.

In this research, we investigated the effects of the agitation method and immersion time on the corrosion performance of the ENIG coatings within the ENP plating process. The experimental approach adopted in this study includes sample preparation by altering the immersion time and agitation method in the ENP bath. A detailed microstructural and compositional analysis was performed using energy-dispersive X-ray spectroscopy (FE-SEM), capturing the morphology and composition of coatings. The corrosion behaviour and protective performance of ENIG coatings were evaluated using both localised and traditional electrochemical characterisation methods, including SECM and potentiodynamic polarisation (PDP), providing comprehensive insights into their electrochemical properties. This approach links structural features to corrosion resistance, providing a comprehensive view of coating performance under harsh conditions.

## **4.2 Experimental procedures**

### **4.2.1 Materials and sample preparation**

#### *4.2.1.1 Electroless nickel immersion gold coating approach*

ENIG coatings were deposited through a multi-stage process. Copper substrates (3x2 cm<sup>2</sup>) were first degreased in an acid solution (METEX Cleaner, MacDermid Enthone) at 50°C for 2 min, then pickled for 2 min at room temperature in a mixed

solution of Macuprep ETCH G-4 (MacDermid Enthone) and 1.0 wt. % sulphuric acid for 2 min at room temperature. Activation was performed in a  $\text{PdCl}_2$  solution (Affinity Activate PDS, MacDermid Enthone) for 30 s at 18°C. Immediately after pretreatment, the copper substrates were transferred into a 500 mL commercial electroless Ni-P plating bath (Planar Ultra Nickel, MacDermid Enthone) at 82°C. Deposition time and agitation methods were varied to study their effects on Ni-P layer thickness and compaction.

Coatings were obtained under ultrasonic agitation in an ultrasonic bath at 100 W acoustic power and 50 kHz for 25 min (ENP-a) or 35 min (ENP-b), as well as under mechanical agitation at 300 rpm for 35 min (ENP-c). Electroless gold plating was subsequently performed by immersing the samples in a 300 mL electrolyte (Affinity Gold 2.0, MacDermid Enthone) at 85 °C for 15 min under mechanical agitation at 200 rpm. A double-distilled water rinse was applied between each process step.

### 4.2.2 Microstructural and compositional analysis

#### 4.2.2.1 *Field-emission scanning electron microscopy and energy-dispersive X-ray spectroscopy (FESEM/EDS) analyses*

The morphological features and compositional details of the samples were meticulously examined using FE-SEM equipped with an Ametek® EDS APOLLO X probe (Model: Carl Zeiss Ultra Plus, manufactured by Zeiss in Jena, Germany). Sample preparation involved a cleansing process using an ultrasonic cleaner, where the samples were submerged in isopropanol for a duration of 10 minutes and subsequently air-dried with high-pressure air.

### 4.2.3 Electrochemical analysis

#### 4.2.3.1 *Potentiodynamic polarisation (PDP) tests*

The electrochemical corrosion behaviour of the samples was evaluated using a 250 mL EG&G Princeton Applied Research three-electrode Flat Cell, controlled by a Solartron Analytical 1287 potentiostat-galvanostat. All measurements were performed in an aerated 3.5 wt.% NaCl solution at room temperature, with a working electrode area of 1 cm<sup>2</sup>. A Pt mesh and a Ag/AgCl (3 M KCl) electrode were used as counter and reference electrodes, respectively. Prior to testing, the samples were cleaned in an ultrasonic bath with isopropanol for 10 min, then



dried with compressed air. Potentiodynamic polarisation measurements were conducted from -0.2 V (vs. OCP) to 0.7 V (vs. Ag/AgCl) at a scan rate of 0.2 mV/s, following a 900 s stabilization period under OCP conditions. Electrochemical measurements were conducted with the electrochemical cell enclosed in a Faraday cage to minimise interference from external electromagnetic signals. Data reproducibility was verified using 3 replicates, with representative results reported.

#### 4.2.3.2 *Scanning electrochemical microscopy (SECM)*

The experimental investigation into the localised corrosion characteristics of the samples designated as AuENP-a, AuENP-b, and AuENP-c was conducted using the SECM technique. A model SCV370 instrument from Princeton Applied Research, part of AMETEK Inc., facilitated this study. To mitigate crevice corrosion risks, an anti-tamper adhesive sealant sourced from Electrolube company was employed to delineate rectangular regions on the ENIG samples, ensuring effective exposure to the corrosive solution throughout SECM measurements. Diverse scan areas were strategically chosen for each sample to enhance the coverage of the SECM scan region. Specifically, 1000  $\mu\text{m}$   $\times$  1200  $\mu\text{m}$  areas were allocated for AuENP-a, 600  $\mu\text{m}$   $\times$  800  $\mu\text{m}$  for AuENP-b, and 900  $\mu\text{m}$   $\times$  1000  $\mu\text{m}$  for AuENP-c. Before each measurement, each sample was levelled by SECM approaching curves at three points of the sample to confirm the absence of tilting. The process was performed with each sample immersed in a non-corrosive aqueous solution containing 2 mM ferrocenemethanol (FcMeOH) and 0.01 M sodium sulphate. After levelling, the SECM was operated in feedback mode, employing an electrolyte solution of 3.5 wt.% sodium chloride and 2 mM FcMeOH to serve as the redox mediator. The experimental setup included a platinum microelectrode with a 10  $\mu\text{m}$  diameter (Sensolytics Inc.), a platinum counter electrode, and a saturated Ag/AgCl reference electrode. The time-dependent electrochemical responses were monitored immediately after sample immersion and subsequently at 2-hourly intervals, along with the 1-, 2-, 3-, and 4-day marks. To prevent the evaporation of the measuring solution, a microliter peristaltic pump was employed to supply deionised water, maintaining a constant solution volume continuously. During these measurements, the

microelectrode was held at a potential of 0.5 V against the Ag/AgCl reference to facilitate the oxidation of the ferrocene mediator. All samples were maintained at open circuit potential (OCP). Prior to each scanning measurement, the SECM tip's proximity to the sample surface was established by approaching curves. The tip-sample separation was fixed at 15  $\mu\text{m}$ . The SECM map scans were performed at a velocity of 20  $\mu\text{m/s}$ , initiated after a stabilization period of 5 minutes post-immersion for each sample.

### **4.3 Results and discussion**

#### **4.3.1 Microstructural and compositional characterisation**

The surface morphology and phosphorus content of ENP coatings were investigated through FE-SEM/EDX analyses. Figure 4.1 shows the surface morphology of the coatings, providing insights into the effect of two agitation conditions and plating times on the surface quality. Specifically, coatings prepared by ultrasonic agitation for 25 and 35 minutes, and by stirring at 300 rpm for 35 minutes, were examined.

Figure 4.1 (a1-a3) and (b1-b3) present the surface morphology of ENP coatings synthesized under ultrasonic agitation, with plating times of 25 minutes and 35 minutes, respectively. For comparison, Figure 4.1 (c1-c3) displays the surface morphology of a sample prepared using mechanical stirring at 300 rpm for 35 minutes. At low magnification (a1-c1), the surface morphology of all three samples appears similar. However, at higher magnification, the mechanically stirred sample shows surface defects, including visible holes. In contrast, the samples produced with ultrasonic agitation exhibit smooth, defect-free surfaces, even at higher magnifications, indicating superior surface quality.

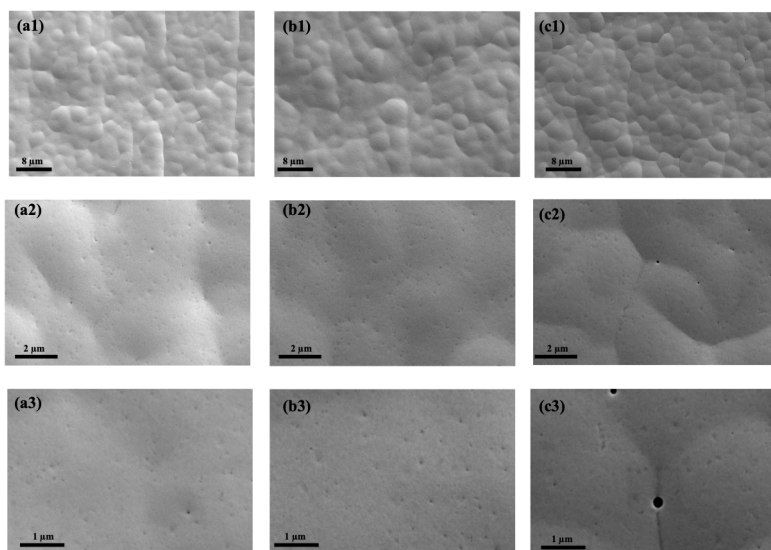


Figure 4.1 Top-view FE-SEM images of the NiP samples coated on Cu substrate showing the impact of deposition time and agitation methods, a1- a3) 25 min with ultrasonic agitation (ENP-a), b1- b3) 35 min with ultrasonic agitation (ENP-b), and c1- c3) 35 min with 300 rpm stirring (ENP-c).

Table 4.1 presents the results of our comparative analysis of the effects of agitation methods and durations on coating thickness and phosphorus content in an ENP plating process. The data indicate that varying the agitation method and duration significantly influences the coating characteristics. The coatings were developed under three different conditions: ENP-a, with 25 minutes of ultrasonic agitation, exhibited a coating thickness of  $4.1 \mu\text{m}$  ( $\pm 0.1 \mu\text{m}$ ) and a phosphorus content of 12.5 wt.% ( $\pm 0.1 \text{ wt.}\%$ ); ENP-b, also subjected to ultrasonic agitation but for 35 minutes, demonstrated an increased thickness of  $5.9 \mu\text{m}$  ( $\pm 0.1 \mu\text{m}$ ) alongside a slightly higher phosphorus content of 13.0 wt.% ( $\pm 0.6 \text{ wt.}\%$ ); and ENP-c, which was mechanically stirred at 300 rpm for 35 minutes, showed the greatest thickness at  $7.4 \mu\text{m}$  ( $\pm 0.1 \mu\text{m}$ ) but a reduced phosphorus content of 11.8 wt.% ( $\pm 0.2 \text{ wt.}\%$ ). The P content of the samples, which are above 10 wt.%, shows that they all are categorised in the high P content ENP category of coatings [42].

The low standard deviation across all samples suggests effective control of the deposition process, yielding uniform coatings regardless of agitation method or duration. However, the phosphorus content differs between the agitation methods, with lower P content in the mechanically stirred sample compared to

that in the ultrasonicated samples. The results indicate that the coating process is significantly affected by both plating time and agitation intensity. Longer plating times allow more material to be deposited on the substrate, resulting in increased coating thickness. However, the decline in phosphorus content with longer plating times suggests that the phosphorus incorporation process may be limited, potentially due to phosphorus diffusion out of the coating.

*Table 4.1 The thickness values and P content of ENP-a, ENP-b, and ENP-c samples*

| <b>Samples</b> | <b>Thickness (<math>\mu\text{m}</math>)</b> | <b>P content (%wt)</b> |
|----------------|---------------------------------------------|------------------------|
| <b>ENP-a</b>   | $4.1 \pm 0.1$                               | $12.5 \pm 0.1$         |
| <b>ENP-b</b>   | $5.9 \pm 0.1$                               | $13.0 \pm 0.6$         |
| <b>ENP-c</b>   | $7.4 \pm 0.1$                               | $11.8 \pm 0.2$         |

XRD measurements were performed to investigate the effect of the plating time and agitation method on the structural characteristics of the samples. As one of the pivotal factors in determining the microstructure of ENP coatings, variations in P content affected by plating bath conditions influence whether the coating consists of a crystalline, amorphous, or hybrid structure. In previous investigations, coatings with medium phosphorus levels exhibited a mixed amorphous-crystalline structure (coexisting  $\beta$  and  $\gamma$  phases) phase, while those with high phosphorus levels showed a predominantly amorphous ( $\gamma$ ) phase [43, 44].

The XRD patterns of ENP coatings with different agitation types and plating times are shown in Figure 4.2. The peak observed at  $2\theta^\circ$  of 45 for all samples corresponds to the characteristic peak of the (111) plane of nickel. Additionally, the sharp peaks marked by the star signs are attributed to the Cu substrate. These Cu peaks were detected since the coating thicknesses were less than the X-ray diffusion depth. The intensity of the Ni (111) peak shows a slight increase in the order of ENP-c > ENP-a > ENP-b, suggesting a trend towards relatively more amorphous structures in the order of ENP-b > ENP-a > ENP-c. This observation aligns with the relative changes in phosphorus content among the ENP samples, as reported in the EDX analyses in Table 4.1.

The broad profile observed near the Ni (111) peak in the  $2\theta$  range of  $40^\circ$  to  $50^\circ$ , along with the absence of other characteristic Ni peaks such as Ni (200), Ni (220), and Ni (311), suggests that the dominant phase in the samples is fully amorphous ( $\gamma$ ) structure, or with a minor presence of nanocrystalline phases in the coatings. The expected positions of Ni (200), Ni (220), and Ni (311) peaks in the XRD spectrum are at approximately  $54^\circ$ ,  $85^\circ$ , and  $108^\circ$  in  $2\theta$ , respectively [30]. Their absence is likely due to the broadness and low intensity of these peaks. The contribution of the nanocrystalline phase to the overall structure of the coatings is minimal; however, their relative abundance follows the order of ENP-c > ENP-a > ENP-b.

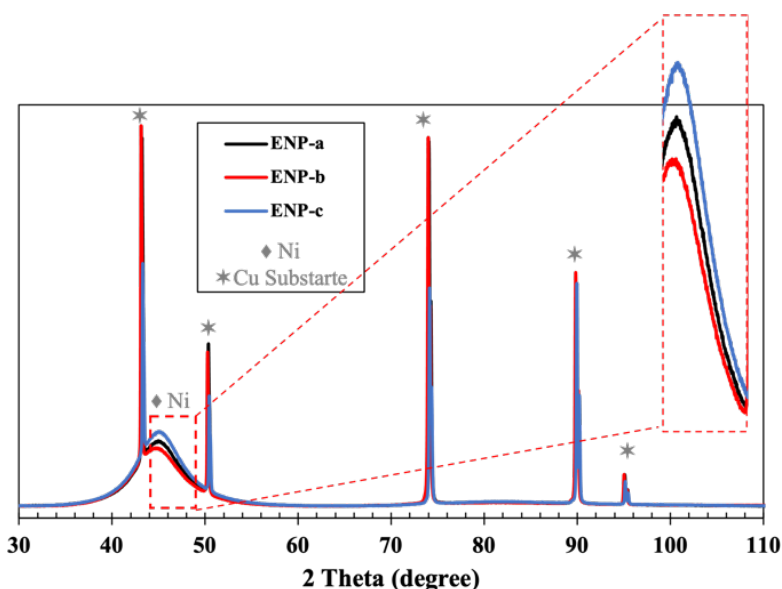


Figure 4.2 The XRD patterns from the top surface of ENP-a, ENP-b, and ENP-c.

#### 4.3.2 Electrochemical study of ENP and AuENP-coated copper samples

In Figure 4.3 (a, b), the potentiodynamic polarisation curves of the ENP coatings and AuENP coatings on the copper substrate in a 3.5 wt.% NaCl solution are shown. The corrosion potential ( $E_{\text{corr}}$ ) and corrosion current density ( $i_{\text{corr}}$ ) values obtained from these curves were calculated using Tafel extrapolation, as presented in Table 4.2. In the aerated near-neutral 3.5 wt.% NaCl solution, the cathodic branch, i.e. the reduction of dissolved oxygen, is expected to be partially

diffusion-controlled, so the assumption of activation control underlying the Tafel extrapolation is therefore not strictly valid. Accordingly, the  $i_{\text{corr}}$  values in Table 4.2 are interpreted as comparative indicators for samples measured under identical conditions rather than as absolute corrosion rates. The relative order of the samples is independently supported by the time-resolved SECM measurements presented in Section 4.3.3 (Figure 4.4), which do not rely on this assumption. The  $E_{\text{corr}}$  values for the coated sample exhibit more negative potentials than those of the bare substrate, indicating improved cathodic protection for the copper substrate in the 3.5 wt.% NaCl solution [27, 45].

The reduction in corrosion current density for all coated samples (ENP and AuENP) relative to the substrate highlights the effectiveness of the coatings in lowering the overall corrosion rate. In Figure 4.3 (a), ENP-b shows the lowest corrosion current density, indicating the slowest corrosion rate among the coated samples. ENP-a and ENP-b coatings, prepared in the same electroless plating bath with nearly identical phosphorus levels, differed primarily in immersion time, resulting in a thinner ENP-a coating. Since both coatings fully cover the substrate, the coating thickness itself is not expected to alter the intrinsic electrochemical response of the coating surface. However, a thinner coating offers a shorter path for localised attack to perforate through the coating towards the substrate, and the shorter deposition time may also result in a less fully developed deposit. Both factors are consistent with the lower corrosion resistance observed for ENP-a compared with ENP-b. On the other hand, ENP-b and ENP-c were subjected to equivalent plating durations, yet ENP-c yielded a thicker coating with reduced phosphorus content compared to ENP-a. This decreased phosphorus concentration is the primary factor contributing to the diminished corrosion resistance observed in ENP-c relative to ENP-a. The mechanical stirring used in ENP-c, although resulting in a higher thickness, does not appear to provide the same level of protection, potentially due to less effective P content or distribution within the Ni matrix, or more irregularities and defects within the coating layer. The anodic branches of the polarisation curves reveal distinct passive behaviours among the coatings. ENP-a and ENP-b display similar passivity behaviour, with ENP-b showing a slightly broader passive region and a higher pitting potential

than ENP-a. The ENP-c samples show a two-step passivity region, with the first region occurring between -280 mV and -120 mV. A second passive region is observed from 0 to +160 mV, transitioning into a transpassive region. Although ENP-c exhibits lower current density in the initial passive region compared to ENP-a and ENP-b, the passive layer in ENP-c proves unstable over a broader range of anodic polarisation. Overall, the passive films in ENP-c were less stable and protective than those in ENP-a and ENP-b.

The potentiodynamic polarisation curves of the specimen after the application of the Au top layer are presented in Figure 4.3 (b). The AuENP samples exhibit positive shifts in  $E_{\text{corr}}$  and significantly reduced  $i_{\text{corr}}$  values, indicating a more noble surface and enhanced corrosion protection. Although the passive behaviours of the AuENP-b and AuENP-c layers appear similar, AuENP-b demonstrates lower  $i_{\text{corr}}$  values and slightly higher pitting potential, signifying superior corrosion performance. In contrast, AuENP-a shows higher  $i_{\text{corr}}$  values compared to the other samples, and the shape of its passive layer in the anodic plot suggests it is less protective. The order of corrosion performance for the Au-incorporated samples is AuENP-b > AuENP-c > AuENP-a, showing a similar trend to that observed in the case of the ENP layers alone. The passive-like character of the anodic branches of the AuENP samples cannot be unambiguously attributed to the Au top-layer itself. Gold does not form a passivating oxide under the present conditions, and the SECM results presented in Section 4.3.3 indicate that the electrolyte reaches the underlying ENP layer during immersion. The observed passive-like response therefore most likely reflects, at least in part, the passivation of the underlying NiP exposed through pores or defects in the Au top-layer. Since the thickness of the Au layer, which governs its pore density, was not determined in this study, the two contributions cannot be separated here, and the interpretation of the anodic branches of the AuENP samples is subject to this limitation.

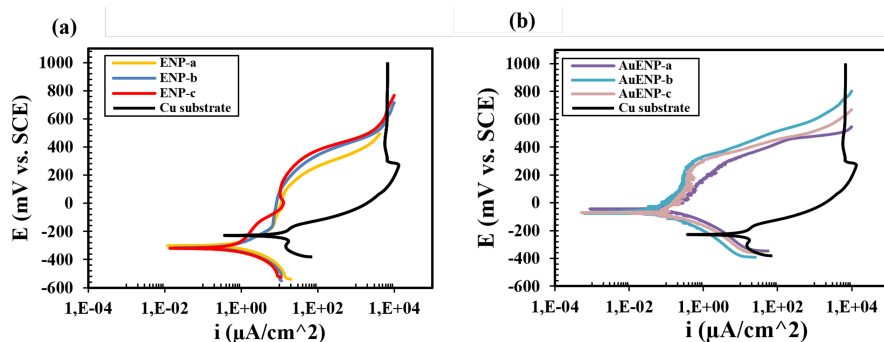


Figure 4.3 Potentiodynamic polarisation curves for (a) the ENP-a, ENP-b, and ENP-c samples, and (b) the Au-coated counterparts (AuENP-a, AuENP-b, and AuENP-c), in a 3.5 wt.% NaCl solution.



Table 4.2. Potentiodynamic polarisation parameter values by Tafel extrapolation for the NP-a, NP-b, and NP-c samples in 3.5 wt.% NaCl solution

| Samples          | $i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ ) | $E_{\text{corr}}$ (mV vs. SCE) |
|------------------|-------------------------------------------------|--------------------------------|
| <b>Substrate</b> | $21.12 \pm 3.00$                                | $-234 \pm 9$                   |
| <b>ENP-a</b>     | $2.80 \pm 0.30$                                 | $-297 \pm 6$                   |
| <b>ENP-b</b>     | $2.50 \pm 0.30$                                 | $-318 \pm 9$                   |
| <b>ENP-c</b>     | $2.60 \pm 0.90$                                 | $-324 \pm 7$                   |
| <b>AuENP-a</b>   | $0.26 \pm 0.05$                                 | $-56 \pm 19$                   |
| <b>AuENP-b</b>   | $0.11 \pm 0.02$                                 | $-68 \pm 8$                    |
| <b>AuENP-c</b>   | $0.13 \pm 0.05$                                 | $-69 \pm 5$                    |

#### 4.3.3 Local electrochemical study of ENIG samples by SECM

SECM measurements were performed to investigate the local electrochemical activity of AuENP samples during immersion in 3.5% NaCl solution (containing 2mM FcMeOH redox mediator). The measurements were conducted in feedback mode, capturing the evolving electrochemical behaviour immediately after immersion and at 2 hours, 1 day, 2 days, 3 days, and 4 days post-immersion.

The SECM maps for the AuENP -a, AuENP -b, and AuENP -c samples are shown in Figure 4.4, designated as subfigures (a1-a6), (b1-b6), and (c1-c6) respectively, displaying the normalised current ( $i/i_{\text{limit}}$ ). In the initial stages of immersion, the SECM maps show a homogeneous signal with no significant variation in the current. Normalised values appear above 1, consistent with the conductive nature of the Au-layer. As the immersion time increases over 1day, localised electrochemical activity emerges, evidenced by the varying intensities of the normalised current values on the maps. As shown in Figure 4.4, after 1 day of immersion, localised current increases begin to appear in the AuENP-a and AuENP-c samples, potentially indicating electrochemical activity associated with corrosion. By the second day, localised events become visible in all samples. For AuENP-a and AuENP-b, these events display dynamic behaviour, with variations

in intensity and location. In contrast, the AuENP-c sample exhibits stable localised activity, suggesting the formation of a persistent pit. Throughout immersion, these signals intensified, indicative of an aggressive corrosion process. The increased tip current suggests active electrochemical behaviour due to the regeneration of redox species on the substrate. During the initial hours of immersion, the corrosive media diffuses toward the underlying ENP layer. Upon reaching this layer and forming stable pits, the SECM signals strengthen with the immersion time. The strong SECM signal correlates with significant electrochemical activity, which is likely due to a large cathode-to-anode surface area ratio, with the gold surface acting as the cathode and the ENP layer as the anode. The varying corrosion performance among the samples can be attributed primarily to differences in the P content and microstructural quality (defect density) of the electroless ENP coatings. The coating thickness plays an indirect role, by determining the length of the through-coating defect path towards the substrate, rather than acting as an independent protective factor.

As indicated earlier by PDP curves, the ENP-c layer did not exhibit passive behaviour, which is consistent with the large limiting current values and strong SECM signals observed on the SECM maps. With increasing immersion time for the AuENP-c sample, the SECM maps suggest the development of localised electrochemical activity at the pit area, potentially indicating changes in the local environment that promote corrosion. For the AuENP-a and AuENP-b samples, the activities noted by the SECM signals also increase over time, but to a lesser extent compared to the AuENP-c. The AuENP-b maps show the most stable SECM, with little local variation throughout the immersion time, indicating better corrosion resistance than AuENP-a and significantly better than AuENP-c. These findings elucidate the influence of ENP layer properties on the corrosion resistance of the samples, with SECM maps effectively visualising the localised electrochemical behaviour and pit-formation dynamics in the AuENP samples over time.

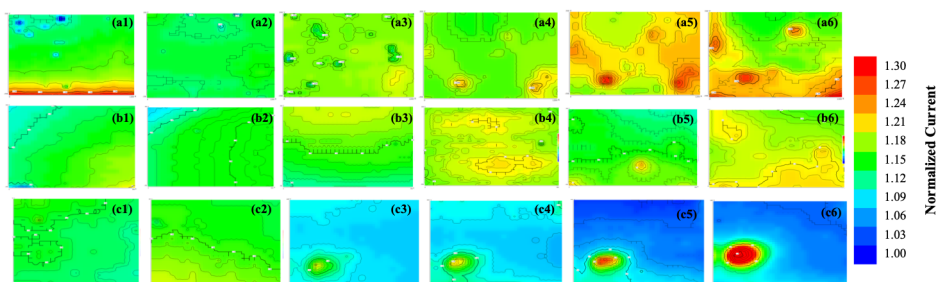


Figure 4.4. The SECM analysis of the AuENP-a, AuENP-b, and AuENP-c samples immersed in 2mM FcMeOH and 3.5% NaCl solution. Subfigures (a1-a6), (b1-b6), and (c1-c6) represent the SECM maps for AuENP-a, AuENP-b, and AuENP-c, respectively, capturing the evolving electrochemical behaviour after immersion, and subsequently at 2 hours, 1 day, 2 days, 3 days, and 4 days post-immersion.

#### 4.3.4 Microstructural and compositional characterisation of post-corroded samples

In Figure 4.5, the top-view FE-SEM/EDX pit analysis of the post-corroded ENIG samples overlapped with the corresponding SECM map is shown to assess the surface morphology and elemental distribution of the post-corroded samples after the four-day SECM measurements. The insets in Figure 4.5 are magnified views of different surface sites that show localised attack and corresponding FE-SEM/EDX compositional analysis. As shown in Figure 4.5 a, the AuENP-a sample exhibited moderate pitting with several localised regions showing corrosion pits. In contrast, the AuENP-b sample in Figure 4.5b displayed a relatively intact surface, suggesting better corrosion resistance. The surface of AuENP-c in Figure 4.5c, however, showed extensive pitting and larger corrosion pits, indicating a higher degree of corrosion and surface damage compared to the other samples. Although the SECM map for the AuENP-c sample shows localised activity related to a surface defect, many other pits were found across the exposed area. This confirms the high reactivity of this sample observed by the SECM experiments. The EDX analysis shows that the pits formed have already reached the copper substrate.

The variations in the severity of the pit formation among the samples can be attributed to the differences in plating conditions, type of agitation, and plating time, which influenced the structural properties and corrosion resistance of the coatings. Specifically, the long deposition time together with ultrasonic agitation

used for AuENP-b likely contributed to its superior surface morphology post-corrosion by promoting a more uniform and denser coating structure during deposition. Ultrasonic agitation during the ENP deposition process (as in AuENP-b) leads to a more uniform coating with slightly higher phosphorus content, enhancing its corrosion resistance in terms of a stable passive layer with high pitting potential. Mechanical stirring (as in AuENP-c) results in less uniform coatings, with more surface defects and lower phosphorus content, thereby reducing overall protective efficacy.

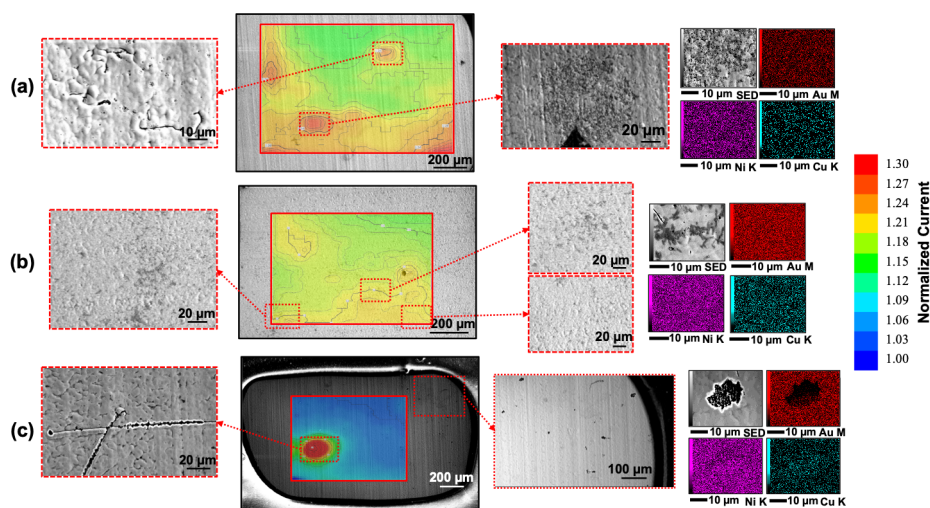


Figure 4.5 Post-corroded FE-SEM and EDS analyses of AuENP samples after four days of immersion in 2 mM FcMeOH and 3.5 wt.% NaCl solution, during which intermittent SECM measurements were performed. Panels (a)–(c) correspond to AuENP-a, AuENP-b, and AuENP-c, respectively. The low-magnification SEM images show the overall corrosion morphology, while the red dashed arrows indicate areas of localised attack that are presented at higher magnification. The accompanying EDS elemental maps (Ni, Cu, and Au) highlight compositional variations within the corroded regions.

#### 4.4 Conclusions

This study provides a comprehensive understanding of the influence of ENP bath parameters, specifically the agitation method and immersion time, on the microstructure and corrosion performance of ENIG coatings on copper substrates in an aqueous chloride-containing environment. Through a combination of microstructural, compositional, and electrochemical analyses, we revealed

critical insights into optimising these parameters to enhance the protective qualities and durability of ENIG coatings.

Ultrasonic agitation during ENP deposition process resulted in coatings with higher phosphorus content (12.5–13.0 wt.%), smoother, defect-free surfaces and improved corrosion resistance compared to those prepared under mechanical stirring. PDP and SECM analyses consistently showed that coatings produced under ultrasonic agitation (ENP-a and ENP-b) exhibited superior corrosion resistance. In contrast, mechanically stirred coatings (ENP-c) were thicker but had lower phosphorus content (~11.8 wt.%) and exhibited inferior corrosion performance and surface defects.

Among all conditions studied, the ENP-b sample (35 min ultrasonic agitation) provided the best overall protection, showing the lowest electrochemical activity and minimal pit formation after prolonged immersion in corrosive media. These results confirm that ultrasonic agitation, combined with optimised immersion time, enhances the corrosion resistance of ENIG coatings by promoting favourable deposition conditions in the ENP bath.

These findings suggest that ENIG coatings prepared under ultrasonic agitation and appropriate plating duration exhibit superior corrosion protection compared to those produced under mechanical stirring. This optimisation of ENP bath parameters offers a reliable route to improving the durability and performance of ENIG surface finishes for electronic applications.

### 4.5 References

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## Chapter 5. Conclusion and Outlook

### 5.1 Conclusions

This thesis has explored the localised corrosion behaviour of electroless nickel immersion gold (ENIG) surface finishes on copper substrates, with a focus on microscale mechanisms relevant to printed circuit boards (PCBs). The primary motivation arises from the increasing miniaturisation in electronic components, where corrosion processes at small scales can critically impact reliability and service life. The work integrated multiple experimental approaches from electrochemical characterisation to advanced microscopic and spectroscopic analyses to reveal how micro-defects, phosphorus content, and deposition parameters govern corrosion initiation, propagation, and overall coating performance.

By investigating ENIG coatings at submicrometric resolution, this work has provided valuable insights into the mechanisms of corrosion initiation and propagation. The findings enhance understanding of failure modes in ENIG-finished PCBs, supporting more accurate root-cause diagnostics and providing valuable guidance for quality control and design improvement. Key microstructural features and environmental triggers of corrosion were identified, enabling the development of targeted mitigation strategies. These strategies include optimised coating composition, refined surface treatments, and improved environmental controls.

Beyond immediate practical implications, this research provides a foundation for the design of more durable and corrosion-resistant electronics. As advancements in the electronics industry continue and devices become even smaller, addressing localised degradation mechanisms becomes more essential. The insights presented here contribute to that endeavour, supporting the

advancement of long-lasting, high-performance electronic systems for a broad range of applications.

The main findings of this thesis can be summarised as follows:

- **Localised aqueous corrosion in commercial ENIG-coated systems.**

In the ENIG-coated copper system studied, corrosion is initiated at pre-existing defects or pores in the thin Au film, which disrupt its continuity and expose the underlying Ni layer. At these sites, a local galvanic cell is established, with the noble Au acting as a large-area cathode and the exposed Ni as the anode; the very high Au/Ni cathode-to-anode surface area ratio produces a strong driving force that causes the Ni to dissolve rapidly. This Ni dissolution evolves into an elliptically shaped pit under the Au, combining lateral undercutting of the Au layer with depth penetration into the Ni. Once the pit breaches the Ni/Cu interface, Ni removal continues along the layer, and the Cu substrate becomes exposed; however, Cu is only weakly attacked under the highly acidic, chloride-rich conditions at the pit bottom. Thus, the overall mechanism is controlled by Au-film integrity and the Au/Ni galvanic coupling. The microstructural and electrochemical studies consistently show that a lack of integrity of the thin Au-layer triggers a Ni-dominated, galvanically driven pit growth, with minimal Cu corrosion occurring only as a secondary, late-stage process.

- **Influence of phosphorus content in electroless nickel coatings.**

Electroless Ni–P coatings showed a clear, phosphorus-dependent sequence of structural and corrosion behaviours. In the examined Cu/Ni–P systems, increasing P content favors an amorphous or nanocrystalline deposit, whereas decreasing P content favors an increasingly crystalline Ni phase. This change in phase state is reflected in the coating's morphology and local Volta potential behaviour. The high-P (amorphous) coatings develop relatively uniform, defect-free surfaces with a smooth, even distribution of electronic potential, while low-P (more crystalline) coatings exhibit many microstructural interfaces or flaws and markedly uneven local surface potentials. These structural and surface potential

heterogeneities, in turn, control corrosion behaviour: the many defect sites and potential differences in low-P coatings create micro-galvanic cells that concentrate anodic dissolution (pitting) at those locations, whereas the high-P amorphous coatings, lacking preferential initiation sites, resist attack and remain largely intact. Overall, higher phosphorus yields a more homogeneous Ni–P microstructure and a higher corrosion resistance, while lower phosphorus content produces a mixed crystalline structure, with attendant surface and electronic inhomogeneities that promote localised corrosion.

- **Optimisation of deposition parameters for enhanced coating performance.** The influence of bath agitation and immersion time on the characteristics of ENIG coatings was systematically examined to clarify how these parameters shape coating quality. More intense agitation enhanced mass transport in the bath, leading to smoother and more homogeneous deposits with higher phosphorus incorporation and fewer surface defects, while milder agitation conditions tended to produce thicker coatings at the expense of uniformity. Increasing the immersion time promoted further growth of the coating and higher phosphorus uptake; however, excessive deposition also increased the likelihood of defects and internal stresses. Together, these results reveal a clear trade-off between coating thickness, composition, and structural integrity. Thicker deposits are often associated with higher phosphorus content but can suffer from reduced mechanical and microstructural stability, whereas lower-phosphorus coatings are generally more robust yet thinner. Achieving an optimal balance between these competing factors is therefore essential. Overall, the findings demonstrate that careful control of both agitation conditions and plating duration is critical for producing ENIG coatings with a well-balanced combination of thickness, composition, and surface quality, ensuring reliable performance in demanding electronic applications.

In conclusion, this research provides a detailed understanding of localised corrosion mechanisms in ENIG surface finishes. It underscores the importance

of microstructural integrity and process control in determining corrosion resistance. Beyond offering valuable scientific contributions to the field, the findings offer practical guidelines for the design and fabrication of more durable and reliable surface finishes for electronic components.

### 5.2 Outlook

This research has laid the groundwork for understanding the localised corrosion behaviour of ENIG final finishes and the influence of processing parameters on their performance. While the findings contribute to improved reliability of PCBs in electronic devices, several promising research directions remain to be explored.

One promising direction for future work is to combine experimental studies with corrosion modelling. While the experiments in this thesis provide clear evidence of localised corrosion initiation in ENIG coatings, they cannot directly resolve the local electrochemical conditions that develop around micro-defects. This is largely due to the spatial resolution limits of the available experimental techniques, which make it difficult to quantify electrochemical parameters at the scale of individual coating defects. Computational modelling could therefore be used to complement the experimental observations by quantifying parameters such as local current density distributions and potential gradients at the gold/nickel galvanic couple. In particular, finite-element (FE) simulations could be applied to study galvanic interactions between the gold layer (cathode) and the nickel layer (anode) in the vicinity of coating defects. Such simulations would allow the influence of defect geometry, cathode-to-anode area ratio, and electrolyte properties on current localisation and nickel dissolution to be systematically evaluated. To ensure that the simulations remain physically meaningful, the modelling results should be validated against experimental data obtained from localised electrochemical techniques, such as SECM measurements, as well as against the corrosion morphologies observed in this work.

Another important direction involves investigating the impact of PCB geometry and circuit design on corrosion susceptibility. The shape and layout of current-

carrying copper traces can introduce localised vulnerabilities, especially in regions with sharp corners, narrow gaps or crevices. These features may promote stress concentration, coating damage and moisture entrapment, factors to accelerate electrochemical degradation.

Another useful direction for future work would be to examine more closely how phosphorus content influences the microstructure of electroless Ni–P coatings and how this, in turn, affects their corrosion behaviour. In particular, it is still unclear what balance between crystalline and amorphous phases provides the best corrosion resistance. While higher phosphorus levels generally lead to more amorphous deposits, the present study could not determine whether the improved performance is mainly due to the phosphorus content itself or to the associated changes in phase structure. Future work could therefore focus on identifying the optimum proportion of crystalline and amorphous phases and understanding how this balance can be controlled through plating conditions. Investigating which bath parameters most effectively influence this phase distribution would not only help clarify the underlying mechanisms but could also provide practical guidance for industry, where simple adjustments to bath conditions may offer a pragmatic way to optimise the properties of electroless nickel coatings.

As PCBs operate under electrical bias in service, it would also be worthwhile for future studies to explore how an applied potential might influence corrosion behaviour. Electrical fields can modify local electrochemical conditions and may affect how corrosion initiates and spreads, especially in fine circuit features.

In summary, advancing our understanding of ENIG degradation through modelling, design-informed research and new mitigation strategies holds great promise for the development of more robust and sustainable electronic systems. Extending the lifespan of electronic components not only improves performance but also contributes to reducing electronic waste and promoting responsible manufacturing practices across the industry.





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## About the author

Mirsajjad Mousavi was born on November 13, 1990, in Tabriz, Iran. He obtained his bachelor's degree in metallurgical engineering from the University of Tabriz in 2013. In 2015, he completed his first master's degree in Corrosion Engineering and Protection of Materials at Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran. In



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# List of publications

## Journal Papers:

1. Mousavi M, Kosari A, Mol JMC, Gonzalez-Garcia Y. Localised aqueous corrosion of electroless nickel immersion gold-coated copper. Corrosion Engineering, Science and Technology. 2022 Sep;57(6):520-30.
2. Mousavi M, Rahimi E, Mol JMC, Gonzalez-Garcia Y. The effect of phosphorus content on the microstructure and localised corrosion of electroless nickel-coated copper. Surface and Coatings Technology. 2024 Sep 30;492:131174.

## Conference Papers:

1. Mousavi M, Mol JMC, Gonzalez-Garcia Y. In-situ study of corrosion phenomena on electronic devices by local electrochemical techniques. EUROCORR 2019 Annual European Corrosion Congress (Seville, Spain, 2019).
2. Mousavi M, Mol JMC, Gonzalez-Garcia Y. In-situ study of corrosion phenomena on electronic devices by local electrochemical techniques. Electrochem 2019 (Glasgow, Scotland, 2019).
3. Mousavi M, Mol JMC, Gonzalez-Garcia Y. Study of corrosion phenomena on contact tracks of SD memory cards with ENIG final finishing. EUROCORR 2020 Annual European Corrosion Congress (Online Presentation).
4. Mousavi M, Mol JMC, Gonzalez-Garcia Y. Study of corrosion phenomena on contact tracks of SD memory cards with ENIG final finishing. EUROCORR 2021 Annual European Corrosion Congress (Online Presentation).
5. Mousavi M, Mol JMC, Gonzalez-Garcia Y. Localized corrosion study of Electroless Nickel (EN) alloys on copper substrate during exposure to aqueous environment: Effect of phosphorous content. EUROCORR 2022 Annual European Corrosion Congress (Berlin, Germany, 2022).

# List of contributions

1. State SP, Costovici S, Mousavi M, Garcia YG, Zanella C, Cojocaru A, Anicai L, Visan T, Enachescu M. Electrodeposited Sn-Cu-Ni alloys as lead-free solders on copper substrate using deep eutectic solvents: The influence of electrodeposition mode on the morphology, composition and corrosion behaviour. Surface and Coatings Technology. 2024 Feb 15;477:130324.



This is the last page of this dissertation.



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