ELECTROCHEMICAL 3D PRINTING OF METALS FOR SENSING APPLICATION

M.Tech. Thesis

By

PROSENJIT MONDAL



DEPARTMENT OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE

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ELECTROCHEMICAL 3D PRINTING OF METALS FOR SENSING APPLICATION

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of

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By

PROSENJIT MONDAL



DEPARTMENT OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **ELECTROCHEMICAL 3D PRINTING OF METALS FOR SENSING APPLICATION** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DISCIPLINE OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from August 2023 to May 2024 under the supervision of Dr. Ajay Kumar Kushwaha, Associate Professor, MEMS, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

31/05/2024

Signature of the student with date (PROSENJIT MONDAL)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

03 06 24

Signature of the Supervisor of M.Tech. (with date) (Dr. Ajay Kumar Kushwaha)

PROSENJIT MONDAL has successfully given his M.Tech. Oral Examination held on 29 May 2024

03/06/24

Signature(s) of Supervisor(s) of M.Tech. thesis Date:

Convener, DPGC Date:

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DEDICATION

Dedicated to my parents

ABSTRACT

The aim of this study is the development and application of electrochemical 3D printing for fabricating metal and alloy structures, focusing on its potential for creating catalytic sensors. The work begins with modifications to a traditional Fused Deposition Modeling (FDM) 3D printer to enable the electrochemical deposition of metals. Copper was initially chosen to test the system, and its deposition was characterized using optical microscopy, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). These techniques revealed the influence of varying voltages and electrolyte concentrations on the morphology and composition of the printed copper structures.

Building on this foundation, the study then shifts to the fabrication of Ni-Co alloy structures on FTO substrates using the developed electrochemical 3D printing technique. The Ni-Co alloy was specifically chosen for its catalytic properties, making it suitable for The fabricated glucose-sensing applications. sensors were characterized and tested for their electrochemical performance in glucose detection, utilizing cyclic voltammetry (CV). The sensors demonstrated significant redox activity, attributed to the Ni(OH)2/NiOOH redox couple, confirming their effectiveness in glucose oxidation.

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NOMENCLATURE

Symbol	Meaning
μ	Micro
m	Meter
nm	Nano Meter
М	Molarity
V	Voltage
A	Ampere
Cu	Copper
Ni	Nickel
Со	Cobalt
E _{pa}	Anodic peak potential
I _{pa}	Peak anodic current

ACRONYMS

AM	Additive manufacturing
DMLS	Direct Metal Laser Sintering
ECAM	Electrochemical Additive Manufacturing
MCED	meniscus-Confined Electrodeposition
SEM	Scanning Electron Microscopy
XRD	X-ray diffraction
PPEK	Polyetheretherketone
SLM	Selective Laser Melting
SLS	Selective Laser Sintering
EFAB	Electrochemical Fabrication
SFF	Solid Freeform Fabrication
MEMS	Micro-Electro-Mechanical Systems
LED	Localized Electrochemical Deposition
EICF	Evaporation-induced convective flow
FDM	Fused Deposition Modeling
PLA	Polylactic Acid
CAD	Computer Aided Design
IPA	Isopropyl alcohol
DI	Deionized water
EDX	Energy Dispersive X-ray spectroscopy
FCC	Face-centered cubic
WHO	World health organization
FTO	Fluorine-doped tin oxide
DC	Direct Current

CV Cyclic Voltammetry

Chapter 1: Introduction

1.1 Background

Additive manufacturing (AM), commonly referred to as 3D printing, represents a transformative approach in the production of objects, distinguishing itself from conventional subtractive Z by building complex three-dimensional geometries layer by layer. This method does not remove material but instead adds it precisely where needed, allowing for the creation of intricate designs that were previously impossible or too costly to achieve with traditional manufacturing techniques [1].

The ability of additive manufacturing (AM) to create intricate structures from materials like stainless steel and titanium, without needing costly tooling, has led to its widespread use across various industries. Sectors such as aerospace [2][3], automotive, and medical [4] have embraced AM for its design flexibility, which enhances product performance while cutting down on lead times and costs[5].

Among the different AM technologies, Direct Metal Laser Sintering (DMLS) stands out as a significant method. DMLS works by selectively sintering layers of metal powder using a high-power laser, resulting in solid metal parts[6]. This process is valued for its ability to create strong, long-lasting parts with complex geometries that are difficult to accomplish in conventional production. Nevertheless, DMLS has limitations that prevent its wider adoption, such as the high cost of materials and equipment, safety concerns with fine metal powders, the need for extensive post-processing, the ability to print only one material at a time, and the requirement for a controlled inert gas environment.[7]. These difficulties highlight the need for creating different metal AM processes that can get above these barriers.

Compared to conventional techniques, electrochemical additive manufacturing, or electrochemical 3D printing, offers a number of benefits. ECAM uses an electrochemical process to reduce metal ions in a solution to deposit thin metal layers onto a conductive substrate. [8]. This process can occur at room temperature and under ambient atmospheric conditions, which can reduce operational costs and simplify equipment requirements.

Meniscus-Confined Electrodeposition (MCED) involves a liquid meniscus between a micropipette and substrate, enabling precise 3D structures. The dynamic scanning-mode integrates horizontal contact lines with a vertical meniscus for smooth copper lines. Layer-by-layer fabrication constructs complex 3D structures through sequential layer deposition. This technique is versatile, accommodating various substrates such as conducting, semiconducting, and insulating materials. These methods underscore the potential of electrochemical 3D printing for high-precision microfabrication in advanced electronic and sensing applications [9]. On the other hand, Localised deposition allows for targeted and controlled metal deposition by using an ultrasharp electrode dipped in an ionically conductive electrolyte close to the deposition spot. [10].

Despite these innovations, both ECAM methods face significant challenges, primarily related to the slow rates of metal deposition. Current speeds range from about 100 nm/s - 0.18 nm/s, translating to volumetric rates of 0.008 to 20.4 μ m³ [11]. These slow deposition rates severely limit the scalability of ECAM from producing small-scale prototypes to larger, functional parts suitable for commercial use. Additionally, the range of geometries possible with ECAM is currently limited, with most products featuring simple, wire-based structures. The surfaces of these products often exhibit rough textures and are typically porous, which may not be suitable for all applications. Moreover, the technology is generally constrained to the use of a single metal, limiting its application in the production of more complex, multi-material parts [12].

To overcome these limitations, ongoing research and development are crucial. Innovations in ECAM technology could lead to faster deposition rates, the ability to produce smoother and more complex geometries, and the capacity to use multiple materials in a single build process. Such advancements could expand the applicability of ECAM in industrial and consumer markets, making it a more competitive alternative to conventional AM techniques like DMLS.

1.2 Research Objective

The central purpose of this study is to engineer a innovative, costefficient electrochemical metal/alloy 3D printer leveraging a meniscusconfined deposition technique. This device aims to markedly elevate the rate and precision of metal depositions, thus refining the overall efficiency of metal 3D printing. To enable precise metal deposition, the procedure makes use of a stable meniscus as a vital contact between the nozzle and the conductive substrate. A significant objective is to enhance this technology's scope to encompass the fabrication of metals and alloys for specific sensing functions, with a particular focus on the catalytic detection of glucose using a Ni-Co alloy.

- Electrochemical 3D Printing System Development:

- Innovate and build a new meniscus-confined print head that ensures a stable meniscus, thus supporting faster deposition rates without sacrificing deposition quality.
- Develop and refine the setup of the electrochemical 3D printer to assure cost-efficiency and operational effectiveness for wider practical adoption.
- Optimization of Printing Parameters:
 - Analyze the limiting factors of current Electrochemical Additive Manufacturing (ECAM) techniques to understand areas for enhancement.
 - Adjust critical printing parameters to enhance the print quality and detail of the metal/alloy components, such as electrolyte concentration, deposition potential, and printing speed.
 - Assessment and Characterization of Printed Outputs:
 - Thoroughly assess the functionality of the engineered printer by producing test structures or patterns.

• Conduct comprehensive examinations using SEM, XRD, and optical microscopy to analyze the microstructure, crystalline structure, and surface morphology of the printed materials, assessing their quality and suitability for intended applications.

— Sensing Application Exploration:

- Broaden the utility of the developed technology to print metal alloys for use in sensing mechanisms.
- Construct and evaluate a catalytic glucose sensor crafted from a Ni-Co alloy, assessing its effectiveness for in-situ health monitoring.
- Achieving these objectives is expected to significantly push forward the capabilities of metal 3D printing technologies and showcase their practical potential, particularly in catalytic sensing applications. This work aims to make substantial contributions to the fields of material science and additive manufacturing, opening new pathways for integrating printed metal components into diverse technological domains.

Chapter 2: Literature Review

2.1 Additive Manufacturing

2.1.1 Electrochemical Additive Manufacturing

Additive Manufacturing (AM) has transformed manufacturing by enabling the precise creation of complex structures with improved material efficiency. Traditional AM methods, such as inkjet printing and material extrusion, often encounter issues like weak interlayer adhesion, limited mechanical strength, and poor resolution. Additionally, problems such as nozzle clogging can interrupt material flow, affecting the overall process. Advances in extrusion-based AM, particularly with materials like polyetheretherketone (PEEK), have addressed these challenges. By optimizing heat management and deposition techniques, these advancements produce high-quality, defect-free structures, demonstrating significant potential for applications in various fields, including biomedical engineering [13]. The study on selective laser melting (SLM) of metallic powder identifies significant challenges due to thermal gradients. High thermal gradients lead to substantial residual stresses, which impact the mechanical properties and dimensional accuracy of the parts. These stresses can cause cracking, particularly during the cooling phase, resulting in warpage and mechanical distortions that limit the minimum feasible thickness of the structures. Additionally, temperature variations affect layer bonding, leading to weak interlayer adhesion and compromising the overall structural integrity of the fabricated parts. These challenges necessitate optimized processing parameters and support structures to mitigate thermal-induced issues [14]. Traditional additive manufacturing (AM) methods like Selective Laser Sintering/Melting (SLS/SLM) face significant challenges due to thermal gradients. These gradients induce substantial residual stresses, which can lead to issues such as warping, cracking, and mechanical distortions, thereby compromising the dimensional accuracy and mechanical properties of the parts.



Figure 2.1 Schematic diagram of SLM fabricating equipment[14]

Additionally, these residual stresses restrict the minimum feasible thickness of the structures, resulting in unwanted mechanical deformations. Optimizing processing parameters and employing effective post-processing techniques are crucial to mitigating these thermal-induced stresses and improving the reliability of SLS/SLM-produced components [15]. The removal of these supports is particularly challenging at micro- and nano-scales, often risking damage to delicate parts and causing distortion [16].

A new method known as electrochemical additive manufacturing (ECAM) deposits tiny, highly adherent metal layers onto a conductive substrate by reducing the amount of metal ions in a solution. [17]. This method offers a new way to production by combining the concepts of AM with the electrodeposition technique. ECAM is a non-thermal method, in contrast to traditional laser- and sintering-based AM processes. This feature significantly minimizes thermal effects and provides precise control over deposition growth, enhancing design flexibility and reducing the reliance on support structures [18]. To date, ECAM has predominantly been utilized in micro- and nano-fabrication due to initially limited deposition rates [19].

Developed by Cohen [20], The EFAB (Electrochemical Fabrication) technology offers a unique approach to microfabrication through the

principles of Solid Freeform Fabrication (SFF), allowing for the creation of high-aspect-ratio metallic microstructures. A critical component of this process is surface [21] planarization, which ensures the precise thickness and flatness of each deposited layer. The first material must be deposited selectively, the second must be deposited blanket-style, and the two-material layer must be planarized as a whole.



Figure 2.2 Stages in the EFAB process [21]

This step is repeated for each layer to achieve the final multi-layer structure. The use of sacrificial materials, such as copper, provides mechanical support during the build process and is later removed through chemical etching. This method is excellent for a range of applications microelectronics and MEMS (Micro-Electroin Mechanical Systems) since it is scalable and can produce complicated geometries with great precision. EFAB is versatile in its compatibility with various electro-depositable metals, with copper and nickel frequently used as sacrificial and structural materials, respectively. Copper is preferred for its ease of removal via chemical etching compared to nickel. This method has been commercialized by Microfabrica.

Recent advances aim to address these challenges, such as the integration of a programmable femtosecond light sheet using DMD technology with EFAB. This combination, known as ultrafast laser-enabled 3D metal printing, facilitates rapid pattern generation

synchronized with laser pulses[22]. EFAB demonstrates proficiency in manufacturing durable micro-metal components, which are utilised in sectors that need micron-scale elements, such coil structures [23], micro-gears [24], including integrated circuit boards [25], tools for invasive surgery [26], adaptive optics [27], and microfluidic devices [28].

With these limitations in mind, there is a rising interest in creating mask-less electrochemical deposition techniques that provide exact control over the rates of diffusive and convective mass transfer through full software control over electrodeposition parameters. [29].

2.1.2 Localized Electrochemical Deposition

Localized Electrochemical Deposition (LED) is a microfabrication technique developed by John D. Madden and Ian W. Hunter [30] to create intricate three-dimensional metal structures at the micrometer scale. This method involves placing an electrode near a substrate in a plating solution with a sharp tip, and then applying a voltage between the two. Because the electric field is localised, metal deposition is limited to the area



Figure 2.3 Schematic localized electrochemical deposition.[30]

beneath the electrode tip. By precisely moving the electrode in relation to the substrate, complex 3D structures are fabricated.

LED achieves vertical deposition rates of up to 6 μ m/s, significantly faster than traditional electroplating methods. The localized electric field and convective flow enhance mass transport to the deposition area, making the process efficient and precise. Demonstrations include the creation of multicoiled helical springs, showcasing the method's capability to produce complex geometries. Theoretical models of mass transport and deposition profiles further support the process, emphasizing its potential for rapid and efficient 3D microfabrication. This method represents a significant advancement in microfabrication, offering a cost-effective and versatile approach to creating highresolution, three-dimensional metallic structures. These ions are deposited at the cathode through a combination of electrochemical reaction kinetics and ion transport mechanisms such as diffusion, convection, and electromigration [31]. This process is characterized by atomic-level control over deposition [32].

The voltage that drives the deposition must be greater than a threshold set by the reaction's thermodynamics. Excessive voltage in aqueousbased processes might cause gas bubbles to develop, which will negatively impact the quality of the structure by forming porous forms. [33]. Numerical studies [34] highlighted how crucial the inter-electrode gap is for regulating diffusion-led deposition and electric field-driven migration. Seol et al. [35] noted that while the gap size critically impacts the dimensional accuracy of deposits, it does not significantly affect structural quality. However, very narrow gaps can lead to electron tunneling, preventing ion deposition [36]. A proposed solution was to use in operando X-ray microradiography to adjust the electrode retraction speed appropriately, maintaining an optimal gap for migration-dominated deposition that results in porous structures, though this method can be impractical due to the complexity of continuous X-ray monitoring [37].

2.1.3 Meniscus-confined electrodeposition

Addressing the constraints of traditional probe-based electrochemical deposition, Suryavanshi and Yu [38] proposed an innovative method for fabricating freestanding copper nanowires using a probe-based electrochemical deposition technique. This approach eliminates the need for traditional plating baths by utilizing a nanopipette filled with CuSO4 electrolyte, allowing precise, localized deposition. The process involves forming an electrolyte meniscus between the nanopipette and the substrate, followed by the application of an electric potential, to induce copper deposition. As the nanopipette retracts at a controlled speed, uniform nanowires with diameters as small as 200 nm [11] and lengths up to 10 µm are grown. This method offers high precision, clean deposition environments, and versatility in creating complex 3D nanostructures. The deposited nanowires exhibit excellent mechanical and electrical properties, making this technique suitable for advanced electronics and nanodevice applications. Challenges include nozzle Blockage, particularly under low humidity conditions (<30%-35%), where copper sulphate crystallises close to the pipette tip due to excessive evaporation rates. Additional research has examined the nucleation and crystallisation of metal salts across a range of durations and timelines on electrode surfaces. [39]. To prevent water electrolysis, deposition potentials were kept low, which inadvertently slowed deposition rates. Although increasing electrolyte concentration could enhance current density and deposition speed, it also exacerbates nozzle clogging.

Hu and Yu [38] developed an advanced meniscus-confined 3D electrodeposition method for directly writing wire bonds. This method creates pure copper and platinum 3D structures in ambient air by using a micro- or nano-scale liquid meniscus. Through the synchronisation of a micropipette's withdrawal speed with the wire's growth rate, they were able to obtain bond sizes under 3 μ m and wire diameters below 1 μ m, together with an impressive breakdown current density of more than 10¹¹A/m². Using a 0.05 M CuSO4 solution, the technique showed the production of complex microscale structures and high-density

interconnects at a growth rate of 0.25 μ m/s. The method's capacity to generate homogeneous wires as small as 100 nm in diameter and bond strengths more than 39 MPa—significantly better than conventional wire bonding standards—was emphasised in the paper. This novel method offers a flexible, affordable alternative for complex metallic designs and promises to make major strides in microelectronics.

In their study, Seol et al. [12] revealed a brand-new process for 3D meniscus-guided electrodeposition printing metallic microarchitectures. This technique allows for fine control of copper deposition at room temperature and ambient settings by using a glass micropipette loaded with copper (Cu) electrolyte to form a meniscus between the pipette tip and a conductive substrate. The researchers demonstrated the capacity to construct hollow and solid objects by adjusting applied electrical potentials. Pulsed potentials (2 V with a 33% duty cycle and 0.8 V at rest intervals) were used to create hollow microstructures, whereas a negative etching step (-0.1 V) was used to create solid ones. The study emphasised how important evaporationinduced convective flow (EICF) is in establishing the density and shape of the structures that are deposited. The experimental results were confirmed by finite element modelling, which highlighted the importance of meniscus diameter and water evaporation rate. The researchers achieved a deposition rate of 20.4 µm³/s and created structures with diameters around 12 µm. This technique holds significant promise for applications in microelectronics and sensors, offering a versatile and cost-effective approach to creating intricate metallic designs.

Xiaolong Chen and colleagues delve into new developments in electrochemical additive manufacturing (ECAM), specifically targeting the production of mesoscale metal objects [17].



Figure 2.4 Schematic of Low Cost ECAM technology[17]

The research targets a critical gap in additive manufacturing—the precise creation of mesoscale objects, a task that has posed challenges due to limitations inherent in powder-based fusion methods and existing ECAM technologies. At the core of this research is the introduction of an innovative, cost-effective ECAM 3D printer that incorporates a microfluidic system alongside a meniscus-guided electrodeposition technique. Using a meniscus that forms between the print head and the substrate, this innovative method enables the controlled deposition of metallic micro-wires.

In their influential research, Pengpeng Liu and colleagues address a notable challenge in additive manufacturing (AM)—the fabrication of mesoscale metal objects [40]. Their work introduces a cutting-edge approach designed to bridge the production gap between microscale and macroscale manufacturing, which has been problematic due to the constraints of powder-based fusion methods for larger scales and the difficulties associated with scaling down current electrochemical additive manufacturing (ECAM) systems for smaller objects. Central to their investigation is the creation of an innovative, economical ECAM 3D printer that incorporates a microfluidic system. This printer features a meniscus-guided electrodeposition method that is key to maintaining stability throughout the printing process.

Julian Hengsteler and colleagues investigate the capabilities and future prospects of electrochemical 3D printing in creating fine conductive structures, pivotal for advancements in electronics and nanotechnology [41]. A major focus of their study is on Meniscus-Confined Electrodeposition (MCED), which employs micro- or nanopipettes as printing nozzles. These nozzles, when positioned near a conductive substrate, form a liquid meniscus that serves as a bridge, confining material growth through electroreduction to the contact point, thereby enabling precise material deposition. The simplicity and costeffectiveness of fabricating MCED nozzles are noted as significant benefits. However, the study also highlights challenges such as nozzle clogging at smaller scales, underscoring the necessity for automated feedback mechanisms to achieve effective nanoscale printing.

Chapter 3: Design and Fabrication of electrochemical 3D printing setup

3.1 Custom head design

FDM 3D Printer's Head and Working Principle

A popular 3D printing technique noted for its ease of use and versatility in item creation is fused deposition modelling, or FDM. The extrusion head, the central part of an FDM printer, melts and deposits the filament material to construct the item layer by layer.

Components and Working Principle of the FDM Printer's Head: Extruder Motor:

• The extruder motor feeds the filament into the hot end. It controls the flow rate of the filament, ensuring consistent material deposition.

Hot End:

• The hot end is where the filament is melted. It consists of a heating element that heats the filament to its melting point. The melted filament is then extruded through a nozzle.

Nozzle:

• The nozzle, attached to the hot end, is responsible for depositing the melted filament onto the print bed. The diameter of the nozzle determines the resolution of the print.

Cooling System:

• A cooling system, often involving a fan, is used to solidify the extruded filament quickly, ensuring that the layers adhere properly and the object maintains its shape.

Working Principle:

- The filament, usually made of thermoplastic materials such as PLA or ABS, is fed into the extruder motor.
- The extruder motor pushes the filament into the hot end, where it is heated to its melting point.
- The melted filament is extruded through the nozzle and deposited onto the print bed.

- The print bed moves vertically (Z-axis), while the nozzle moves horizontally (X and Y axes), allowing the printer to build the object layer by layer.
- The cooling system solidifies each layer before the next one is deposited, ensuring structural integrity and precision.

Modifications for Electrochemical 3D Printing

To facilitate electrochemical 3D printing, a standard FDM (Fused Deposition Modeling) 3D printer was modified to accommodate an electrochemical deposition system. The key modification involved designing and 3D printing a custom holder for the micropipette, which is essential for the electrochemical process.

Custom Holder Design and Installation:

The holder, designed specifically for this application, was created using CAD software and subsequently printed using a commercial FDM 3D printer. The design and dimensions were carefully considered to ensure compatibility with the existing 3D printer and to securely hold the micropipette in place. The Fig 3.1 below illustrate the design from multiple perspectives: top, front, and side views.

- Top View: The top view shows the overall shape and the positioning of the screw holes (label A) and the micropipette holder (label B). The screw holes are strategically placed to align with the mounting points of the 3D printer's x-axis movement assembly.
- Front View: This view highlights the alignment of the screw holes (label A) with the printer's head mount. It also shows the orientation of the micropipette holder (label B), ensuring that the micropipette is held vertically and securely.
- Side View: The side view provides a clearer understanding of the holder's depth and how it positions the micropipette relative to the x-axis movement assembly. This view also confirms the holder's ability to maintain the micropipette's stability during the printing process.

Installation and Setup :

- Removal of Original Extrusion Head: The original extrusion head of the 3D printer was carefully removed to make space for the custom holder.
- Mounting the Custom Holder: The custom-designed holder was then screwed into place using the pre-drilled holes (label A) shown in the design. These holes were aligned with the original mounting points of the printer's x-axis movement assembly.
- Inserting the Micropipette: The micropipette was inserted into the holder through the large hole (label B). This ensures that the micropipette is held firmly and accurately positioned for the electrochemical deposition process.



Figure.3.1 Front view, Top view and side view of the customed designed print head

The electrochemical 3D printing setup is finished with the micropipette positioned and the custom holder firmly fixed. With this modification, the printer can now accurately move the micropipette over the substrate by executing G-code instructions. The necessary threedimensional structures are produced by reducing and depositing metal ions from the electrolyte solution onto the substrate surface by applying a positive voltage between the anode (inserted into the micropipette) and the substrate.

3.2 Cotton-assisted electrochemical 3D printing

In the electrochemical 3D printing process, controlling the flow of the liquid electrolyte through the micropipette onto the conducting substrate is crucial. The challenge lies in preventing the uncontrolled free flow of the electrolyte from the 400-micrometer pipette tip while ensuring a steady, controlled deposition of metal ions onto the substrate.

To address this, a piece of cotton is pressed and placed inside the micropipette, near the tip opening. This cotton piece serves as a back pressure regulator, controlling the flow rate and ensuring that only the necessary mass transfer of electrolyte occurs. This method ensures that the electrolyte is delivered in a controlled manner, maintaining a stable meniscus at the tip of the micropipette.

Mechanism of Flow Control :

The flow control mechanism in the micropipette can be understood through principles of fluid dynamics, specifically considering the balance between hydraulic pressure and surface tension effects. When the micropipette is brought close to the substrate's surface, the electrolyte solution flows out of the pipette tip and forms an electrical connection with it. The cotton inserted inside the micropipette creates a resistance to the free flow of the electrolyte, thereby controlling the back pressure. This ensures that the electrolyte does not flow out uncontrollably due to gravity or capillary action.

The flow rate Q of the electrolyte through the micropipette can be described by Darcy's Law, which is given by:

$$Q = -kA(p_b - p_a)/\mu L$$

Where:

Q is the flow rate (m³/s) κ is the permeability of the medium (m²) p_b-p_a is the pressure drop (Pa) A is the cross-sectional area that the flow (m^2)

 μ is the dynamic viscosity of the electrolyte (Pa·s)

L is the length over which the pressure drop acts (m)

Additionally, the pressure drop (p_b-p_a) can be related to the height difference $(Z_b - Z_a)$ and the specific weight (γ) of the electrolyte by the equation:

 $pb - pa = -\gamma (Z_b - Z_a)$

Practical Implementation :

- Insertion of Cotton: A piece of cotton is carefully inserted into the micropipette near the tip. The cotton acts as a porous medium that regulates the flow of electrolyte by creating a back pressure. This back pressure is essential to maintain a controlled flow rate and prevent the electrolyte from freely dripping out of the pipette tip.
- Creation of Stable Meniscus: The cotton's presence aids in the micropipette's tip's ability to generate a stable meniscus. The electrolyte solution's curved surface at the liquid-air contact is known as the meniscus. For the metal ions to be deposited into the substrate precisely and under control, this meniscus must remain stable.
- Controlled Electrolyte Delivery: As the micropipette moves over the substrate according to the G-code instructions, the controlled flow of the electrolyte ensures that metal ions are deposited accurately on the substrate. The back pressure created by the cotton ensures that the electrolyte is delivered only when needed, minimizing wastage and improving the precision of the deposition process.

Electrical Connection and Deposition: The reduction of metal ions in the electrolyte results in their deposition onto the substrate surface when a positive potential is provided between the conducting substrate and the anode (held within the micropipette). The electrolyte's regulated flow guarantees that the deposition happens exactly, consistently, and in the appropriate pattern. By incorporating this flow control mechanism, the electrochemical 3D printing process can achieve high precision and accuracy in metal and alloy deposition. This approach ensures that the electrolyte is delivered in a controlled manner, maintaining the stability of the meniscus and allowing for precise control over the deposition process.

3.3 Printer set up for material

fabrication

Figure 3.2 shows a schematic of the developed electrochemical 3D printer. The print head, or nozzle assembly, is fixed to a carriage that may move in both the x and z axes. Under the guidance of G-code commands, the stationary platform can move in the y direction in the interim.



Figure.3.2 Schematic of the developed electrochemical 3d printer



Figure.3.3 (a) shows the original FDM 3D printer, (b) shows the print head assembly of the FDM type 3D printed and (c) shows the customed head assembly for electrochemical 3D printing

Components and Configuration

1. Nozzle Assembly (Print Head):

The print head is designed to accommodate a micropipette containing the electrolyte solution and the counter electrode.

The assembly is mounted on a movable carriage, enabling precise movements in the x and z directions.

2. Stationary Platform:

The platform is stationary in the x and z directions but moves in the y direction as per the G-code instructions.

This movement allows for the creation of complex 3D structures through coordinated motion with the print head.

3. Counter Electrode:

Suspended within the electrolyte, the counter electrode is the source of metal ions to be deposited onto the substrate.

The counter electrode is held in an insulated holder to maintain dimensional accuracy.

A copper wire is wrapped around the counter electrode, ensuring a stable electrical connection.

4. Working Substrate:

The working substrate, either stainless steel or fluorine-doped tin oxide (FTO), is the surface on which the metal or alloy structures are printed.

The substrate remains stationary during the deposition process, providing a stable base for building the desired structures.

Fabrication Process

1. Initiation:

The print head is brought into contact with the working substrate.

A small amount of electrolyte solution is oozed out of the micropipette, forming a stable meniscus at the tip of the print head.

2. Electrochemical Deposition:

A positive potential is applied between the working and counter electrodes using a DC power supply.

Metal ions (M^{2+}) in the electrolyte are reduced and deposited onto the substrate, forming the desired structure.

3. Simultaneous Replenishment:

If the counter electrode is made of the same metal as the one being deposited, the M^{2+} ions are simultaneously replenished from the counter electrode.

This occurs through an oxidation reaction, creating a concentration gradient that is controlled by a combination of diffusion and migration.

4. Controlled Movement:

The print head moves in the x and y directions according to the Gcode instructions, enabling precise deposition of material layer by layer.

The coordinated motion of the print head and the platform ensures the accurate formation of 3D structures

Chapter 4: Electrochemical 3D Printing of Metal

4.1 Electrochemical 3D

printing strategy for lines

During the experiment, a specific piece of G-code was executed to control the movement of the nozzle in the electrochemical deposition apparatus. Initially, the G91 command was employed to switch the system to relative positioning mode, essential for the looping movement required in the deposition process. This mode ensured that all subsequent movements were relative to the current position of the nozzle. A feed rate of 5mm/min was set using the G1 F5 command, allowing for slow and precise movements of the nozzle.



Figure 4.1 shows the custom-written G-code for printing line-based structures

This reduced speed was crucial for ensuring uniform deposition of material. The experiment involved eight passes of the nozzle over the substrate. In each pass, the G1 command was used to move the nozzle. For the first pass (pass 1), the command 'G1 X10 Y0' moved the nozzle 10mm forward. This was followed by 'G1 X-10 Y0' for the second pass (pass 2), which moved the nozzle 10mm backward, returning it to its initial position. This pattern of alternating forward and backward movements was repeated for subsequent passes (passes 3 to 8), ensuring consistent coverage over the same area of the substrate. Throughout these passes, no lateral (Y-axis) or vertical (Z-axis) movements were programmed, maintaining the focus of deposition on a specific, predefined area. The repetitive forward and backward

motions facilitated by the G-code were pivotal in achieving a uniform layer of electrochemically deposited material on the stainless steel substrate.

4.2 Materials and Instruments

4.2.1 Electrolyte preparation

Material Preparation :

For the single line experiments, a 0.5 M solution of copper(II) sulfate pentahydrate (CuSO4·5H2O) was prepared using deionized water and Cupric sulfate Pentahydrate (CuSO4·5H2O) extrapure AR, 99.5% from SRL. The chemicals were used directly without any further processing.

Experimental Setup :

The experimental conditions were maintained at room temperature, approximately 25°C. The nozzle, integral to the printing process, was placed firmly onto the substrate, ensuring no electrolyte leakage. The print head was programmed to traverse the x-axis over an 8 mm distance in a repetitive back-and-forth motion at a speed of 5 mm/min. Each printing session involved 8 passes to achieve a uniform deposition of copper lines.

4.2.2 Stainless Steel surface preparation

The stainless steel substrates were prepared by cutting them into dimensions of 2 cm x 1 cm x 1.5 mm. The cut pieces were then polished using a Metco BAINPOL grinding/polishing machine. The polishing process began with an initial coarse grinding using 80-grit sandpaper, followed by a finer grinding with 200-grit sandpaper to achieve a smooth surface.

4.2.3 Devices and Instruments

After polishing, the substrates underwent a thorough cleaning process involving ultrasonication using a Multifunctional Ultrasonic Cleaner from Athena Technology. This cleaning sequence included the use of soap, isopropyl alcohol (IPA), acetone, and deionized (DI) water to ensure the complete removal of impurities and contaminants. This meticulous surface preparation was essential to prevent any hindrance during the electrochemical 3D printing process, ensuring high-quality deposition and adhesion of the printed materials

4.3 Characterization Techniques

4.3.1 Scanning electron microscope

Field Emission Scanning Electron Microscopy (FE-SEM) is an advanced imaging technique that provides high-resolution images of a sample's surface. The "JOEL7610F Plus" FE-SEM used in this study is a sophisticated instrument that employs a field emission gun to generate a finely focused electron beam. As the sample's surface is scanned by this electron beam, precise pictures that show the surface shape and structural features at the nanoscale level are produced.

The working principle of FE-SEM involves the generation of a highly coherent and focused electron beam by the field emission gun. Field emission refers to the extraction of electrons from a sharp metallic tip by applying a strong electric field, producing a beam with a small spot size and high current density, essential for achieving high-resolution imaging. The concentrated electron beam interacts with the sample's atoms as it moves in a raster pattern across its surface, producing the emission of a variety of signals, such as secondary electrons, backscattered electrons, and distinctive X-rays.

A detector gathers secondary electrons, which are low-energy electrons released by the surface atoms, to create the primary picture, which offers comprehensive topographical details about the sample surface. Compositional contrast is produced by high-energy electrons called backscattered electrons, which are reflected back from the material. Additionally, X-rays generated from the electron-sample interaction can be used for elemental analysis through energy-dispersive X-ray spectroscopy (EDS). The detected signals are processed to create high-resolution images displaying the surface morphology and structural details of the sample. The high depth of field and magnification capabilities of FE-SEM allow for the observation of three-dimensional surface features with great clarity. Utilizing the "JOEL7610F Plus" FE-SEM, detailed images of the electrochemically 3D printed metal/alloy

structures are obtained, which are critical for analyzing the morphological characteristics, such as texture, topography, and any present defects, ensuring the quality and precision of the printed materials.

4.3.2 XRD

X-ray diffraction (XRD) is a powerful technique used to analyze the crystalline structure of materials. In this study, the XRD pattern was collected using a Panalytical Empyrean X-ray diffractometer with Cu K α radiation, having a wavelength of 1.54 Å. XRD works by directing X-rays at the sample and measuring the intensity and angles of the diffracted beams. When X-rays interact with the crystal lattice, they are scattered in specific directions based on the lattice spacing and wavelength.

The Panalytical Empyrean diffractometer scans the sample over a range of angles, recording the diffraction pattern. Peaks in this pattern correspond to specific crystallographic planes, providing information about the crystal structure and phase composition. By analyzing these patterns, researchers can identify crystalline phases, calculate lattice parameters, and assess crystallinity. This data is crucial for understanding the structural properties of electrochemically 3D printed metals and alloys, optimizing the printing process, and developing high-quality materials.

4.3.3 Profilometry

An Optical surface profilometer (Filmetrics, Profilm 3-D) was used to determine the surface profile. This technique is essential for measuring the thickness of the electrochemically 3D printed structures. The profilometer works by scanning the surface of the sample with a light beam, which reflects off the surface and is detected to create a detailed 3D map of the surface topography.

By analyzing the surface profile data, the thickness of the printed structures can be accurately measured. This information is crucial for assessing the uniformity and consistency of the deposition process, ensuring that the printed materials meet the desired specifications and quality standards. The use of the Filmetrics Profilm 3-D profilometer provides precise and reliable measurements, contributing to the overall evaluation and optimization of the electrochemical 3D printing process.

4.3.4 Optical Microscopy

Optical characterization of the printed structures was performed using a ZEISS Axio optical microscope. This microscope works by illuminating the sample with a light source, which is focused onto the sample through a condenser lens to ensure even illumination. The light reflected from the sample passes through objective lenses with varying magnification powers, typically ranging from 4x to 100x, to magnify the image. The magnified image is then viewed through eyepiece lenses or captured by a digital camera for further analysis. This technique allows for detailed inspection of the printed structures, enabling the detection of uniformity issues, micro cracks, and other surface defects. The high-resolution images obtained are crucial for assessing the quality and consistency of the electrochemically 3Dprinted metals and alloys.

4.4 Results and Discussion

4.4.1 Surface Morphology of the Electrochemically 3D printed Copper Structure

Figure 4.2 (a), (b), and (c) depict copper structures electrochemically printed at a constant concentration of 0.3 M CuSO4 solution, with applied voltages of 5V, 7V, and 9V, respectively. These images illustrate the significant impact of voltage on the quality and uniformity of the deposited copper structures. At 5V, the deposited copper structure is markedly non-uniform, characterized by numerous empty spaces where deposition has not occurred. This lack of uniformity can be attributed to the lower electric field strength generated at this voltage. In electrochemical deposition, the electric field strength is crucial as it drives the reduction of Cu^{2+} ions from the electrolyte onto the substrate. A lower voltage results in a weaker electric field, which is insufficient to facilitate the consistent reduction

of ions across the substrate surface. Consequently, the incomplete coverage indicates that the applied voltage of 5V is not adequate to ensure a uniform and continuous deposition process, leading to sporadic and patchy deposition.



Figure 4.2 The figure shows a grid of optical images of electrochemically 3D-printed copper line-based structures with varying voltages and concentrations.

Increasing the voltage to 7V results in a noticeably more uniform copper deposition, as evidenced by the reduced number of empty spaces. This improvement suggests that the higher voltage generates a stronger electric field, which enhances the electrochemical reduction process. A stronger electric field increases the rate at which Cu²⁺ ions are reduced and deposited onto the substrate. This more effective reduction results in better coverage and a more continuous copper layer. The images show that at 7V, the deposition process becomes more reliable and consistent, indicating that this voltage is more suitable for achieving uniform copper structures in this process.

At 9V, the deposition of copper continues to improve in uniformity compared to the lower voltages. However, it was observed that excessively high voltage can introduce new challenges. Specifically, the rapid reduction of Cu^{2+} ions at 9V can cause the newly formed copper atoms to not adhere well to the substrate. This phenomenon occurs because the high electric field strength at 9V accelerates the reduction process, leading to a rapid accumulation of copper atoms on the substrate. If the deposition rate is too high, the atoms do not have sufficient time to form strong bonds with the substrate, resulting in poor adhesion. This can lead to the detachment of deposited material, creating inconsistencies and defects in the copper layer. Moreover, the inefficient use of power at this voltage can result in the loss of ions, as some of the deposited material fails to integrate into a coherent structure, thus leading to wastage.

The photos' observations highlight how crucial it is to maximise the applied voltage throughout the electrochemical 3D printing process. At lower voltages (5V), the electric field is too weak to drive a uniform deposition, leading to incomplete and patchy coverage. As the voltage increases to 7V, the deposition improves significantly, indicating that this voltage range is more effective for achieving a consistent and uniform copper layer. However, further increasing the voltage to 9V introduces rapid ion reduction issues, leading to poor adhesion and potential material wastage. These findings highlight the delicate balance required in selecting the appropriate voltage for electrochemical deposition. An optimal voltage must be strong enough to ensure efficient ion reduction and uniform deposition, but not so high that it causes rapid reduction and adhesion problems. The results suggest that 7V is a more suitable voltage for the electrochemical 3D printing of copper at a concentration of 0.3 M CuSO4, providing a good balance between deposition efficiency and material quality. By understanding the influence of voltage on the deposition process, researchers and engineers can optimize the electrochemical 3D printing parameters to produce high-quality metal structures with desired properties. This foundational knowledge is essential for advancing the and applications of electrochemical capabilities 3D printing technology.

Influence of Concentration on Copper Deposition :

The first column of images (a), (d), and (g) shows structures printed at a constant voltage of 5V with varying concentrations of the CuSO4 solution: 0.3 M, 0.5 M, and 0.7 M, respectively. These images illustrate the significant impact of electrolyte concentration on the quality and uniformity of the deposited copper structures. At a concentration of 0.3 M, the copper deposition is notably non-uniform, characterized by significant voids and empty spaces where copper has not been deposited. This lack of uniformity can be attributed to the insufficient availability of Cu²⁺ ions in the electrolyte. With fewer ions available for reduction, the electrochemical process does not produce a continuous copper layer across the substrate, resulting in incomplete coverage. The observed gaps and irregularities indicate that a concentration of 0.3 M is inadequate for achieving a uniform deposition, as the limited ion supply cannot support consistent and thorough electrochemical reduction.

Increasing the concentration to 0.5 M improves the uniformity of the copper deposition. The image shows a smoother and more consistent copper layer, indicating that the higher concentration provides a greater number of Cu^{2+} ions, which enhances the electrochemical reduction process. With more ions available in the electrolyte, the deposition process becomes more effective, leading to better substrate coverage. The increased ion concentration supports a more continuous and uniform copper layer, minimizing voids and ensuring a more homogeneous deposition.

At a concentration of 0.7 M, the deposition is even more uniform and smoother. However, higher concentrations also present challenges. The increased viscosity of the electrolyte at this concentration can hinder the flow of the solution through the micropipette tip, causing blockages that affect the deposition process. Additionally, the higher concentration may lead to the formation of micro-cracks in the deposited layer due to stresses induced during the rapid deposition process. While the high ion concentration supports a more uniform and smooth deposition, it also increases the viscosity of the electrolyte, potentially causing flow issues and defects in the copper layer. The visual observations highlight how crucial it is to maximise the electrolyte concentration during the electrochemical 3D printing procedure. At lower concentrations (0.3 M), the ion supply is insufficient to produce a uniform copper layer, leading to incomplete and patchy coverage. Increasing the concentration to 0.5 M improves the deposition significantly, providing better coverage and a smoother copper layer. However, further increasing the concentration to 0.7 M introduces new challenges, such as increased viscosity and potential micro cracks due to rapid deposition stresses. These findings highlight the delicate balance required in selecting the appropriate concentration for electrochemical deposition. An optimal concentration must provide sufficient ions for consistent and uniform deposition while avoiding issues related to high viscosity and rapid deposition-induced stresses. The results suggest that 0.5 M is a more suitable concentration for the electrochemical 3D printing of copper at a constant voltage of 5V, providing a good balance between deposition efficiency and material quality. By understanding the influence of concentration on the deposition process, researchers and engineers can optimize the electrochemical 3D printing parameters to produce high-quality metal structures with desired properties. This foundational knowledge is essential for advancing the capabilities and applications of electrochemical 3D printing technology.

Thickness of Printed structure :

The Figure below shows the profile of the printed copper line-based structure on a stainless steel substrate. Based on the analysis, the thickness of the printed structure is determined to be 18 micrometres.



Figure 4.3 Profile analysis of the printed lined-based copper structure The 3D view and line profile clearly illustrate the height distribution and surface topology, confirming the successful deposition of a uniform copper layer on the substrate.

While optical microscopy images provided insights into surface cracks and uniformity, a more detailed examination of the surface structure at higher magnification is essential. This is achieved through Field Emission Scanning Electron Microscopy (FE-SEM). The (Fig 4.4) presents FE-SEM images of the electrochemically printed copper lines, focusing on the width of the printed structures. The FE-SEM images of the printed copper lines, taken at a magnification of 50X. Each image provides a detailed view of the surface morphology and structural characteristics. The scale bar in each image indicates 500 μ m, allowing for precise measurement of the printed lines' width. It was observed that the approximate width of the lines, on average, is 850 μ m, indicating the spread of the meniscus from a 400 μ m micropipette tip opening



Figure 4.4 FE-SEM images of electrochemically printed copper lines at a magnification of 50X. Demonstrating the spread of the meniscus from a 400 µm micropipette tip opening.

Influence of Voltage on Surface Morphology :

At 5V, as depicted in Fig 4.5 (a), the surface morphology is characterized by well-shaped octahedral grains. These grains indicate that the reduced Cu^{2+} ions have sufficient time to arrange themselves into well-defined shapes during the deposition process. The lower voltage allows for a slower and more controlled reduction of ions, enabling the copper atoms to organize into these distinct octahedral structures. This orderly arrangement is a result of the optimal balance between the rate of ion reduction and the time available for the atoms to form stable, regular geometries.

As the voltage is increased to 7V, shown in image (d), there is a noticeable change in the grain structure. The initially formed octahedral grains become larger and lose their well-defined shapes. This shift can be explained by the higher voltage speeding up the reduction process. A higher voltage creates a stronger electric field, which in turn increases the rate at which Cu^{2+} ions are reduced and

deposited onto the substrate. While this results in larger grains due to the rapid accumulation of copper atoms, it also disrupts the orderly formation seen at lower voltages. The grains become less regular and more irregular in shape, reflecting the faster but less controlled deposition process.

At 9V, as illustrated in Fig 4.5 (g), the surface morphology undergoes a further transformation. The higher potential results in secondary growths are observed on top of the previously formed structures. This phenomenon occurs because the elevated voltage forces the ions to reduce rapidly, leading to the formation of new grains on top of the existing ones.



Fig 4.5 The influence of voltage and concentration on the morphology of the printed structures are shown in the image grid

The rapid reduction process at this voltage not only causes the initial grains to lose their defined shapes but also triggers additional layers of copper to deposit on the surface. This secondary growth is a direct consequence of the excessive ion reduction rate, which outpaces the ability of the atoms to form stable and uniform structures. As a result,

the surface becomes more complex, with overlapping layers and increased irregularities.

Influence of Concentration on Surface Morphology :

The first column of images (a), (b), and (c) in Fig 4.5 illustrates the structures printed at a constant voltage with increasing concentrations of 0.3 M, 0.5 M, and 0.7 M, respectively. These images highlight the significant impact of electrolyte concentration on the surface morphology of the electrochemically printed copper structures.

At a concentration of 0.3 M, as depicted in image (a), the surface morphology is characterized by well-formed octahedral grains. These grains indicate that the reduced Cu^{2+} ions have sufficient time to arrange themselves into well-defined shapes during the deposition process. The lower concentration means fewer ions are available in the electrolyte, allowing for a slower and more controlled reduction process. This slower reduction rate provides ample time for the copper atoms to organize into stable, regular octahedral structures, reflecting an optimal balance between ion availability and deposition rate.

As the concentration is increased to 0.5 M, shown in image (d), there is a noticeable increase in the number of grains observed on the surface. These grains mostly retain their octahedral shapes, although they are more numerous compared to the lower concentration. The higher concentration provides a greater number of Cu^{2+} ions available for deposition, which enhances the reduction process. This results in a more densely packed arrangement of grains, as the increased ion availability facilitates more frequent and efficient deposition of copper atoms. The grains remain relatively well-formed, indicating that the deposition process is still controlled, despite the increased ion concentration.

At a concentration of 0.7 M, as illustrated in image (g), the surface morphology undergoes significant changes. The octahedral shapes are no longer prevalent, and the grains become larger, forming rock-like structures. This change is due to the higher ion concentration, which accelerates the reduction process and leads to rapid accumulation of copper atoms. The increased deposition rate causes the grains to grow larger and lose their defined shapes, as the atoms have less time to organize into regular structures. Additionally, secondary growth of smaller grains is observed on top of the previously formed grains. This secondary growth occurs because the high ion concentration leads to an excess of available Cu²⁺ ions, which continue to reduce and deposit on the surface even after the initial grains have formed. This results in a more complex surface morphology, with overlapping layers and irregular grain shapes.

EDX analysis of the printed Structure:

To confirm the presence and determine the elemental composition of the copper structures, EDS of the electrochemically 3D printed samples printed with 0.3 M and 0.7 M CuSO4 solutions at a printing potential of 7V. The EDS analysis provided insights into the purity and composition of the printed copper structures.



Figure 4.6 (a) and (b) Shows the edx of printed copper structure at 0.3M and 0.7M and the corresponding elemental compositions respectively

The results, presented in Figure 4. 6, include both FE-SEM images and corresponding EDX spectra for the two concentrations. For the 0.3 M CuSO4 solution, the EDX spectrum (Spectrum 2) shows a copper content of 96.4 atomic percent (At%) with 3.6 At% oxygen. This

indicates that the printed structure is predominantly composed of pure copper with minimal oxide formation, suggesting an efficient electrochemical reduction process.

For the 0.7 M CuSO4 solution, the EDX spectrum (Spectrum 3) reveals a copper content of 90.9 At%, with oxygen at 9.1 At%. Although the oxygen content is slightly higher, copper remains the dominant element, comprising over 90% of the composition.

These EDX results verify the excellent purity of the printed copper structures, with copper constituting the bulk of the elemental composition. The minimal presence of oxides indicates that the conditions used for electrochemical printing at 7V are optimal for achieving high-purity metal deposits, essential for applications requiring conductive and reliable copper structures.

4.4.2 Structural analysis of the electrochemically 3D printed copper structure

Figure 4.7 displays the printed copper structure's XRD pattern. To perform the structural analysis of the copper that was electrochemically printed, an XRD examination was conducted. The copper crystallographic planes are represented by separate peaks in the XRD pattern. The (111), (200), and (220) planes of copper correspond to the conspicuous peaks found at 20 values of around 43.3°, 50.4°, and 74.1°, respectively. These peaks align with the typical diffraction pattern for face-centered cubic (FCC) copper and verify that the



Figure 4.7 represent the X-ray Diffraction (XRD) patterns of copper 3D printed on stainless steel substrates.

The presence of these peaks indicates that the electrochemical 3D printing process successfully produces crystalline copper. The intensity and sharpness of the peaks suggest good crystallinity, which is essential for achieving desirable mechanical and electrical properties in the printed structures. This XRD analysis provides further validation of the quality and integrity of the electrochemically printed copper, supporting its potential use in various applications requiring high-purity and well-defined crystalline materials.

4.5 Conclusions

The comprehensive analysis using optical microscopy, FE-SEM, EDX, and XRD reveals that the electrochemical 3D printing process produces high-purity, crystalline copper structures. Optical microscopy highlighted surface uniformity and cracks influenced by voltage and concentration. FE-SEM provided detailed morphological insights, showing well-defined octahedral grains at lower voltages and concentrations, transitioning to larger, irregular structures at higher values. EDX confirmed copper content above 90%, indicating minimal oxide formation. XRD verified the crystalline nature of the copper with peaks corresponding to the (111), (200), and (220) planes. Optimal printing parameters balance voltage and concentration to ensure uniform and high-quality copper deposits.

Chapter 5: Electrochemical 3D printing of Ni-Co alloy for Glucose sensing

5.1 Introduction

Cells require glucose as an energy source since it is crucial to metabolism. When glucose levels are too high, they can cause cytotoxicity and damage to cells, which can result in diabetes mellitus. Conversely, too little glucose can cause energy starvation and fast cell death. Diabetes is a long-term metabolic illness that mostly affects the body's microcirculation and is currently incurable. It can lead to consequences such retinopathy, nephropathy, peripheral neuropathy, and cardiovascular disorders. According to the World Health Organisation (WHO), the number of diabetics increased sharply from 108 million in 1980 to 422 million in 2014, and this increase is to blame for millions of deaths annually. According to WHO projections, diabetes will rank among the world's top causes of death by 2030, underscoring the serious public health issue it poses. [42][43].

Blood glucose levels are a major sign of diabetes. For diabetic patients to prevent crises and diabetes-related complications, regular monitoring of these levels is essential. Therefore, it is essential to build extremely sensitive and selective glucose sensors. Numerous techniques for detecting glucose have been investigated, including spectroscopy [44], chemiluminescence[45], optical methods[46], fluorescence, and electrochemistry[46]. Because of its benefits, which include low instrument cost, easy operation, and disposable sensor technology, electrochemical detection is the most popular among them. Based on their catalytic processes, electrochemical glucose sensors are categorised as enzymatic or non-enzymatic.

The majority of commercial glucose sensors work using enzymatic techniques, detecting glucose using redox-active enzymes such as glucose oxidase (GOx) or glucose dehydrogenase. Enzyme immobilisation on the electrode surface necessitates intricate multistep procedures, notwithstanding the excellent sensitivity and selectivity of enzymatic sensors. Enzymatic sensors also have limitations, such as low stability caused by environmental factors including pH, humidity, and storage temperature, as well as denaturation of the enzymes.

These shortcomings are addressed by non-enzymatic glucose sensors, which are based on the direct electrocatalytic oxidation of glucose on the electrode. Non-enzymatic glucose sensing has attracted more interest recently. [47]. For the purpose of detecting glucose, a variety of electrode materials have been studied, including noble metals, transition metals, and their oxides. [48], Composites and metal alloys [49], with the goal of achieving superior catalytic activity. Through electrodeposition, the transition metals nickel and cobalt can combine to produce a stable layer of Ni-Co alloy. For electrodes, this alloy is a more affordable option than noble metals. As a result, a lot of research has been done on non-enzymatic glucose sensors based on Ni-Co. Nevertheless, further research is necessary to fully understand the Ni-Co alloy's catalytic effects on glucose oxidation.

In this work, a non-enzymatic glucose sensor based on Ni-Co was created for the quantitative measurement of glucose. The Ni-Co alloy was printed using the electrochemical 3D printing technique on substrates made of FTO. To comprehend the catalytic performance of the in-situ produced electrochemically 3D printed Ni-Co alloy on glucose, its material characteristics were examined.

5.2 Chemical preparation

Ni-Co alloy preparation :

To prepare the Ni-Co alloy, a solution of Nickelous Chloride Hexahydrate(NiCl2 \cdot 6H2O), extrapure AR, 99% from SRL and cobalt(II) chloride hexahydrate (CoCl2 \cdot 6H2O), 98% was used. The concentrations were 0.15 M for NiCl2 \cdot 6H2O and 0.08 M for CoCl2 \cdot 6H2O, both dissolved in DI water. The pH of the solution was adjusted to 2 by gradually adding 0.5 M hydrochloric acid (HCl).

To prepare the mixture, 10 ml of DI water was measured out. Then, 356.53 mg of NiCl2·6H2O and 190.34 mg of CoCl2·6H2O were added to the water. The solution was thoroughly mixed using a magnetic

stirrer for about 10 minutes, during which 0.5 M HCl was gradually added to adjust the pH to 2. This preparation ensured a homogeneous mixture suitable for the subsequent electrochemical 3D printing process.

Glucose sensing :

For glucose sensing, a total of six solutions were prepared. The first solution was a 0.1 M sodium hydroxide (NaOH) solution, while the other five solutions consisted of 0.1 M NaOH mixed with varying concentrations of glucose: 1 mM, 2 mM, 3 mM, 4 mM, and 5 mM. To prepare the 0.1 M NaOH solution, 20 mg of NaOH was dissolved in 5 ml of deionized (DI) water. This base solution was then used to prepare the glucose solutions. The same 0.1 M NaOH solution was prepared five more times, and to each, glucose was added to achieve the desired concentrations. The Glucose used here is Dextrose (C₆H₁₂O₆), extrapure AR, ACS from SRL The solutions were as follows: 0.1 M NaOH with 1 mM glucose, 0.1 M NaOH with 2 mM glucose, and 0.1 M NaOH with 5 mM glucose. Each solution was thoroughly mixed to ensure complete dissolution of the glucose, providing a range of glucose concentrations for subsequent sensing experiments.

5.3 Electrochemical 3D printing of Ni-Co alloy and Fabrication strategy of the sensor

NiCl2·6H2O and CoCl2·6H2O mixed solution was put into the tip of the micropipette. A platinum (Pt) electrode was positioned as the counter electrode above the micropipette tip within an insulating holder to ensure precise geometrical alignment. After that, this arrangement was fastened to a specially made holder, which served as the printing head. A DC power supply's negative terminal was linked to the counter electrode, and the substrate—a fluorine-doped Tin Oxide (FTO) substrate that had been prepared beforehand—was connected to the power supply's positive terminal. The FTO substrate was prepared by making two parallel scratches to demarcate the working, counter, and reference electrode areas, ensuring precise deposition and electrode formation. During the printing process, the micropipette dispenses the Ni-Co alloy electrolyte solution onto the FTO substrate. A liquid meniscus develops at the tip aperture and makes contact with the substrate when the print head and micropipette approach the substrate surface. The printing process starts as soon as power is applied, concurrently decreasing the metal ions on the surface to create the Ni-Co alloy.

The sensor is fabricated by printing line-based structures using the provided G-code. This method ensures the precise and controlled deposition of the Ni-Co alloy, forming the desired sensor structure on the FTO substrate.

5.4 Morphological and Structural analysis of the electrochemically 3D printed Ni-Co alloy

Surface Morphological analysis:

After the deposition, Scanning Electron Microscopy (SEM) images were captured to learn more about the morphology of the printed Ni-Co alloy. The SEM micrographs in Figure 5.1 clearly show the formation of nanomaterials within the deposited alloy.



Figure 5.1 SEM image of electrochemically 3D printed Ni-Co alloy Observing these SEM images, it is evident that the deposited alloy consists of nanoparticles. These nanoparticles exhibit a high surface-tovolume ratio, which is advantageous for catalytic activity, particularly in glucose-sensing applications. The increased surface area provided by the nanoparticles enhances the catalytic efficiency, making the Ni-Co alloy an effective material for non-enzymatic glucose sensors.

EDX analysis:

The EDS analysis of the Ni-Co alloy confirms the elemental composition and the ratio in which the alloy is formed. The EDX spectrum, shown in Figure 5.2, indicates the presence of cobalt (Co) and nickel (Ni) in the deposited material. The quantitative analysis from the EDX spectrum reveals that the alloy consists of 52.3% Co and 47.7% Ni. This composition confirms that the desired ratio of Ni to Co has been achieved in the electrochemical deposition process. The accurate formation of this alloy ratio is crucial for optimizing the catalytic properties of the sensor for glucose detection.



Figure 5.2 EDX analysis of the Ni-Co alloy.

Structural Analysis:

Figure 5.3 shows XRD pattern of the Ni-Co alloy The electrochemically 3D printed on a FTO substrate revealed distinct peaks at 44.362° and 51.69°, which are indicative of FCC crystal structure, corresponding to the (111) and (200) planes, respectively. These results confirm the successful formation of the FCC phase of the Ni-Co alloy, suggesting a uniform crystalline structure with potential high mechanical stability and good conductivity. The precise peak positions and their associated planes are consistent with typical FCC structures, which are crucial for applications requiring excellent mechanical and electrical properties. The analysis not only demonstrates the phase purity of the printed alloy but also underpins the effective integration of Ni and Co in a well-defined crystalline lattice on the conductive FTO substrate, highlighting the capability of the electrochemical 3D printing technique in producing functionally tailored materials for advanced technological applications.



Figure 5.3 represent the X-ray Diffraction (XRD) patterns of electrochemically 3d printed Ni-Co alloy

5.5 Glucose sensing using the Electrochemically 3D printed Ni-Co alloy as the electrode

The image shows a Fluorine-doped Tin Oxide (FTO) substrate divided into three sections. The middle section, where three lines of the Ni-Co alloy are printed, serves as the working area of the sensor. The left and right sections are designated for the reference and counter electrodes, respectively.



Figure 5.4 Image of the FTO substrate with three sections, working, reference and counter

In this configuration, the fabricated Ni-Co alloy sensor is used for glucose sensing. The Ni-Co alloy, known for its excellent catalytic properties, facilitates the electrochemical oxidation of glucose. When a glucose-containing solution is applied to the sensor, the glucose undergoes oxidation at the working electrode (middle section). This reaction generates a measurable electrical signal proportional to the glucose concentration.



Figure 5.5 Schematic of electrochemical measurements of fabricated sensor

The reference electrode maintains a stable potential, ensuring accurate measurement, while the counter electrode (right section) completes the electrical circuit. This configuration makes use of the high surface-tovolume ratio and catalytic efficiency of the Ni-Co alloy to provide accurate and dependable glucose detection. The fabricated Ni-Co alloy sensor is utilized for cyclic voltammetry (CV) measurements by connecting it to a Potentiostat, as illustrated in the schematic. The setup resembles a screen-printed electrode, with three connections made to the working, counter, and reference electrodes.

To perform electrochemical sensing, the analyte solution containing glucose in an electrolytic medium is drop-casted onto the surface of the sensor electrode. This solution spreads across the entire electrode surface, establishing an electrical connection between the three electrodes. The Potentiostat then measures the electrochemical response, allowing for the detection and quantification of glucose in the solution.



Figure 5.6 (a) shows CV of bare FTO with and without Glucose in the presence of 0.1M NaOH solution and (b) shows CV of bare FTO and the Ni-Co printed sensor in the presence of 0.1M NaOH, the scan rate is 10mV/s for both (a) and (b)

The cyclic voltammetry (CV) data provide several key insights into the electrochemical behavior of the fabricated Ni-Co alloy sensor. The bare FTO substrate, both with and without glucose in the presence of 0.1 M NaOH as shown in Figure 5. 6 (a), shows no characteristic redox peaks, indicating its passive nature and lack of contribution to electrochemical reactions within the studied potential range.

Figure 5. 6 (b) compares the redox behaviour of the bare FTO substrate with that of the Ni-Co printed sensor. The cyclic voltammetry results indicate that the bare FTO substrate exhibits no characteristic redox peaks, highlighting its passive behaviour towards electrochemical sensing. This lack of electrochemical activity in the bare FTO suggests that it does not participate in redox reactions within the studied potential range when in the presence of the 0.1 M NaOH electrolytic solution.

On the other hand, in comparable circumstances, the Ni-Co printed sensor exhibits significant redox activity. Changes in the oxidation states of Ni nanostructures were indicated by the unique quasi-reversible redox peaks displayed by the Ni-Co sensor. The well-defined E_{pa} observed at 472 mV is ascribed to the transformation of various complex oxidation species of Ni-Co in an alkaline medium. Under these alkaline conditions, Ni(II) and Co(II) are converted to Ni(III) and Co(III), respectively, with Co(III) further oxidizing to Co(IV) at higher potentials. And the cathodic sweep (Epc) found at 335 mV is due to the conversion of Ni(III)/Ni(II) and Co(IV)/Co(III) [50]. These peaks indicate the active involvement of the Ni-Co alloy in electrochemical reactions, confirming its catalytic properties. The presence of these redox peaks in the Ni-Co printed sensor, absent in the bare FTO, underscores the enhanced electrochemical performance of the sensor due to the Ni-Co alloy deposition.



Figure 5.7 (a) CV of Ni-Co printed electrode in 0.1M NaOH with varying concentrations of glucose at a scan rate of 50mV s-1, (b) CV of 3D Printed Ni-Co electrode in 0.1M NaOH in the presence of 1mM glucose with different scan rates ranging from 20 to 100mV s-1

This comparison clearly illustrates the superior electrochemical behaviour of the Ni-Co printed sensor, which is essential for effective glucose detection. The observed redox peaks validate the sensor's ability to facilitate electrochemical reactions, making it a suitable candidate for non-enzymatic glucose sensing applications.

The cyclic voltammograms (CV) of Ni-Co in 0.1M NaOH solution are shown in Figure 5. 7 (a), where glucose concentrations range from 1 to 5 mM, and the scan rate is 50 mV s⁻¹. Anodic peak potential (E_{pa}) and anodic peak current (I_{pa}) both exhibit a discernible rise with increasing glucose content. This distinct, fouling-effect-free glucose electrooxidation activity at the Ni-Co electrode emphasises its potential as a great platform for the amperometric I-t determination of the manufactured sensors. [50]. The results elucidate the electrochemical oxidation of glucose as follows [51]:

 $Ni + 2OH^{-} \rightarrow Ni(OH)_2 + 2e^{-}$

 $Co + 2OH^{-} \rightarrow Co(OH)_2 + 2e^{-}$

 $Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-$

 $Co(OH)_2 + OH^- \rightarrow CoOOH + H_2O + e^-$

 $CoOOH + OH^{-} \rightarrow CoO_2 + H_2O + e^{-}$

NiOOH + glucose \rightarrow Ni(OH)₂ + gluconolactone

 $2CoO_2$ + glucose \rightarrow 2CoOOH + gluconolactone

An active Ni(III) oxide species forms on the electrode surface during the electrochemical oxidation of glucose on the Ni-Co printed sensor. This process occurs at potentials near 310 mV, and it is established that NiOOH generally forms at a potential close to 0.45 V vs. SCE [52]. Strong oxidation is exhibited by the Ni(III) surface, which combines with glucose to create gluconolactone. Usually, the production of Ni(III) oxide and the electrochemical oxidation of glucose on Ni electrodes happen at the same voltage. [53].The Ni(OH)₂/NiOOH redox pair mediates the electron transfer involved in this oxidation process. Ni(III) is a strong oxidant of glucose in this redox system, which helps to oxidise glucose. Irreversibility of the glucose oxidation process is shown by the observed rise in peak current with increasing glucose concentrations, restricted to the anodic scan. This feature demonstrates how well the Ni-Co printed sensor works to encourage glucose's electrochemical oxidation, making it a promising platform for glucose-sensing applications.

Figure 5.8 (a) shows the relationship between the square root of the scan rate $(v^{1/2})$ and the current (I_{pa}) for the oxidation of 1 mM glucose in a 0.1 M NaOH solution, with scan rates ranging from 20 to 100 mV/s. The voltammograms show that a quasi-reversible electrochemical mechanism is some way related in the glucose oxidation at the Ni-Co alloy electrode. A strong R value of 0.999 indicates a linear rise in the peak current (I_{pa}) with the scan rate $v^{1/2}$, $v^{1/2}$ indicating direct link between and а Ipa



Figure 5.8 (a) $v^{1/2}$ vs. current (mA) at 1mM glucose in 0.1M NaOH solution and the scan rate ranging from 20-100 mV/s (b) I_{pa} vs. log(v)for the oxidation of 1mM glucose at a scan rate ranging from 20-100 mV/s

This suggests that the electrode response kinetics at the CV peak potential have an impact on the process. In order to investigate the diffusion-controlled aspect of glucose oxidation at the Ni-Co alloy electrode more thoroughly, an analysis was conducted on the correlation between the logarithms of the current (log Ipa) and the scan rate (log v). Figure 5.8(b), which presents the study's findings, shows a linear relationship with a high correlation coefficient of 0.999 and a logarithmic curve slope of about 0.81. A slope of 0.81 suggests that the process is not solely diffusion-controlled. Instead, reaction kinetics might be affected by factors such as adsorption/desorption processes, surface reactions, or charge transfer kinetics at the electrode interface. The process likely exhibits characteristics of both diffusion-controlled and kinetically controlled behaviour, explaining the deviation from the ideal slope value of 0.5. This mixed control indicates that glucose oxidation at the Ni-Co alloy electrode is governed by a combination of diffusion and kinetic factors.

Chapter 6: Conclusion and Future Scope

6.1 Conclusion

This study successfully demonstrated the implementation of electrochemical 3D printing for fabricating metal structures and in situ electrocatalytic glucose sensors. The research journey started with modifications to a commercially available 3D printer and advanced to developing high-performance glucose sensors using Ni-Co alloys. The comprehensive investigation included detailed steps, from device modification and copper line printing to the characterization of printed metal structures and utilizing this method for fabricating glucose sensors.

The first phase of the study involved modifying a commercially available 3D printer to enable electrochemical deposition. The original extrusion head was replaced with a custom-built holder designed to accommodate a micropipette. This modification allowed for the precise dispensing of electrolyte solutions necessary for metal deposition.

The initial experiments focused on printing copper lines on a stainless steel substrate using a 0.5 M CuSO4 electrolyte solution. The printing process involved careful control of parameters such as the movement speed of the nozzle and the back-and-forth passes to ensure uniform deposition. The substrate preparation included cleaning with soap, acetone, isopropyl alcohol, and deionized water to remove contaminants.

The printed copper structures were characterized using various analytical techniques. Optical microscopy provided an initial assessment of surface morphology, revealing uniform deposition without significant defects. SEM analysis offered detailed insights into the surface structure, showing nanostructured copper particles that enhance the catalytic surface area. EDX confirmed the high purity of the deposited copper, with no significant impurities detected. XRD analysis verified the crystalline nature of the deposited copper, showing peaks corresponding to the face-centred cubic structure of copper. Building on the successful copper line printing, the research advanced to fabricating a Ni-Co alloy-based electrocatalytic glucose sensor. The Ni-Co alloy was chosen for its excellent catalytic properties and cost-effectiveness compared to noble metals. A mixed solution of NiCl2·6H2O and CoCl2·6H2O was prepared in deionized water with concentrations of 0.15 M and 0.08 M, respectively. The pH was adjusted to 2 using 0.5 M HCl. The prepared solution was dispensed onto a FTO substrate using the modified 3D printer. The substrate was preprocessed by making two parallel scratches to separate the working, counter, and reference electrode areas, ensuring precise deposition and electrochemical deposition, the micropipette tip was brought in close proximity to the substrate surface, a liquid meniscus was formed, and a voltage was applied.

Characterization and Performance Evaluation

The Ni-Co alloy printed structures were thoroughly characterized to assess their suitability for glucose sensing. SEM analysis revealed the formation of nanostructured particles, indicating a high surface-tovolume ratio that is beneficial for catalytic applications. EDX analysis confirmed the desired elemental composition, with a Co to Ni ratio of approximately 52.3% to 47.7%. XRD analysis further validated the crystalline structure of the alloy, showing distinct peaks corresponding to the face-centred cubic structure. The fabricated Ni-Co alloy sensor was employed for glucose sensing using cyclic voltammetry (CV). The CV studies were conducted in a potential range of -100 to 600 mV, with glucose concentrations ranging from 1 to 5 mM in a 0.1 M NaOH solution. The results demonstrated high sensitivity and selectivity towards glucose, with clear redox peaks indicating active glucose The oxidation. bare FTO substrate showed no significant electrochemical activity, highlighting the superior performance of the Ni-Co alloy sensor.

Further analysis of the CV data revealed that the glucose oxidation process is influenced by both diffusion and kinetic factors. The observed linear relationship between the peak anodic current (I_{pa}) and

the square root of the scan rate $(v^{1/2})$ suggests quasi-reversible electrochemical behaviour. Additionally, the positive shift in the anodic peak potential (E_{pa}) with increasing scan rates indicates complex kinetic processes. Analysis of the log I_{pa} versus log v plot revealed a mixed control mechanism, with a slope of approximately 0.81, highlighting that the oxidation process involves both diffusioncontrolled and kinetically controlled characteristics.

6.2 Future scope

The promising results obtained from this study highlight the significant potential of electrochemical 3D printing technology. Several future research directions can be pursued to enhance and expand the capabilities of this technology:

- Investigate a broader range of materials, including various metal alloys, composites, and doped materials, to enhance the properties of printed structures.
- Optimize electrochemical deposition parameters, such as applied voltage and electrolyte composition, for improved precision and quality of printed structures.
- Develop techniques for multi-material printing to create complex, integrated structures with varied functionalities.
- Focus on miniaturizing printed devices to enable applications in microelectronics, medical implants, and lab-on-a-chip systems.
- Conduct comprehensive characterization and long-term stability tests to assess the performance and durability of printed devices.

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