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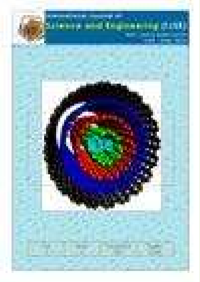

Initial study of Nickel Electrolyte for EnFACE Process

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Abstract - *Nickel electrolyte for a micro-pattern transfer process without photolithography, EnFACE, has been developed. Previous work on copper deposition indicated that a conductivity of ~2.7 Sm^{-1} is required. Electrochemical parameters of electrolyte i.e. current density and overpotential are also crucial to govern a successful pattern replication. Therefore, the investigation focused on the measurement of physicochemical properties and electrochemical behaviour of the electrolyte at different nickel concentrations and complexing agents of chloride and sulfamate. Nickel electrolytes containing sulfamate, chloride and combined sulfamate-chloride with concentrations between 0.14 M and 0.3 M were investigated. Physicochemical properties i.e. pH and conductivity were measured to ensure if they were in the desired value. The electrochemical behaviour of the electrolytes was measured by polarisation experiments in a standard three-electrode cell. The working electrode was a copper disc (surface area of 0.196 cm^2) and the counter electrode was platinum mesh. The potential was measured againts a saturated calomel reference electrode (SCE). The experiments were carried out at various scan rate and Rotating Disc Electrode (RDE) rotation speed to see the effect of scan rate and agitation. Based on the measured physicochemical properties, the electrolyte of 0.19 M nickel sulfamate was chosen for experimentation. Polarisation curve of agitated solution suggested that overall nickel electrodeposition reaction is controlled by a combination of kinetics and mass transfer. Reduction potential of nickel was in the range of -0.7 to -1.0 V. The corresponding current densities for nickel deposition were in the range of -0.1 to -1.5 mA cm^{-2}.*

Keywords—*Electrodeposition; Enface technology; Nickel plating; Maskless patterning process; Pattern transfer*

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I. INTRODUCTION

A rapid growth of modern technologies in various areas such as micro-electromechanical system (MEMS) (Tadigadapa and Najafi, 2003; Grayson et al., 2004), microelectronics (Van Noije et al., 2001; Wong et al., 2006), medical (Betancourt and Brannon-Peppas, 2006), biomechanics (Baudoin et al., 2007) *etc*. is mainly due to a continuing advancement of the microfabricated devices. The recent dimensions of microdevices have been miniaturised down to nano scale *i.e.* 0.02 µm (Franssila, 2010; Madou, 2002; Anwar et al., 2010; Jung et al., 2003). The miniaturisation leads to a reduction of raw material usage (Krebs et al., 2012; Chen et al., 2007), a decrease in production cost (Chen et al., 2007; Tolfree, 1998), a minimisation of waste (Franke and Achim Wixforth, 2008; O'Donnell-Maloney and Little, 1996), and optimisation of the device performance (Anwar et al., 2010; Jung et al., 2003; Chen et al., 2007; O'Donnell-Maloney and Little, 1996). A microfabrication via photolithography, by far, is the most extensively used technology in manufacturing such microdevices (Franssila, 2010; Madou, 2002; Wu et al., 2011). In this method, patterning process is the most crucial step as the quality and reliability of the pattern on the devices are essential in imparting their functionality (Franssila, 2010; Madou, 2002; SchÖnenberger and Roy, 2005). The desired pattern shape and structure is obtained initially by coating each individual substrate by photosensitive resin. The pattern master is created by exposing the resin-covered substrate to UV light through predesigned mask, thereafter metallisation is achieved by plating or etching. Hence, this standard technology is a multistage and expensive process, generates copious waste, uses a large amount of water, and requires specialised tools (*e.g.* clean room).

A mask-less microfabrication process, Enface (Electrochemical nano and micro-fabrication by Flow and Chemistry), has been proposed to potentially minimise the problem. In this technology, photolithography of each individual substrate is not required, instead the master pattern is defined on a tool. The tool and a fully exposed substrate are electrodes, placed in an electrochemical cell facing to each other with a narrow gap (~300 µm). By imposing current or voltage, deposited metals are selectively formed to define the desired pattern. This method has been comprehensively described in a number of publications (Roy, 2007; 2009; 2010; SchÖnenberger, 2004; Nouraei and Roy, 2008). Enface process is advantageous as a single patterned tool can be used for a number of pattern replications so that the operating cost decreases. However, Enface requires electrolytes of particular properties *i.e.* high resistance and low conductivity (~2.7 Sm^{-1}). Therefore, development of a new electrolyte is required.

In this work, a new electrolyte for nickel pattern transfer using EnFACE technology was developed. Nickel was chosen for experimentation due to its unique properties which are applicable in various industrial products such as a diffusion barrier, wear and corrosion resistance (Shina, 2008; Harper, 2004). It was also to see the usefulness of Enface technology in a system with a relatively slow kinetic (Grujicic and Pesic, 2006; Saraby-Reintjes and Fleischmann, 1984).

Electrolytes of high concentration of nickel ions i.e. 0.8 M – 1.4 M are utilised in conventional nickel deposition process. A successful nickel deposition using Enface would establish this technology to be a resource efficient process as much lower concentrations of nickel salts is required. Electrolyte composition has also been shown to determine the deposited nickel properties (Dini, 1993; Sabine et al., 2005), therefore electrolyte formulation is important stage in electrodeposition process.

In this work, the investigation focused on the measurement of physicochemical properties of the developed electrolye baths (pH and conductivity). Various nickel concentrations and two different complexing agents *i.e.* chloride and sulfamate have been examined to determine a concentration and composition that is appropriate for Enface. Electrochemical behaviour of the electrolytes was also measured including the effect of agitation and scan rate on electrochemical polarisation.

II. THEORY

2.1 Physicochemical properties: Conductivity

Prior works on copper etching and deposition have shown that the best pattern replication was achieved for an electrolyte conductivity of around 2.7 Sm^{-1} (SchÖnenberger and Roy, 2005). To predict the concentration and the composition of nickel electrolyte where its conductivity was at the low range, the conductance formula for fully ionised solution was used (Watson et al., 1996; Atkins and De Paula, 2009).

$$\kappa = c_+ \upsilon_+ \lambda_+ + c_- \upsilon_- \lambda_- \qquad (1)$$

In equation 1, κ is molar conductivity (Sm^{-1}), λ is ionic conductivity (Sm^{2}mol^{-1}), and υ_+ is number of cations moles whilts υ_- is number of moles of anions, both are obtained from one mole dissolved electrolyte. Table 1 lists Ionic conductivities of cation and anion involved in the electrolytes.

2.2 Physicochemical properties: pH

pH scale represents the acidity of solutions. pH is determined by the concentration of hydrogen ions (H$^+$) in the solution. A logarithmic reflection of the H$^+$ concentration is used to express the pH value due to low concentration of hydrogen ion. pH is typically estimated by the following equation:

$$pH = -\log[H^+] \qquad (2)$$

$$[H^+] = 10^{-(pH)} \qquad (3)$$

In fact, H$^+$ presents as H_3O^+ in aqueous solution, therefore pH is also often expressed as:

$$pH = -\log[H_3O^+] \qquad (4)$$

Equations 2 and 4 show that the value of pH depends on the concentration of H$^+$. pH value decreases as concentration H$^+$ increases (Beier and Hede, 2010; Whitten et al., 2009). In the experimentation, pH of a solution is often measured by either indicator method or using a pH meter (Whitten et al., 2009).

Table 1 Ionic conductivity of cation and anion involved in the electrolytes

Cation	**λ_+ / λ_- (mSm^{2}mol^{-1})**	**μ (10^{-8}m^{2}s^{-1}V$^-$**
Hydronium (H_3O^+)	34.97	36.23
Nickel (Ni^{2+})	4.96	4.99
Anion		
Sulfamate (SO3.NH2)$^-$	4.83	7.91
chloride (Cl$^-$)	7.63	8.29

(Atkins and De Paula, 2009)

H$^+$ ions in the electrolyte affect the conductivity of the solution due to its high ionic mobility (μ) (Atkins and De Paula, 2009), thus H$^+$ is included in the estimation of conductivity. Ionic mobility of some cations and anions involved in the process is presented in Table 1.

The ionic and molar conductivity of the solution relates to the ionic mobility by equation 5

$$\lambda_\pm = z\mu_\pm F \qquad (5)$$

$$\kappa = F\sum_i |Z_i| \mu_i C_i \qquad (6)$$

Where, z = charge, = ionic mobility, F = Faraday's constant. As z and F are constant, the value of λ_+ is dependent on its ionic mobility (Atkins and De Paula, 2009), and the molar conductivity is determined by ionic mobility and the solution concentration.

The electrolyte pH is crucial in the nickel electrodepotion process as the reaction mechanism is greatly affected (Grujicic and Pesic, 2006). In addition, a pH-electrode potential curve on thermodynamic equilibrium of nickel-water system (Pourbaix diagram) shows that a pH value between 4 and 7.5 is required (Gamburg and Zangari, 2011; Pourbaix, 1974). At this pH range, pure, high conductive, and hydrogen free nickel deposit is obtained (Gamburg and Zangari, 2011; Pourbaix, 1974). At pH higher than 7.5, hydroxide would be co-deposited with nickel. Nickel hydroxide must be avoided due to its properties (i.e. high resistivity) which are not suitable for application in micrelectronic. Hydrogen evolution is easy to occur at pH less than 4 causing pH rise near the electrode surface (Gamburg and Zangari, 2011), current efficiency decrease, and poor deposit properties ((Gamburg and Zangari, 2011; Nasirpouri et al., 2011).

2.3 Electrochemical polarisation

When an electrical charge is imposed to the system, over potential (η) serves as the driving force for electrodeposition process to take place.

$$\eta = E - E_e \tag{7}$$

Where E is applied potential and E_e is equilibrium potential.

$$E_e = E^{0'} + \frac{RT}{nF}\ln\frac{C_{Oxd}}{C_{\mathrm{Red}}} \tag{8}$$

The value of the overpotential determines the electrode reaction as indicated by Nernst's equation (8). At negative overpotential ($E<E_e$), the reaction equilibrium is re-established by an electron transfer governing a reduction reaction. In this case, the electron (ne^-) is supplied by the cathodic current. At positive potential ($E>E_e$), anodic current flows leading to oxidation reaction

The overpotential drives the electrochemical reaction to take place, the net current density (j) can be defined as:

$$j = \vec{j} + \overleftarrow{j} \tag{9}$$

Where, j is a current density which is a normalised form of current respect to an electrode area (a current flow per unit area of a respected electrode). $\vec{j}$ and $\overleftarrow{j}$ are partial cathodic and anodic current density respectively. A general relationship of overpotential and current density is represented by Butler-Volmer equation (eq 10).

$$j = j_0\left[\exp\left(\frac{\alpha_A nF\eta}{RT}\right) - \exp\left(\frac{-\alpha_C nF\eta}{RT}\right)\right] \tag{10}$$

j_0 is the exchange current density, α_A and α_C are anodic and cathodic charge transfer coefficients respectively, where $\alpha_A + \alpha_C = 1$. The exchange current density refers to an equilibrium partial current density at which the anodic and the cathodic partial current densities are equal. The value of the exchange current density is determined by the electrochemical reaction and the electrode material and surface (Paunovic and Schlesinger, 1998). Butler-Volmer equation (10) shows that a number of parameters affect the current density including temperature, charge transfer coefficient, overpotential and exchange current density. A rise in overpotential increases the current density leading to an increase in the rate of electrochemical reaction.

III. MATERIALS AND METHODS

3.1 Electrolyte Development

The nickel electrolyte solutions were prepared from analytical grade of nickel (II) sulfamate tetrahydrate ($Ni(SO_3NH_2)_2.4H_2O$ 98 %, Sigma-Aldrich) and nickel (II) chloride hexahydrate ($NiCl_2.6H_2O$ 99 %, Fisons Scientific) in a high purity deionised water *i.e.* 18 MΩ. Various composition and concentration of nickel ions investigated in this work are listed in Table 2

3.2 Apparatus

Polarisation experiments were carried out in a standard three-electrode cell constructed of a vertical-cylindrical glass with diameter of 6.5 cm and 8.5 cm height (Figure 1). A luggin capillary tube was inserted into the cell through a side neck to locate a reference electrode.

Table 2 various nickel solutions containing different composition and concentrations of Ni^{2+}

No.	Composition	
	Nickel Sulfamate (M)	Nickel Chloride (M)
1	0.30	-
2	0.20	-
3	0.19	-
4	0.15	-
5	0.29	0.01
6	0.19	0.01
7	0.14	0.01

Rotating disk electrode (RDE, EDI101 Radiometer Analytical) and a counter electrode were introduced through its lid. An approximately 250 ml of nickel solution was used to sufficiently fill up the cell. RDE is a tool usually used to characterise an electrochemical reaction including the mass transfer effect (Durbha and Orazem, 1998). To investigate force-convective mass transfer, an agitation is achieved by mechanically rotating the electrode that is an externally controlled to set the rotation speed (0 – 5000 rpm). The rotation produces a uniform axial velocity and well defined fluid flow due to a centrifugal effect.

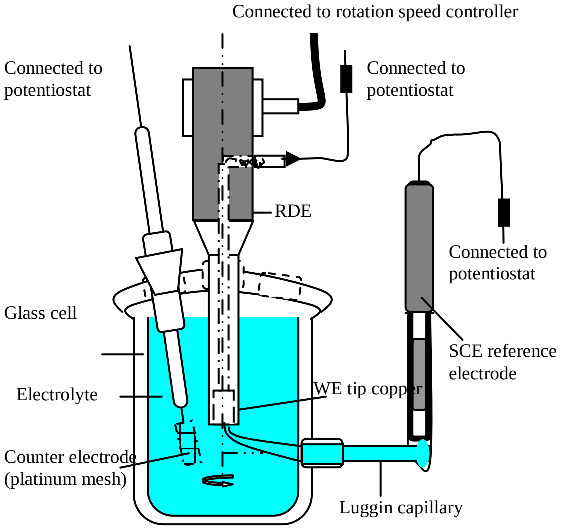


Figure 1 Diagram of three-electrode cell for electrochemical investigation

3.3 Electrode Preparation

The working electrode (WE) was a copper disk (5 mm diameter, Radiometer Analytical) surrounded by a PTFE shroud (10 mm diameter). Prior to each experiment, the disk surface was cleaned using a dilute nitric acid solution (5 %) and then gently polished by wet silicon carbide papers with fineness of #2400 and #4000 grit (Struers Ltd, UK) to obtain a mirror finish. Impurities were removed from the electrodes surface by washing thoroughly using acetone and deionised water. Thereafter, the disk was mounted onto the RDE shaft and immediately immersed to the electrolyte. A platinum mesh (99.9 % purity, 1 cm width and 2 cm length, Goodfellow) was used as a counter electrode (CE). The counter electrode was cleaned up using a dilute nitric acid solution (5%) and thoroughly washed using deionised water before each experiment. The potential was measured against a saturated calomel reference electrode (SCE) supplied by Thermo Scientific. The electrode potential of SCE is $E^0 = +0.241$ V vs normal hydrogen electrode (NHE) at 25 °C. The reference electrode was placed at a point approximately 3 mm away from the working electrode surface using a luggin capillary glass probe so that the ohmic drop was minimised.

3.4 Procedure

In order to determine the concentration and composition of the nickel solution to obtain the desired conductivity value (e.g. 2.7 Sm^{-1}), Equation (1) was used. The actual pH and conductivity were experimentally measured at a temperature range between 18 and 22 °C by using an S47 SevenMulti™ dual pH and conductivity meter (Mettler-Toledo).

Polarisation data was recorded at a temperature of 18 - 22°C by linear sweep voltammetry (LSV) technique using a potentiostat of Autolab PGSTAT30 supported by GPES software for data acquisition. Due to an excessive hydrogen evolution generated at overpotential higher than -1.0 V, the potential range was set between open circuit potential (OCP) and -1.0 V. The scan rates were 0.5, 1, 2, 5, and 10 mVs^{-1} to see at which steady state condition was reached. The rotation speeds were from 0 to 3500 rpm to measure the effect of convective-diffusion mass transfer. These experiments aimed to determine an onset potential and current density for nickel electrodeposition.

Despite the interelectrode gap was narrow, the ohmic drop might be significant due to the high resistive solution. Potential values in the polarisation curves were corrected by incorporating the uncompensated resistance of the solution to the polarisation data.

IV. RESULTS AND DISCUSSIONS

The calculated conductivity values (Table 3) shows that the concentration of nickel salt needs to remain within 0.15 – 0.2 M. The electrolytes of 0.19 M nickel sulfamate with and without addition of 0.01 M nickel chloride were chosen for experimentation.

Table 3 Calculated conductivities for the nickel solutions in different concentrations of Ni^{2+}

No.	Composition		Calculated Conductivity (Sm^{-1})
	Ni-Sulfamate, $Ni(SO_3.NH_2)_2$ (M)	Nickel Chloride, $NiCl_2$ (M)	
1	0.30	-	4.39
2	0.20	-	2.92
3	0.19	-	2.78
4	0.15	-	2.19
5	0.29	0.01	4.44
6	0.19	0.01	2.98
7	0.14	0.01	2.24

The measured pH of the chosen electrolyte had been in the expected range, no further pH adjustment was required (Table 4). Nickel sulfamate and chloride were not fully ionised due to the fact that the measured conductivities were lower than the calculated.

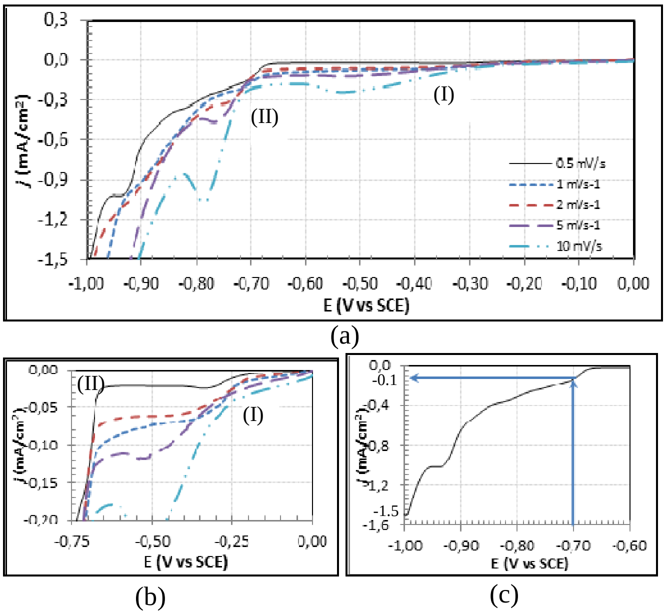
Since the present of chloride caused a spontaneous dissolution of copper electrode thereby contaminating the solution, in the subsequent experiments, only 0.19 M nickel sulfamate without nickel chloride was used.

Table 4 Conductivities (calculated and measured) and pH for the selected nickel solutions

Electrolyte	Calculated Conductivity (Sm^{-1})	Experimental Data (20±2 °C)	
		Conductivity (Sm^{-1})	pH
0.19 M $Ni(SO_3.NH_2)_2$ + 0.01 M $NiCl_2$	2.98	2.37 ± 0.04	6.45 ±0.14
0.19 M $Ni(SO_3.NH_2)_2$	2.78	2.19 ± 0.06	6.70 ± 0.22

A set of linear sweep voltammetry (LSV) experiments were carried out for the electrolyte in the three-electrode cell at scan rates of 0.5 – 10 mVs^{-1} and at a rotation speed of 0 rpm. Figure 2 (a) shows linear sweep voltammograms for the reduction of 0.19 M nickel sulfamate at various scan rates. The steady state polarisation condition was assumed to be at the scan rate of 0.5 mV/s.

The steady state polarisation curve is characterised by two identifiable potential waves marked (I) and (II). A cathodic current commences to flow at an overpotential of around -0.015 V (Figure 2 (b)). The current density slowly increases to reach the first wave at a potential of about -0.2 V. Thereafter, the current density level off until the second wave at overpotential of approximately -0.7 V where the current density rapidly increases (Figure 2 (b) and(c)).



(a)

(b) (c)

Figure 2 (a) Cathodic Polarisation Curves for 0.19 M nickel sulfamate at various scan rates, the RDE rotation speed was 0 rpm on copper substrate, (b) zoom of the low current density region to show the steady state condition (c) zoom of nickel deposition region for 0.5 mVs^{-1} scan rate.

However, nickel deposit was not obtained at potentials between the two waves. Nickel deposit was observed at potentials greater than -0.7 V up to -1.0 V. This suggests that nickel deposition takes place via a multiple step. Two consecutive one-electron transfers are assumed to involve in the overall nickel depostion reaction represented by the two waves. The wave (I) may represent the first electron transfer, and the second electron transfer may relate to the second wave (II). This result is in agreement with previous works (Cui and Lee, 1995; Grujicic and Pesic, 2006).

Hydrogen evolution was observed to occur at overpotentials exceeding –1.0 V. Therefore, the reversible potential for nickel deposition was estimated to be in the potential range of -0.7 to -1.0 V. The corresponding current densities for nickel deposition were expected to be in the range of -0.1 to -1.5 mA cm^{-2} (Figure 2 (c)).

Uncompensated ohmic drop of the system was incorporated to the polarisation curve so that the potential – current density data was corrected. No significant difference is observed in the corrected polarisation curve (Figure 3). The close proximity of the reference electrode to the working electrode was found to effectively minimise the potential drop.

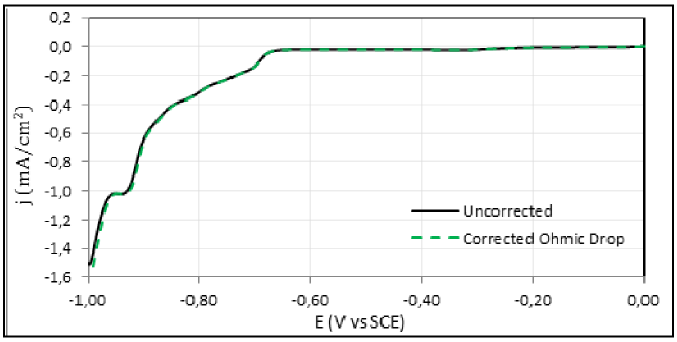


Figure 3. Comparison between cathodic polarisation Curves for 0.19 M nickel sulfamate with and without ohmic drop correction on copper substrate at 0.5 mV/s scan rate and 0 rpm RDE rotation speed.

Current density has been shown to moderately increase at RDE rotation speed of 700 rpm as compared to that for stagnant solution (Figure 4).

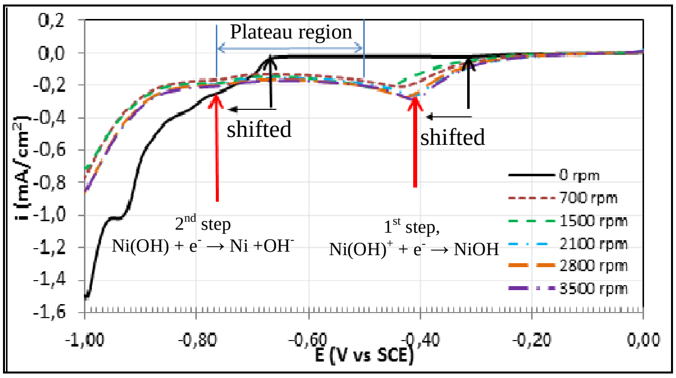


Figure 4. Cathodic Polarisation Curves for 0.19 M nickel sulfamate on copper substrate at 0.5 mV/s scan rate, the RDE rotation speed varied between 0 and 3500 rpm.

This is an indication that the agitation improves the electrochemical reaction rate due to convective-diffusion mass transfer. However, only a slight increase in current density was observed when the RDE rotation speed was increased up to 3500 rpm. This suggests that nickel deposition reaction is not solely controlled by mass transfer (Zoski, 2007). Mixed kinetics and mass transfer tends to control the nickel deposition process. This finding is supported by some other works (Xu, *et al.*, 2009; Dolgikh *et al.,* 2009; Seo, *et al.,* 2005). The agitation is also found to shift the nickel deposition and hydrogen evolution potential approximately 0.10 V to more negative region.

V. CONLUSIONS

A systematic approach to develop a new nickel electrolyte for use in Enface system has been shown. Based on the conductivity and pH value, an electrolyte of 0.19 M nickel sulfamate ($Ni(SO_3.NH_2)_2$) has been chosen. The electrolyte has advantages of lower metal ion concentration, neutral pH, room temperature operation, and no acidifying agent required.

Steady polarisation data for the electrolyte of 0.19 M nickel sulfamate confirmed that the electrodeposition of nickel takes place via multiple stages including two consecutive single-electron transfers. The data at various RDE rotation speeds suggested that overall nickel electrodeposition reaction is controlled by a combination of kinetics and mass transfer. Reduction potential of nickel has been found to be in the range of -0.7 to -1.0 V with corresponding current densities are in the range of -0.1 to -1.5 mA cm^{-2}.

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