

Title: Electroforming in the Industry 4.0 Era

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Abstract:

In the Industry 4.0 Era big data and automation will require precise knowledge that allows one to control, monitor and predict a process. Electroforming, which is the fabrication of free-standing components using electrodeposition, is rapidly gaining acceptance as a sustainable additive manufacturing technology. However, current knowledge of electroforming is based on empirical data, and academic engagement in this area has been limited. This paper throws light on some of the complex issues surrounding the electrochemical and chemical behaviour during electroforming which are yet unresolved. The differences between cathodic reactions in sulphamates and sulphates, ambiguities related to the role of boric acid, and paucity of data on anode reactions are highlighted.

1.1 Introduction

Industry 4.0 refers to the revolution involving increased digitisation, automation and control of production processes in manufacturing [1]. An overarching definition has been suggested; *“Industry 4.0 can be summarised as an integrated, adapted, optimised, service-oriented and interoperable manufacturing process which can correlate with algorithms, big data and high technologies”* [2]. There have been several papers on this subject over the past 5-10 years, which have tried to explore industry readiness [2], impact on businesses [3, 4], society [4, 5], and sustainability [6]. While many of these ideas have yet to mature, Industry 4.0 will affect all manufacturing. Its impact has also been highlighted in manufacturing journals citing cross-technology innovation involving electrochemical processes [7-10]. These publications focused on electrochemical deposition as an “additive” forming technique [8-10]. Novel manufacturing techniques have also featured in electrochemical publications citing inkjet printing of fuel cells [11], laser writing of electrocatalysts for textile manufacture [12], as well as algorithms for optimising micro-fabricated structures [13].

Electrochemical forming (or electroforming), in particular, is rapidly gaining recognition as an additive and sustainable manufacturing process which uses electrochemistry to build a structure layer by layer [14]. Currently many of the complex parts for printing, holography, sound reproduction etc. are produced by electroforming [14, 15]. A number of bespoke components in the aerospace industry also rely on electrochemically formed Ni and its alloys [16, 17]. Despite the continued exploitation of electroforming in manufacturing, academic and scientific interest in the area remains limited, which is now impeding the transition to automated production.

For Industry 4.0 capability, one requires reliable data feeding into algorithmic and artificial intelligence protocols needed to model and predict process behaviour. However, mechanisms for cathodic nickel reduction as well as accompanying anodic reactions, which can critically influence the physical and mechanical properties of the deposit, have remained ambiguous. Furthermore, some of these reactions can induce changes in the electrolyte that, in turn, can modify electrode reactions. This paper throws light on some of the complex issues surrounding the electrochemical and chemical behaviour during electroforming to highlight aspects that require reinvestigation.

1.2 Background and Empirical Experience

Electroforming is defined as the fabrication of free-standing components using electrodeposition. An electroformed part is fabricated using a mould (termed as mandrel) and has to be easily detachable without deformation whilst retaining its shape (*c.f.* Figure 1). Most electroformed parts are thick (>250 μm and often >1 mm) for mechanical strength. Forming thick deposits without deformation imposes a requirement of low internal stress on the material. This *unique* functionality is achieved when nickel is reduced from an electrolyte containing almost only nickel sulphamate and boric acid (*c.f.* Table 1).

Industrial development has provided copious empirical process data [19], including operating parameters required for stable operation [15, 19] as well as methods of monitoring bath chemistry [20]. Understandably, much of that work focused on optimising deposit internal stress as a function of operating parameters [18, 21], anode material [22], growth rate and grain size [23] as well as identifying chemicals lowering internal stress [24]. Further refinements of the process focused on achieving high rates of deposition [25, 26] and better knowledge of the effect of process parameters on deposit morphology and crystallinity [27, 28]. Innovations to extend technology capability focused on pulse deposition [29-31], micro-scale manufacturing [32] using LIGA techniques [33, 34], and mask-less microfabrication [35]. Numerical models to predict Ni-Co alloy composition [36] and feasibility of Ni recovery from spent electrolytes [37] have also been developed.

However, scientific endeavours to elucidate, verify or interpret empirical data are lacking. Currently, much of our understanding on electrochemical reduction of Ni is borrowed from sulphate electrolytes. However, the fact that the internal stress of Ni deposits obtained from sulphamate and sulphate differ by more than an order of magnitude [19] suggests that the reduction processes differ. Again, although it is widely accepted that anode reactions play a critical role in maintaining low stress [22, 24], there is no substantive investigation to elucidate this phenomenon. Furthermore, while much of the empirical literature states boric acid addition as a means for pH control, other studies provide a more complex picture. The implications of these differences are elaborated in the forthcoming sections.

2.0 Process and Analysis

Table 1 shows the chemical constituents of a sulphamate electrolyte [19,37]. As a comparison, the main constituents of a sulphate electrolyte is also included, which at first glance look similar. However, the first difference between the two solutions is the concentration of Cl^- , which is much lower in the sulphamate bath. A second difference is that sulphamate systems are additive free, whereas sulphate electrolytes use a variety of addition agents. Furthermore, surface adsorption by ions such as $[\text{Cl}]^-$, $[\text{SO}_4]^{2-}$, $[\text{OH}]^-$ are strictly avoided in sulphamates [18,21,22,31] since they increase internal stress. A fourth difference is that the operational current during electroforming is low; typically, between 5 and 20 $\text{mA}\cdot\text{cm}^{-2}$ (0.5-2 ASD) vs. 50 $\text{mA}\cdot\text{cm}^{-2}$ (5 ASD) for sulphate systems. At these low currents, hydrogen evolution is low and current efficiency for Ni deposition is consistently close to 100% [19, 22, 38]. Ni content in the bath is replenished via the dissolution of specialised Ni anodes, which again, operate close to 100% current efficiency. These myriad differences set the two electrolyte systems apart, and their electrochemical and chemical reactions should be viewed in this perspective.

2.1 Cathode Reactions

The debate around the mechanism of nickel electro-reduction has mainly centred on sulphate and chloride based electrolytes [39, 40, 41], where NiSO_4 and NiCl_2 are the source of nickel ions, respectively. The proposed sequence of reactions for nickel reduction for those electrolytes is shown in Table 2 (*c.f.* Reactions 1-3). The key points are that the second reaction step rate determining, although it has been argued that either $[\text{OH}]^-$ [39, 41] or $[\text{Cl}]^-$ [40, 42] can be the active intermediate.

This mechanism has been tested experimentally, where possible. It has been shown that either $\text{Ni}(\text{OH})_{\text{ads}}$ or NiCl_{ads} could be the adsorbed intermediate [39, 40-45] depending on Cl^- concentration. Analyses of Tafel slopes have revealed that Reaction 3a and 3b, involving a single or two electron transfer are favoured at low and high overpotentials [39, 42, 43, 45, 46]. Electrochemical Impedance spectroscopy (EIS) data have provided indirect support to these Tafel slope measurements [43, 44]. The generality of this mechanism has also been tested using perchlorate and methanesulphonic acids [45]. One could argue that since sulphamate ion is a poor complexant [37], that nickel discharge follows a similar mechanism

to that shown in Table 2 and since $[\text{Cl}^-]$ concentration is low, $\text{Ni}(\text{OH})_{\text{ads}}$ is the adsorbed intermediate.

However, there are some major differences between cathodic processes in sulphamate and sulphate systems. For example, sulphate systems encounter co-reduction of protons and oxygen during nickel deposition leading to cathode passivation [41, 44]. This issue has been countered by maintaining high levels of chloride ions, as opposed to sulphamate systems. Other researchers have also attributed hydrogen evolution to catalysis by nickel [41, 42, 46] via reactions 4-6 in Table 2. While these reactions can lead to low current efficiencies, it remains unclear why they should lead to oxidised nickel. One explanation offered is that this is due to co-adsorption of species such as $[\text{OH}]^-$, $[\text{SO}_4]^{2-}$, which is supported somewhat by impedance data to [44]. However, sulphamate systems have low $[\text{Cl}^-]$ concentration, no addition agents, and avoids the formation of $[\text{SO}_4]^{2-}$. The current efficiency too is nearly 100% within the operational range cited in Table 1. This means that Reactions 4-8 are suppressed during nickel electroforming by other means.

Direct measurement of mass and charge using an electrochemical quartz crystal nano balance (EQCN) [47] for sulphate and chloride electrolytes, on the contrary, show that most of the hydrogen formed via reaction 5 is out-gassed, and very little β -nickel is deposited. Their results also show that that $\text{Ni}(\text{OH})_2$ forms at the electrode surface right from the beginning of Ni deposition leading to oxidised nickel, indicating that the pH near the electrode is always high. Another independent experimental investigation using cyclic voltammetry shows that low current efficiencies and nickel oxides are obtained in only aerated solutions [48]. These data point towards reaction 7 (and 8 at high overpotentials) being the main cause of high surface pH. These EQCN results provide evidence that the other bath constituent, namely boric acid, may be blocking these reactions.

2.2 Role of Boric Acid

Since the formation of $[\text{OH}]^-$ is undesirable, boric acid (H_3BO_3) is added to nearly all nickel electrodeposition solutions [39, 41-44, 47]. The use of boric acid was recorded in 1954 [49], and process descriptions of sulphamate electrolytes recommend the use of boric acid as a buffering agent to obtain current efficiencies of 100% [18-24]. The buffering action of boric acid near the electrode surface however, has been contested by other researchers [50, 51]

since pK_a of the boric acid was calculated to be 9.3 [52], and nickel precipitation occurs at pH exceeding 5.5. The role of boric acid in sulphamate electrolytes has been examined by collecting polarization data [53]. Tafel behaviour was found to be qualitatively similar to those in sulphate systems and current efficiency for nickel deposition remained high almost up to the limiting current ($180 \text{ mA}\cdot\text{cm}^{-2}$), showing that hydrogen evolution was suppressed even at high currents. In addition, micro sensor measurements close to the electrode (between 10-100 μm) showed that the pH value remained close to that in the bulk when boric acid was present in the electrolyte.

These results build upon the EQCN findings [47] mentioned in the previous section showing that Ni deposition is facilitated by H_3BO_3 . This also compares well with EIS analysis of sulphate-based systems that propose that a single reaction, identified as Ni reduction, proceeds in the presence of boric acid, [43, 44]. Further evidence can be found in cyclic voltammetry and chronopotentiometry measurements by Hoare [50, 51], whose data show the suppression of both oxygen as well as proton reduction reactions when boric acid is present. The mechanism for maintaining pH at the electrode surface, therefore, is not via classic solution side buffering, but through modification of surface and reactions which has never been investigated for a sulphamate electrolyte.

2.3 Anode Reactions

The use of appropriate anodes for Ni electrodeposition from sulphamate electrolytes was recognised as early as 1965 [22]. It was demonstrated that, depending on the choice of anode, the internal stress of the deposit could vary. Specifically, sulphurised anodes, where Ni dissolves at low potentials, have been observed to produce products of low internal stress. Other anodes such as platinised Ti and pure Ni, have been correlated with increased amount of $[\text{SO}_4]^{2-}$ in the solution as well as incorporation of sulphur in the deposit. Since the bulk decomposition of sulphamate is slow [18, 24, 31], formation of $[\text{SO}_4]^{2-}$ is assumed to be via anodic reactions. A detailed study by Greene [24] proposed that several electrochemical reactions can occur at the anode, depending on the potential; these reactions are listed in Table 2(b). Greene [23] identified this compound by UV-Vis analysis as azodiphulphonate, $[\text{O}_3\text{S N} = \text{N SO}_3]^{2-}$, although other authors have suggested other compounds [54, 55].

It is the rate of generation (and consumption) of this product is what controls the internal stress of the deposit [18, 19, 56]. Therefore, one needs to tailor and control anodic reactions such that Ni dissolution is the main reaction (Reaction 10), and small amounts of $[\text{O}_3\text{S N} = \text{N SO}_3]^{2-}$ are co-produced (Reaction 13). Whilst the first reaction replaces Ni^{2+} ions consumed at the cathode, the latter enters the electrolyte as a stress reducer. A polarisation analysis suggests that the stress reducer is formed only at intermediate potentials [57]; this cannot be attained at desulphurised Ni, but were produced using pure Ni anodes where the electrode partially passivated [57]. However, reactions 14 and 17 may also occur on Ti, Ti-Pt or Pt which are deleterious to process operation.

However, during a process one needs to control the production and consumption of the stress reducer in the solution so as to optimise the internal stress. This would require the quantification of product generation and consumption which is lacking. As an example, Figure 2 shows the overall cell potential gathered in authors' laboratory during nickel electroforming, where pure Ni electrodes were used. The cell potential is low for the first 400s sustaining a current of $20 \text{ mA}\cdot\text{cm}^{-2}$ (2.0 ASD) after which passivation of the anode begins. Once passivation has occurred, the cell potential shoots up to 10 V (compliance voltage) and the current drops to $< 0.3 \text{ ASD}$ or $3 \text{ mA}\cdot\text{cm}^{-2}$. Presumably these currents correspond to the formation of a myriad of products shown in Reactions 12-17. One needs to identify and monitor the products formed and rates of formation, which, in practice, is difficult, owing to their low concentrations. However, since these chemical changes govern deposit stress (which has often been measured), quantification of these reactions is needed if one were to develop a controllable process.

3.0 Outlook

In the Industry 4.0 Era, big data and automation will require precise knowledge that allows one to control, monitor and predict a process. Electroforming has been identified as one of the processes that requires transition into the Industry 4.0 era. We have highlighted the paucity of systematic, reliable and validated scientific data for electroforming. Although there is a plethora of empirical data, they need scientific analysis that is amenable to predictive modelling and monitoring. As a starting point, key electrochemical and chemical reactions

governing the process and product quality need to be identified and their rate equations derived. Mass balances based on chemical monitoring is required, which needs to be correlated to grain structure and internal stress. Use of high-grade electrochemical equipment, coupled with gravimetry offered by EQCN need to be coupled with modern surface analysis offered by atomic scale microscopy, chemical analysis such as spectroscopy. These approaches would provide credible correlated information, which is currently lacking. Based on these findings, verifiable models as well as new methodologies for monitoring deposit growth and shape evolution of electroforms could be developed.

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Table 1: Process parameters and properties for nickel sulphamate and sulphate electrolytes. Derived process parameters using these values are also included. Non-scientific units are included for ease of comparison with literature. Molecular weight for nickel sulphamate is 250.86, Nickel chloride 237.69 and Boric acid 61.83 g mol⁻¹.

Chemicals/Parameters	Units	Sulphamate Electrolyte	Sulphate Electrolyte	Role
Nickel Sulphamate	M/g L ⁻¹	2.1/519	1.5/300	Ni ²⁺ source
Nickel Chloride	M/g L ⁻¹	0.028/6.7	0.25/60	Depassivator
Boric Acid (H ₃ BO ₃)	M/g/L ⁻¹	0.57 /35	0.57/40	Buffering agent*
pH	Dimensionless	4.0±0.36	2-4	
Temperature	K / °C	318-323/ 55-60	None	
Current Density	mA cm ⁻² / ASD	5-20 / 0.5-2	50-100/5-10	
Current Efficiency	%	99-100%	<< 100%	
Rate of Growth	µm/hr	25 – 61	NA	
Limiting Current	mA cm ⁻² / ASD	2081/208	NA	
Dissolved Oxygen	M / g L-1	Present	Present	
Ammonium Ions	M / g L-1	Avoided	NA	
Sulphate	M / g L-1	Avoided	Present	
Additives	M / g L-1	Self generated	Many	

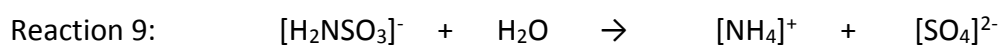
* The role mentioned in most of the literature.

Table 2:

(a) Chemical and Electrochemical reactions expected to occur in Sulphamate Systems.

Reaction Number	Possible Reactions at the Cathode	Reference
(1)	<i>Ni Deposition:</i> $\text{Ni}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Ni(OH)}^+ + \text{H}^+$	39-42 45, 46
(2)	$\text{Ni(OH)}^+ + \text{e}^- \leftrightarrow \text{Ni(OH)}_{\text{ads}} \text{ rate determining step(RDS)}$	
(3a) or	$\text{Ni(OH)}_{\text{ads}} + \text{e}^- \leftrightarrow \text{Ni} + \text{OH}^-$	
(3b)	$\text{Ni(OH)}_{\text{ads}} + \text{Ni}^{2+} + 2\text{e}^- \leftrightarrow \text{Ni} + \text{Ni(OH)}_{\text{ads}}$	
	Note that Cl ⁻ replaces OH ⁻ in electrolytes where significant amounts of chloride is present.	
(4)	<i>Proton Reduction:</i> $\text{Ni} + \text{H}^+ + \text{e}^- \rightarrow \text{Ni-H}_{\text{ads}}$	
(5a) or	$2 \text{Ni-H}_{\text{ads}} \rightarrow 2 \text{Ni} + \text{H}_2$	
(5b)	$\text{Ni-H}_{\text{ads}} + \text{H}^+ + \text{e}^- \rightarrow \text{Ni} + \text{H}_2$	
(6)	$\text{Ni-H}_{\text{ads}} \rightarrow \text{Ni(H}_{\text{ads}})$	
	Reaction (6) allows the formation of β-Ni phase. In effect two different Ni phases are formed which have been detected by cyclic voltammetry [47].	
(7)	<i>O₂ Reduction:</i> $\text{O}_2 + 2 \text{H}_2\text{O} + 4\text{e}^- \leftrightarrow 4 \text{OH}^-$	
(8)	<i>H₂O Electrolysis:</i> $2 \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	

Chemical Hydrolysis reaction can take place in the bulk solution via reaction 9



(b)

Reaction Number	Possible reactions at the anode	Reference
10	Ni Dissolution (active): This reaction can only take place in the presence of Cl ⁻ ions or when sulphur-depolarised Ni is used or pure Ni anodes are used. Ni → Ni + 2e ⁻	[22, 24]
11	<i>Anode reactions involving sulphamate</i> 2 [H ₂ NSO ₃] ⁻ → [O ₃ S NH = HN SO ₃] ²⁻ + 2H ⁺ + 2e ⁻ (Proposed intermediate)	[23]
12	[O ₃ S NH = HN SO ₃] ²⁻ → [O ₃ S N = N SO ₃] ²⁻ + 2H ⁺ + 2e ⁻ (azodisulphonate)	[23]
13	Overall reaction: 2 [H ₂ NSO ₃] ⁻ → 2 [O ₃ S N = N SO ₃] ²⁻ + 4 H ⁺ + 4 e ⁻	[23]
14	<i>At high anode over potentials:</i> 2 [H ₂ NSO ₃] ⁻ + H ₂ O → N ₂ + 2 [SO ₄] ²⁻ + 8 H ⁺ + 6 e ⁻	[23]
15	2 [SO ₄] ²⁻ → [S ₂ O ₃] ²⁻ + 2 e ⁻	[22]
16	<i>Reactions involving Cl⁻:</i> Cl ⁻ → Cl ₂ + 2e ⁻	
17	2 [NH ₂ SO ₃]H + 3 Cl ₂ + 2 H ₂ O → N ₂ + H ₂ SO ₄ + 6 HCl	[24]

Figure Captions

Figure 1: Illustration of electrochemical forming of nickel showing some of the operating parameters, such as cell potential, temperature and agitation in a laboratory scale experiment. The anode is usually Ni pellets in a Ti basket and the cathode is a steel mandrel which is detached after plating. The chemical structure of sulphamate and sulphate are included to show the chemical similarity.

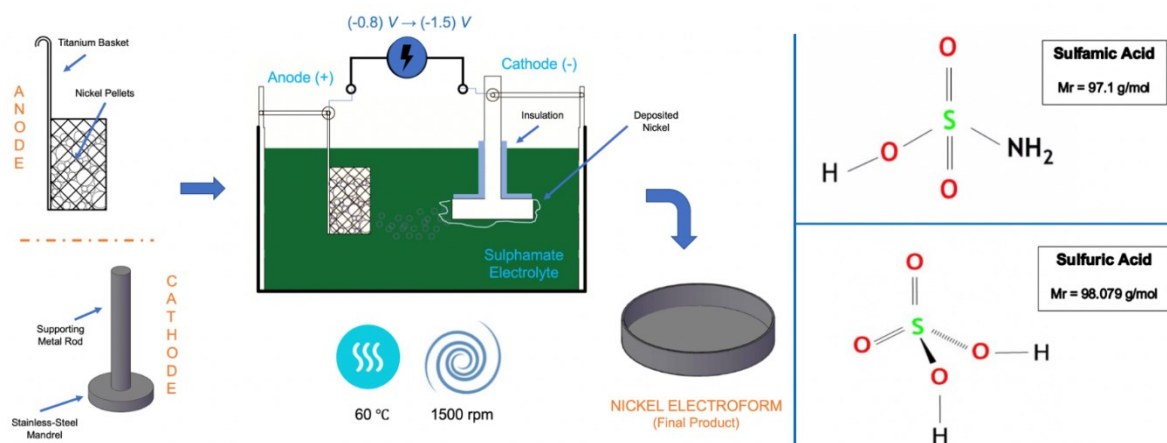


Figure 2: Cell Voltage (in black) and current (in red) as a function of time during electrochemical deposition from a sulphamate electrolyte of composition stated in Table 1. Applied current density at start was 20 mA.cm⁻² (2 ASD) and was applied for a time period of 2 h. Solution temperature 50 °C.

