Induced Codeposition of Mo and W from Aqueous Electrolytes

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By

Shaopeng Sun

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ABSTRACT

Mo and W alloys are recognized for their outstanding corrosion, wear resistance and catalytic properties towards the generation of hydrogen. The electrochemical codeposition behavior of Mo or W with iron-group elements (i.e., Ni, Co, Fe) exhibits induced codeposition, since they cannot be reduced alone, but only with iron group elements. Although Mo and W have been intensively investigated, their reaction mechanisms remain not well understood.

In the work presented here, Mo induced codeposition with Ni was explored when the concentration of nickel ions in the electrolyte was much lower than molybdate. Their composition and deposit thickness were characterized by X-ray fluorescence. Mo-rich alloys were obtained, setting a new record, with > 80 wt. % Mo content. Catalytic properties were investigated and exhibited Tafel behavior consistent with their hallmark feature as a catalyst for electrolytic hydrogen evolution. NiMoW alloys were also electrodeposited, where the nickel preferentially induced the deposition of molybdenum over that of tungsten. The tungsten partial current density, hence reaction rate, was inhibited when deposition was compared to a molybdenum free electrolyte. A mechanism to describe this observation was raised for both Mo and W induced codeposition.

To probe the intermediate of induced codeposition, intensity modulated photocurrent spectroscopy (IMPS) was performed to assess the intermediate species occurring during induced codeposition of NiW. Results support the presence of adsorbed intermediates that form during electrodeposition that is photoactive. Pulse electrodeposition was also conducted to investigate the induced codeposition. It was observed that duty cycle decreased Mo content and increased W content in deposit, but
didn’t significantly change Ni content, attributed to differences in adsorbed molybdenum and tungsten intermediate species. Additionally pulse electrodeposition helps to tune the density of cracks in the deposits.

In this work, the composition range of electrodeposited NiMo from aqueous solution was expanded to a new limit, 80 wt.%. Also, a new mechanism of Mo and W induced codeposition was suggested, where adsorbed intermediates was identified as the key species that induces molybdate and tungstate ion reduction. For the first time, IMPS was applied to an electrodeposition system, and used to verify adsorbed intermediates during NiW codeposition.
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1.0 INTRODUCTION

Tungsten alloys are of interest for their outstanding corrosion resistance [1-4], extraordinary wear resistance [5-7] and high hardness [7-10]. NiW alloys were considered as a potential material for microelectromechanical systems (MEMS) [11, 12]. Tungsten alloys are also well known to enhance hydrogen evolution reactions as a catalyst [13-15]. Molybdenum alloys are recognized for their corrosion [16-20] and wear [21-23] resistances and considered as an outstanding catalyst for hydrogen evolution reaction [24-39]. Mo alloys with iron group elements have wide applications as promoters of catalyst for several important reactions, such as hydrodesulfurization, hydrodenitrogenation, dehydrogenation and hydrodeoxygenation in organic chemistry and in the oil industry [40-42].

Fabricating Mo and W alloys by electrodeposition from aqueous solutions have two major advantages: low investment cost and capability of easily handling complicated shaped substrates. Hence, investigation on Mo and W alloys electrodeposition has practical significance for industry. However, Mo [6, 13, 17, 19, 24, 25, 27, 31, 33, 34, 38, 43-68] and W [47, 54, 69-102] alloy electrodeposition have been mainly investigated empirically, and could only achieve a limited range of deposit composition. Expanding the composition range and the understanding of Mo and W electrodeposition from aqueous electrolytes can enable us to gain more control on the production, and broaden the design of Mo and W alloys e.g., electrodepositing multiple layers NiW, where the composition of each layer is well designed, that could maintain, or even improve, the
properties of interest over those obtained for NiW (or NiMo) deposits of a uniform composition.

Extraordinary wear resistance [5-7, 103] and high hardness [7-10] make W alloys used widely in industry for the protection layer of soft materials, such as Ni. e.g. Sriraman et al. [7] showed that adding W into Ni to form NiW alloy decreased wear rate from 3.92 to 1.14 mm$^3$N$^{-1}$m$^{-1}$×10$^{-5}$, and increased hardness from 277 to 536 HV. Hence, in manufacturing the parts which are constantly scratched, such as the connector of USB and the pistons in engines, W alloys have clear advantages. Mo alloys don’t have as good mechanical properties as W alloys, but they have outstanding catalytic properties, such as a catalyst for hydrogen generation [24-39, 104]. Hence, Mo alloys are considered as a potential material for the cathode in hydrogen generation industry. In the manufacturing hydrogen by electricity, the cathode is in a corrosive environment. Mo alloys don’t only offer an outstanding catalytic properties, but also good corrosion [16-20] and better wear [21-23] resistance than some other catalysts, such as Ni. As a result, Mo alloys can cut maintenance costs. Compared to a platinum cathode, Mo alloys can also cut the investment cost dramatically.

Since W alloys have outstanding mechanical properties and Mo alloys have extraordinary catalytic properties, if W and Mo alloys can be combined, an improved material can take advantage of both W and Mo alloys, such NiMoW. This ternary element alloy may have good catalytic properties of NiMo for the hydrogen evolution reaction, and improved mechanical properties by introducing W. This will be of great interest for commercialization. Moreover fabricating it by electrodeposition can offer a
relatively low cost process, which can also easily coat complicated shaped substrates to increase surface area.

The electrodeposition of Mo and W alloys was coined by Brenner [105] as “induced codeposition” in his comprehensive review of alloy electrodeposition, because they cannot be electrodeposited alone from aqueous solution, but they require to be codeposited with iron group elements, such as Ni, Co and Fe. Although Mo [6, 13, 17, 19, 24, 25, 27, 31, 33, 34, 38, 43-68] and W [47, 54, 69-102] induced codeposition with iron group elements have been extensively investigated experimentally, the reaction mechanisms are still not well understood. In 2002, an overall reaction of NiW induced codeposition was raised by Younes and Gileadi [87]. They proposed that a complex species of Ni(II), W(VI) and a citrate ligand is the precursor of the NiW induced codeposition. However they also admitted that there is no direct evidence to support this argument. Their conclusion was drawn from the partial current densities and estimated concentration of this precursor. Since Mo and W share the same unique property of induced codeposition [105], the mechanism of Mo induced codeposition could be analogous with W induced codeposition. For Mo induced codeposition, mechanisms were suggested by Fukushima et al. [67], Chassaing et al. [64] and Podlaha and Landolt [58, 60]. In the work of Fukushima et al. [67], they raised a two-step reaction mechanism of NiMo and suggested two characteristic composition of Mo alloys with iron group elements electrodeposited from aqueous solution, the composition with the highest current efficiency and the composition of the limiting Mo content. They also suggested that these two characteristic compositions were related with the numbers of unpaired 3d electrons in the iron group element which was codeposited with Mo. Chassaing et al. [64]
developed an overall mechanism for NiMo induced codeposition, where a product of MoNi$_3$ was the final product. This also infers a maximum of Mo content in NiMo alloys electrodeposited from aqueous solution being 25 at %. Others [59, 63] have found significantly higher Mo percentages. They observed when potential was not sufficiently negative, e.g. at -1.35 V vs SSE, Mo can be only partially reduced to Mo(IV) in the form MoO$_2$Ni$_4$, which was examined *ex situ* by Auger electron spectroscopy, AES, and energy-dispersive X-ray spectroscopy, EDAX. Podlaha and Landolt [58-60] did a comprehensive investigation on Mo induced codeposition. They raised a mechanism [60], where Mo reduction was a separated reaction, Ni ions acted as a catalyst for Mo reduction, and the reaction took place via an adsorbed intermediate formed by Mo(IV), Ni(II) and citrate. This mechanism was expanded to include Co and Fe as an inducing element [58]. The intermediates suggested by Podlaha and Landolt was further proved by *in situ* surface Raman spectroscopy by Zeng *et al.* [52] and Niu *et al.* [57].

In this work, Mo and W induced codeposition will be explored by varying the concentration of the electrolyte and electrodeposition method to expand the composition range of the deposits. Also it will be the first time that Mo and W reductions are compared together in one electrodeposition bath and a mechanism will be raised to describe the observations. Since the intermediates formed during Mo and W induced codeposition are essential to understand induced codeposition, intensity modulated photocurrent spectroscopy will be applied to examine the intermediates.
2.0 CRITICAL LITERATURE REVIEW

Induced codeposition was defined in 1963 by Brenner [105]. It describes a type of electrodeposition reaction where an element cannot be reduced by itself in an aqueous electrolyte, but requires another element to induce this element. Since these two elements are electrodeposited together, an alloy is formed. Systems that exhibit induced codeposition include Mo or W with the iron group elements (Ni, Co and Fe).

2.1 Induced Codeposition of Mo Alloys with Iron Group Elements

2.1.1 Research Interests of Mo Alloys with Iron Group Elements

Mo alloys with iron group elements are recognized as outstanding catalysts for several type reactions. In organic chemistry, CoMo and NiMo with a support of alumina, alumina oxide or silicon dioxide are considered as good catalysts for hydrodesulfurization, hydrodenitrogenation, dehydrogenation and hydrodeoxygenation [40-42]. Introducing Ni or Co to Mo will extraordinarily enhance the catalytic property. Bataille et al. [42] investigated the promoter effect of Co or Ni on the hydrodesulfurization activity of Mo on a support of alumina for dibenzothiophene and 4,6-dimethyldibenzothiophene. They observed that on the unpromoted catalyst, Mo supported on alumina, dibenzothiophene and 4,6-dimethyldibenzothiophene have similar reactivity. After the Co or Ni promoter was introduced, dibenzothiophene was much more reactive than 4,6-dimethyldibenzothiophene.

Platinum is the conventional catalyst for hydrogen evolution reactions. Since NiMo is considerably less expensive than Pt and exhibits a high catalytic potential catalyst for hydrogen evolution reaction in industry [24-39, 104]. Navarro-Flores et al. [104] conducted a comprehensive examination on the electrodeposited NiMo alloys’
catalytic properties on hydrogen evolution reactions. They observed that introducing Mo into Ni to form NiMo alloys can significantly enhance the catalytic property toward hydrogen evolution reactions by decreasing the Tafel slope and increasing the exchange current density. They compared two compositions of NiMo alloys, 12 and 25 at. % and found that smaller Mo content resulted in a better catalytic property. They also compared NiMo with NiW, NiFe and pure Ni, where all the deposits were electrodeposited, and investigated two important factor for catalysts; surface roughness and intrinsic electrocatalytic activity. It was of interest that Ni$_{7.3}$Mo, (Mo content of 12 at. %), had the overall best electrocatalytic activity. However, Ni$_{3.4}$W, (W content of 23 at. %), had the best intrinsic electrocatalytic activity. This indicated that the reason why Ni$_{7.3}$Mo is better than Ni$_{3.4}$W is larger surface roughness, which was also confirmed by scanning electron microscope. NiMo of larger range compositions was examined by Jaksic et al. [32]. All the NiMo deposits in their work were prepared by arc melting of the pure components (Ni, Mo) under argon atmosphere, so the catalytic property investigated by them can be considered as intrinsic. They found the best composition of NiMo is 50 at. %. Also they suggested that the hydrogen evolution reaction mechanism on NiMo should follow Volmer–Heyrovsky with the rate determining step of Heyrovsky. Raj and Vasu [39] examined several combination of Ni based ternary alloys, including NiMoFe, NiMoCu, NiMoZn, NiMoCo, NiMoW, NiMoCr and pure Ni. They found that NiMoFe was a better catalyst for hydrogen evolution reaction than the others. It was noted that for each ternary alloy, only one composition was investigated, in other words, the effect of composition was not considered in their work.
Mo alloys are also of interest for their wear [21-23] and corrosion [16-20] features, Lima-Neto et al. [17] examined the corrosion resistance and influence of heat treatment of electrodeposited NiMo coating. They found that the annealing temperature can help to increase microhardness of the Ni-Mo coatings. They compared NiMo with Cr and found that Cr had better corrosion resistance in chloride medium, however they also observed that Ni\textsubscript{13}Mo could be a potential replacement for Cr coatings when the operating temperature is higher than 100 °C and high microhardness is required.

2.1.2 Induced Codeposition of Mo Alloys with Iron Group Elements

An early comprehensive review of alloys containing Mo and Ni, Co or Fe was written by Brenner, a pioneer in this area in his book, *Electrodeposition of Alloys* [105]. Several bath and operation conditions were discussed in detail. Brenner suggested that the practical value of Mo alloys was limited, since its physical properties are not as good as W alloys. But, today, it is recognized that Mo alloys, especially NiMo alloys, are superior catalyst for the hydrogen evolution reaction [24-39, 104], and the electrodeposited NiMo was better than NiW in overall electrocatalytic activity due to its larger surface roughness [104].

Most of the investigation on Mo electrodeposition were from alkaline baths, but it also can be electrodeposited from acid baths with very low efficiency and low Mo content in the deposit [106]. The alkaline baths usually can be divided into following types: citrate, pyrophosphate, carbonate and ammoniacal baths. A list of selective electrolyte conditions for Mo induced codeposition is listed in Table 1. Ammonia is believed to have a significant effect on Mo induced codeposition. It can significantly increase current efficiency and decreases the Mo content [59].
**Table 1: Typical baths for induced codeposition of Mo alloys**

<table>
<thead>
<tr>
<th>No.</th>
<th>MoO$_4^{2-}$ (M)</th>
<th>Iron Group Element (M)</th>
<th>Complexing Agent (M)</th>
<th>Others (M)</th>
<th>pH</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02</td>
<td>Fe: 0.23</td>
<td>Citric Acid: 0.31</td>
<td>-</td>
<td>6</td>
<td>[106]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni: 0.22</td>
<td>Monohydrate Citric Acid: 0.31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Co: 0.22</td>
<td>Monohydrate Citric Acid: 0.31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0 – 0.073</td>
<td>Ni: 0.14</td>
<td>Sodium Pyrophosphate: 0.36</td>
<td>Ammonium chloride: 0.37; 2-Butyne-1,4-diol: 0.0006; Rokafenol N10: 100 μl/L</td>
<td>8.5 - 9.75</td>
<td>[107]</td>
</tr>
<tr>
<td>3</td>
<td>0.17</td>
<td>Fe: 0.033</td>
<td>Sodium Pyrophosphate: 0.1; Sodium Bicarbonate: 0.9</td>
<td>-</td>
<td>8</td>
<td>[108]</td>
</tr>
<tr>
<td>4</td>
<td>0.005</td>
<td>Ni: 0.7</td>
<td>Sodium Citrate: 0.7</td>
<td>Ammonia: adjusted by pH</td>
<td>7.4</td>
<td>[59]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Co: 0.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe: 0.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.03</td>
<td>Ni: 0.2</td>
<td>Sodium Citrate: 0.2</td>
<td>Ammonia: 0.28</td>
<td>-</td>
<td>[63]</td>
</tr>
</tbody>
</table>
Table 1: Typical baths for induced codeposition of Mo alloys (continuation)

<table>
<thead>
<tr>
<th>No.</th>
<th>MoO$_4^{-2}$ (M)</th>
<th>Iron Group Element (M)</th>
<th>Complexing Agent (M)</th>
<th>Others (M)</th>
<th>pH</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0-0.03</td>
<td>Ni: 0.2</td>
<td>Sodium Citrate: 0.25</td>
<td>pH Adjusted by Ammonia</td>
<td>9.5</td>
<td>[64]</td>
</tr>
<tr>
<td>7</td>
<td>0.005</td>
<td>Ni: 0.35</td>
<td>Sodium Citrate: 0.4; Ammonia: 0.28</td>
<td>-</td>
<td>8.5</td>
<td>[51]</td>
</tr>
<tr>
<td>8</td>
<td>0.005-0.012</td>
<td>Co: 0.3</td>
<td>Sodium Citrate: 0.2</td>
<td>-</td>
<td>3-5</td>
<td>[45]</td>
</tr>
<tr>
<td>9</td>
<td>0.003-0.024</td>
<td>Ni: 0.2</td>
<td>Sodium Citrate: 0.3</td>
<td>pH Adjusted by Ammonia</td>
<td>8</td>
<td>[109]</td>
</tr>
<tr>
<td>10</td>
<td>0.01-0.1</td>
<td>Ni: 0.2</td>
<td>Citric Acid: 0.35; Ammonia Sulfate: 0.7</td>
<td>Sodium Chloride: 0.37</td>
<td>8.5</td>
<td>[110]</td>
</tr>
<tr>
<td>11</td>
<td>0.012 - 0.02</td>
<td>Co: 0.1</td>
<td>Sodium Citrate: 0.2</td>
<td>-</td>
<td>6.6</td>
<td>[49]</td>
</tr>
<tr>
<td>12</td>
<td>0.003-0.006</td>
<td>Ni: 0.2-0.24; Co: 0.06-0.1</td>
<td>Sodium Citrate: 0-0.306</td>
<td>Sodium Chloride: 0.5</td>
<td>4-10</td>
<td>[111]</td>
</tr>
<tr>
<td>13</td>
<td>0-0.1</td>
<td>Ni: 0.01-0.1</td>
<td>Sodium Citrate</td>
<td>-</td>
<td>4</td>
<td>[112]</td>
</tr>
</tbody>
</table>
Some organic additives, like butyne-1,4-diol and rokafenol N10, were also examined to improve the roughness of deposits. In the work of Denten et al., [107] NiMo alloys were deposited from a pyrophosphate bath. Scanning electron microscope was applied to examine the morphology of the deposit. It was observed that the organic additive, butyne-1,4-diol and rokafenol N10, improved the surface roughness and eliminated bumps and cracks on the surface. They also found that molybdate in the electrolyte improved the Mo content in the deposits as expected, but decreased the Mo reaction rate. It was due to higher Mo content in the deposits enhanced the side reaction, hydrogen evolution reaction, which inhibited Mo reaction rate. They observed that the organic additive decreased Mo content in the deposits at a given applied current density.

Pulse electrodeposition is also widely applied in Mo induced codeposition. [24, 48, 49, 51, 56, 62, 65, 66]. In 1988, Nee et al. [65] investigated NiMo induced codeposition by pulse electrodeposition method. They reported that pulse electrodeposition can affect the composition and internal stress of the deposit. An increase of the pulse current density can increase the Mo content in the deposit. They attributed the increase in Mo content to the enhanced side reactions at high current densities, which generated hydrogen, and more hydrogen reduced more Mo. They believe this also explained why the current density could decrease the current efficiency. They also found that pulse electrodeposition decreased deposit stress, which was due to the desorption of hydrogen during each off-time. When the pulse current density is 25 mA/cm², changed in the pulse frequency increased yield and tensile strengths.

In 1995, Chassaing et al. [62] investigated NiMo induced codeposition by reverse pulse electrodeposition. They found that the length of cathodic and anodic pulse affected
the composition of the deposits. When the anodic pulse is less than 30 ms, the cathodic pulse time decreased the Mo content in the deposits. They attributed changes in composition to the influence of the diffusion control of that Mo electrodeposition. In the anodic pulse range of 10 to 160 ms, when the cathodic pulse was 100 ms, they observed that when the anodic pulse length was short, it increased Mo content in the deposit. In the range of 50 to 100 ms for the anodic pulse, the anodic pulse didn’t significantly influence the composition. When the anodic pulse was longer than this range, it decreased Mo content dramatically. When anodic pulse was very long, > 160 ms, no deposit was observed. They attributed this behavior to reactions or processes during the anodic pulse other than ions replenishment and hydrogen oxidation. They also observed that reverse pulse electrodeposition generated a nodular morphology and the thickness of deposits didn’t increase the roughness.

In 2002, Marlot et al. [51] investigated pulse electrodeposition of NiMo in an electrolyte where Ni ions were in excess and molybdate was mass transport limited. They showed that smaller duty cycles and large frequency increased Mo content in the deposits considerably, which was due to Mo reduction being under diffusion control. Compared to d.c. electrodeposition, when the duty cycle was between 0.4 and 0.6 at high frequency, pulse electrodeposition enhanced the current efficiency. However, when duty cycle was decreased to 0.2, high frequency decreased current efficiency dramatically. During the off-time, no deposit was significantly oxidized, which was confirmed by rotating electrochemical quartz crystal microbalance and Auger electron spectroscopy.

Although Mo alloy induced codeposition has been investigated intensively, the mechanistic theories of Mo induced codeposition are still debatable. As early as 1958, a
mechanism was raised by Ernst and Holt [113] to describe Mo alloy electrodeposition from ammonia citrate electrolytes [113]. In this mechanism, MoO$_4^{2-}$ was believed to first reduce to an oxide, then the oxide was subsequently reduced to the alloy of a metal surface of Ni, Fe and/or Co, as given as reactions (2.1.1) and (2.1.2):

$$\text{MoO}_4^{2-} + 4\text{H}_2\text{O} + \text{n}e^- \rightarrow \text{Mo(OH)}_{(6-n)} + (2 + \text{n})\text{OH}^- \quad \text{(2.1.1)}$$  

$$\text{Mo(OH)}_{(6-n)} + (6 - \text{n})\text{H} + \text{M} \rightarrow \text{M} \bullet \text{Mo} + (6 - \text{n})\text{H}_2\text{O} \quad \text{(2.1.2)}$$

Their mechanism assumed that when a layer of oxide, Mo(OH)$_{(6-n)}$, was formed by reaction 2.1.1 and covered the original metal cathode, it is possible that the oxides can’t supply the right lattice for Mo ions to be discharged. Hence, the overpotential on the cathode would increase, and become high enough for hydrogen evolution reactions. During the hydrogen evolution reaction, the intermediate, atomic hydrogen, could reduce Mo oxide to metallic Mo with M, such as Ni, and then it offered a new position for Mo ion in the electrolyte to be reduced to another Mo oxide. But the theoretical basis of this process is questionable, since there was no evidence to show that Mo oxide was reduced by hydrogen.

The role of hydrogen in the mechanism of Mo induced codeposition is still not in agreement. Since the current efficiency of induced codeposition is not 100%, sometimes as low as 10%, there are always plenty of hydrogen generated by the side reactions. Hence, it is very difficult to find out whether hydrogen evolution reactions affect induced codeposition. Fukushima et al. [67] proposed that hydrogen is part of the mechanism of Mo induced codeposition. In 1979, they proposed a mechanism as:

$$\text{MoO}_4^{2-} + (6 - \text{n})\text{e} \rightarrow \text{Mo}^{\text{n}}\text{oxide (hydroxide)} \quad \text{(2.1.3)}$$
\[ \text{Mo}^{n+} \text{oxide (hydroxide )} + n\text{H(M)} \rightarrow \text{Mo(M)} \]  \hspace{1cm} (2.1.4)

\[ \text{M}^{2+} + 2e \rightarrow \text{M} \]  \hspace{1cm} (2.1.5)

\[ \text{H}^+ + e(\text{M}) \rightarrow \text{H(M)} \]  \hspace{1cm} (2.1.6)

where \( n \) is the valence of Mo and M stands for the iron group elements. They attribute the role of the iron group elements in inducing Mo ions to the unpaired 3d electrons of iron group elements. The number of unpaired 3d electrons of Ni, Co and Fe are 0.6, 1.6 and 2.2 respectively. They tried to connect the number of unpaired 3d electrons of iron group elements with Mo content in the deposits by an equation, as follows:

\[
\text{Mo wt\%} = \left[\frac{(95.94N/n)}{(W + 95.94N/n)}\right] \times 100
\]  \hspace{1cm} (2.1.7)

where \( N \) is the number of unpaired 3d electrons of iron group elements, \( n \) is the valence of the Mo in the intermediate, and \( W \) is an atomic weight of the iron-group metal. It was assumed that the iron group elements only participate once in Mo induced codeposition.

Fukushima et al. \[67\] suggested that the valence of Mo in the intermediate is 4. The valence of Mo in the intermediate also agreed well to other researchers \[58, 60, 64\] and was supported by \textit{in-situ} Raman spectroscopy studies \[52, 57\]. A maximum of Mo content in the alloys was derived by:

\[
\text{Mo wt\%} = \left[\frac{(95.94mN/n)}{(W + 95.94mN/n)}\right] \times 100
\]  \hspace{1cm} (2.1.8)

where \( m \) is iron group elements participation frequency. The maximum participation frequency of iron group elements to Mo reduction is 3. Hence, a maximum of Mo content in the deposit was proposed to be: 42 wt.% for MoNi, 66 wt.% for MoCo and 73 wt.% for MoFe.

The mechanism presented by Chassaing \textit{et al.} \[64\] for NiMo induced codeposition follows:
\[
\text{MoO}_4^{2-} + 3\text{Ni}^{2+} + 8\text{e}^- + (4 + n)\text{H} \rightarrow \text{MoNi}_3 + 4\text{OH}^- + n\text{H}_{\text{included}} \quad (2.1.9)
\]

where MoNi\textsubscript{3} was the only product of Mo reduction. This indicated a maximum Mo content in deposits was 25 at.%. They found this overall reaction happened when the applied potential was more negative than -1.5 V vs SSE. When the applied potential was not negative enough, an oxide of Mo was formed:

\[
\text{MoO}_2 + 4\text{Ni}^{2+} + 8\text{e}^- \Leftrightarrow \text{MoO}_2\text{Ni}_4 \quad (2.1.10)
\]

where this oxide contain both Mo and Ni and the ratio of Mo : Ni is 1:4.

In both mechanisms of Fukushima \textit{et al.} and Chassaing \textit{et al.}, hydrogen acted as a reducing agent to reduce Mo with Ni. Crousier \textit{et al.} [114] investigated the role of hydrogen during induced codeposition. They used three substrates: glassy carbon, pure Ni and palladium. On glassy carbon substrates, it was hard for hydrogen to diffuse into it. But on palladium substrates, hydrogen could rapidly diffuse into it. The Ni substrate was in between these two extremes. It was found that NiMo couldn’t be deposited on palladium. So the authors reached a conclusion that NiMo induced codeposition required the presence of hydrogen. Crousier \textit{et al.} thus points to the important role of hydrogen in reducing molybdate ions. Hydrogen could affect the induced codeposition, but may not be a determining factor, as Pd, Pt and Ni all can have different effects on adsorbed intermediates.

Podlaha and Landolt [59] examined induced codeposition of NiMo. They found that rotation rate significantly increased the Mo content in the deposits when molybdate was mass transport limited in the electrolyte. The rotation rate also increased current efficiency, when applied current density was high. However it didn’t affect the deposition considerably when current density was low, as expected for a kinetic controlled regime.
They observed that molybdate in the electrolyte decreased Mo content in the deposit at the concentration range of 0.015 to 0.045 M, when the applied current density was small, < ~ 40 mA/cm². More citrate in the electrolyte increased Mo content in the deposits, but decreased current efficiency. They also investigated the effect of ammonia on Mo induced codeposition and found that ammonia significantly improved current efficiency, but decreased Mo content in the deposits. They also examined the electrolyte with limited concentration of Ni. It was observed surprisingly that the rotation rate didn’t significantly affect the composition in the deposits. However, rotation rate enhanced the partial current densities of Ni and Mo equivalently. They concluded that this was due to the low concentration of Ni in the electrolyte limiting the Mo reduction rate. Podlaha and Landolt [60] raised a new mechanism of NiMo induced codeposition, reactions 2.1.11, 2.1.12 and 2.1.13. In this mechanism, Mo reduction was separated from the Ni reduction, in other words, Ni acted as a catalyst for Mo reduction. An adsorbed intermediate, $[\text{NiCitMoO}_2]^-$, was suggested.

\[
\text{NiCit}^- + 2e^- \rightarrow \text{Ni(s)} + \text{Cit}^-^3 \\
\text{MoO}_4^{2-} + \text{NiCit}^- + 2\text{H}_2\text{O} + 2e^- \rightarrow [\text{NiCitMoO}_2]^{}_{\text{ads}} \\
[\text{NiCitMoO}_2]^{}_{\text{ads}} + 2\text{H}_2\text{O} + 4e^- \rightarrow \text{Mo(s)} + \text{NiCit}^-
\]

2.2 Induced Codeposition of W Alloys with Iron Group Elements

2.2.1 Research Interests of W Alloys with Iron Group Elements

Tungsten is of interest of its outstanding physical properties, including highest elemental melting point, 3410 °C, the lowest coefficient of linear thermal expansion, $4.3 \times 10^{-6}/^\circ \text{C}$ and the highest tensile strength, 410 kg/mm². W alloys with iron group
elements are well-known for their superior corrosion [1-4, 93] and wear [5-7] properties and high hardness [7-10]. W alloys are also recognized as a remarkable catalyst for hydrogen evolution reaction [13-15, 104], which have potential wide applications in industry due to its prominent physical properties. W alloys are also considered as a potential material for microelectromechanical systems (MEMS) [11, 12]. Recently, W alloys were comprehensively reviewed by Tsyntsaru et al. [115].

In 1996, Yao et al. [116] examined the corrosion resistance of NiP, NiW, NiWP and FeW in hydrochloric and sulfuric bathes and compared them with type 304 stainless steel. They observed that introducing W into Ni-based deposits significantly improved the corrosion resistance by decreasing the anodic dissolving current. Also, the passivation enhanced corrosion property of amorphous NiW in sodium chloride solution at 30 °C. In the immersion experiments, they found the corrosion rate of type 304 stainless steel had much faster corrosion rate than amorphous NiWP and NiW deposits in hydrochloric acid solution at 30 °C. At 30 °C, type 304 stainless steel had a lower corrosion rate than Ni-based deposits in sulfuric acid solution, but at 60 °C its corrosion rate increased dramatically and became much larger than the amorphous deposits.

Since the passivation is essential for W alloys’ corrosion resistance, in 1993, Donten et al. [117] conducted an intensive examination on the passivation of CoW in variable pH solutions. They observed that the passivation of amorphous CoW were mainly influenced by pH in noncomplexing solutions. In acidic solutions, the process of passivation was relatively fast and the thickness of the layer was about 0.4 µm. They suggested that both Co and W contributed to the passivation and crystalline tungsten-oxide species were observed at the surface. In the alkaline solutions, the passive layer
was also formed, which was not as fast as in the acidic solutions, but thicker. They observed that W was dissolved during the passive process, so the W content in the passive layer was lowered. In neutral solutions, they didn’t observe passivation formed on any of their CoW samples. They also found that oxidation could damage the passive layer.

Another investigation of NiW corrosion properties was conducted by Obradovic et al. [118]. They observed that Ni was preferentially dissolved from the surface at OCP. Eventually, only W was left on the surface. They found NiW of the highest W content had the lowest corrosion rate. High W content deposits had better corrosion resistance in the solutions without oxygen than with oxygen.

Capel et al. [103] examined the wear and corrosion resistance and hardness of CoW and CoWFe and compared them with chromium. They observed that the hardness of CoW was significantly improved by heat treatment. As a result, the wear resistance was close to the electrodeposited chromium. However, the heat treatment decreased the corrosion resistance. The electrodeposited CoWFe of 30 wt.% Fe content had a hardness close to electrodeposited chromium and improved corrosion resistance, but its wear resistance was not as good as the electrodeposited chromium.

Chianpairot et al. [4] examined the corrosion properties of nanocrystalline NiW with the grain size of 5 to 63 nm in NaCl solutions. They showed that there were two major factors that affected corrosion. One is the W content in the deposits, since W formed a corrosion resistant oxide layer. The other one is the grain boundary volume where corrosion can happen. They found that in the grain size range of their work, the
grain size decreased the corrosion resistance in the alkaline environment, but, in the acidic environment, it went to the other way, enhancing corrosion.

W alloys with iron group elements also are well-known as catalysts for hydrogen evolution reactions [13-15, 104]. In 2011, Marceta Kaninski et al. [15] examined the catalytic properties of CoW for hydrogen evolution reactions and compared it with standard pure Ni substrate. They concluded that CoW was a much better hydrogen evolution catalyst than a standard pure Ni substrate. It saved more than 20% energy per mass unit of hydrogen generated. Their rate determining step of hydrogen evolution reaction on CoW was the discharge step, Volmer reaction, and the exchange current density was in the order of magnitude of $10^{-3}$ A/cm$^2$, having as apparent energy of activation was 28.1 kJ/mol. They partially attributed the outstanding catalytic property of CoW to the larger active surface area. They also examined the stability of CoW deposits in alkaline solution at 343 K with an applied current density of 300 mA/cm$^2$, which showed throughout 45 days that the measured potential was stable.

### 2.2.2 Induced Codeposition of W Alloys with Iron Group Elements

Induced codeposition of W alloys was well reviewed and defined by Brenner in 1963 [105], and recently it was reviewed by Eliaz et al. [47] and Tsyntsaru [115]. All of them reviewed the operating baths and electrodeposition conditions that can be applied in induced codeposition of W alloys. In the review of Eliaz et al., they noted that it is possible that Fink and Jones are the first group who report electrodeposition of pure W, although it was readily proved untrue with a suspicion that contaminants in the water contained the inducing element [119].
Induced codeposition of W alloys has been intensively investigated around world. Similar as Mo induced codeposition, the following factors affect the electrodeposition of W alloys: W and iron group elements content in the electrolyte, complexing agent and its concentration in the electrolyte, pH, temperature and, if the species are under mass transfer control, electrolyte agitation [47, 54, 69-102, 115]. Generally, a basic bath is better than an acidic bath for W alloys induced codeposition due to its better deposit [47]. Selective baths are listed in Table 2. Also, the electrodeposition method, e.g. pulse electrodeposition and reverse pulse electrodeposition, can also affect the electrodeposited W alloys, especially if they are pulsed deposited [70, 93, 97].

In the acidic bath, according to Brenner [105], the ratio of W concentration over iron group elements concentration in the electrolyte could increase W content in the deposit, especially for FeW. But it could also decrease current efficiency. Applied current density could affect W content in FeW significantly, but not for NiW and CoW. In a basic bath, citrate is widely applied as a complexing agent. The most influent factor is ratio of W concentration in the electrolyte over the iron group elements.

A comprehensive investigation was performed by Vaaler and Holt [101]. They performed electrodeposition of NiW in a citrate bath, pH was fixed at 8. They compared the function of ammonia in the induced codeposition of NiW. They found that ammonia increased the current efficiency from < 3% to > 30% and decreased W content in the deposits. When citric acid concentration was 66 g/L, W concentration increased the W
Table 2: Typical baths for induced codeposition of W alloys

<table>
<thead>
<tr>
<th>No.</th>
<th>WO$_4^{2-}$ (M)</th>
<th>Iron Group Element (M)</th>
<th>Complexing Agent (M)</th>
<th>Others (M)</th>
<th>pH</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.076</td>
<td>Ni: 0.038</td>
<td>Citric Acid: 0.34</td>
<td>pH Adjusted by Ammonia or Sodium Hydroxide</td>
<td>6.2 - 8.6</td>
<td>[102]</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>Co: 0.013</td>
<td>Ammonium Citrate: 0.26</td>
<td>Boron Phosphate: 0.165; pH adjusted by ammonia</td>
<td>9.2</td>
<td>[100]</td>
</tr>
<tr>
<td>3</td>
<td>0.12</td>
<td>Ni: 1.58</td>
<td>Ammonium Citrate: 0 - 0.16; Citric Acid: 0.17</td>
<td>Nickel Ions were Added as Nickel Ammonium Sulfate</td>
<td>1.59 - 1.95</td>
<td>[95]</td>
</tr>
<tr>
<td>4</td>
<td>0.02</td>
<td>Co: 0.02</td>
<td>Triammonium Citrate (0.01 - 0.1) or Dimethyl Sulphoxide (0.01 - 0.1) or Both</td>
<td>Sodium Sulfate: 0.01; Boric Acid: 0.05</td>
<td>8</td>
<td>[54]</td>
</tr>
<tr>
<td>5</td>
<td>0.14</td>
<td>Ni: 0.06</td>
<td>Citrate: 0.3 - 0.5; Ammonium Chloride: 0.5</td>
<td>Sodium Bromide: 0.15</td>
<td>8.5</td>
<td>[92]</td>
</tr>
<tr>
<td>6</td>
<td>0 - 0.5</td>
<td>Ni: 0.1</td>
<td>Citrate: 0.2</td>
<td>-</td>
<td>8</td>
<td>[91]</td>
</tr>
</tbody>
</table>
Table 2: Typical baths for induced codeposition of W alloys (continuation)

<table>
<thead>
<tr>
<th>No.</th>
<th>WO$_4^{2-}$ (M)</th>
<th>Iron Group Element (M)</th>
<th>Complexing Agent (M)</th>
<th>Others (M)</th>
<th>pH</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.265</td>
<td>Ni: 0.02</td>
<td>Citrate: 0.135; Citric Acid: 0.065; Phosphoric Acid: 0.014; Boric Acid: 0.4; pH adjusted by Ammonia; 2-butyn-1,4-diol and Rokafenol N-10 as the Brightner</td>
<td>8.5</td>
<td>[89]</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.25</td>
<td>Ni: 0.02</td>
<td>Co: 0.02; Fe: 0.02</td>
<td>Sodium Citrate: 0.2; Phosphoric Acid: 0.11; Boric Acid: 0.365; pH adjusted by Ammonia; 2-butyn-1,4-diol and Rokafenol N-10 as the Brightner</td>
<td>8.5</td>
<td>[85]</td>
</tr>
<tr>
<td>9</td>
<td>0.2</td>
<td>Ni: 0.075</td>
<td>Citric Acid: 0.314</td>
<td>pH Adjusted by Ammonia</td>
<td>8.15</td>
<td>[84]</td>
</tr>
<tr>
<td>10</td>
<td>0.4</td>
<td>Ni: 0.01 - 0.1</td>
<td>Citrate: 0.25 - 0.6</td>
<td>-</td>
<td>8</td>
<td>[9]</td>
</tr>
</tbody>
</table>
content in the deposits, but not as much as in the electrolyte of 132 g/L citric acid. In both citric acid concentration electrolytes, Ni concentration of the electrolyte decreased W content in the electrolyte significantly, but enhanced the current efficiency. Tungstate increased current efficiency slightly in the electrolyte of low citric acid concentration, though decreased current efficiency in the electrolyte of high citric acid concentration. The concentration of citric acid decreased current efficiency. This effect was enhanced by the concentrations of nickel salt and tungstate in the electrolytes. The concentration of citric acid also decreased W content in the deposits. They also observed that temperature improved W content in the deposits, but only helped current efficiency in the electrolyte of limited concentrations of Ni ions and tungstate. Applied current density didn’t significantly affect the composition of deposits. When citric acid concentration was high, the applied current density enhanced current efficiency. In the low citric acid concentration electrolyte, no significant difference was observed. In the pH range 6 to 9, pH decreased W content in the deposit. Current efficiency reached a maximum at pH 7.5. They also tried codeposited elements with W other than iron group elements. Only Ag₂O, 8.8 g/L, successfully codeposited with W, but the deposit showed grey and spongy.

Younes et al. [90] investigated NiW induced codeposition in a similar citrate bath as Vaaler and Holt did, but they eliminated the ammonia. Younes et al. electrodeposited a deposit of up to 50 at.%, equivalently 76 wt.%, W content from aqueous solutions. When the concentration of Ni ions was 0.1 M, W concentrations in the electrolyte increased of W content in the deposit from ~2 to ~50 at.% at applied current density of 15 mA/cm². However, when ammonia was added, W in the electrolyte only increased W content in the deposit to ~10 at.%. They also found that in the pH range of 6.0 to 8.5, there was a
maximum W content of ~ 35 at.% at pH of 7.5 – 8.0. They also examined the crystalline structure of their deposits by X-ray diffraction. They suggested that an amorphous alloys were obtained when W content was from 20 at% to 40 at%. At lower W content deposits, a fcc solid solution $\text{Ni}_{(1-x)}\text{W}_x$ was detected. When W content was high, a 1/1 Ni/W alloy was observed.

Younes and Gileadi [87] investigated NiW electrodeposition. They observed that when ammonia is in excess and the concentration of citrate, 0.4 M, was bigger than the sum of W and Ni ions in the electrolyte, the concentration of Ni ions in the electrolyte increased current efficiency, potential and partial current densities of both Ni and W, but decreased W content in the deposits and partial current density of hydrogen evolution reactions, or the side reactions. Younes and Gileadi highlighted the effect on W partial current density. It indicated Ni ion was involved in the reduction of W reduction. Concentrations of W in the electrolyte were investigated in two electrolytes, one had 0.1 M Ni ions, and the other had 0.2 M Ni ions. Both electrolytes had excess ammonia and 0.6 M citrate. As expected, tungstate in the electrolytes increased W content in the deposits and reached a limit at ~ 0.3 M. It was also observed that when concentration of tungstate was small, < 0.2 M, W partial current density was not significantly affected by Ni ions concentrations in the electrolyte. Beyond this range, Ni ion concentration in the electrolyte increased W partial current density. The effect of citrate was investigated in the baths containing tungstate, 0.1 M; Ni ions, 0.1 M and excess ammonia. Younes and Gileadi showed that when citrate concentration was larger than 0.2 M, the sum of tungstate and Ni ions, the current efficiency dropped dramatically. It was observed that <~ 0.5 M citrate increased W content slightly, but when citrate concentration was larger
than that, it decreased W content dramatically, which was accompanied with that partial current density of hydrogen evolution reaction stopped increasing and reached a limit. This result suggests that W induced codeposition is related to the hydrogen evolution reaction. Mass transfer was investigated by varying rotating rate in the two electrolytes: one had 0.4 M tungstate and 0.04 M nickel sulfate, and the other had 0.04 M tungstate and 0.4 M nickel sulfate. In both electrolytes, rotation rate slightly increased W content in the deposits and W partial current density. It was of interest that the W partial current density increased more in the former electrolyte of less Ni ions than the latter of less tungstate. Applied current density was examined in the same electrolyte. They found that the applied current density increased W partial current density and the current efficiency. The current efficiency reached a limit at 30 mA/cm². In the electrolyte of high Ni ion concentration, the limit was close to 90%, but in the other electrolyte, this limit was ~40%. Then they examined the role of ammonia in electrolytes of pH 8. Ammonia was varied from 0 to 2 M. In this range of ammonia concentrations, ammonia decreased W content in the deposit from ~33 to ~13 at.%. Current efficiency reached a maximum at ~0.8 M. They also investigated the role of pH in this system, they highlighted the pH range from 8 to 9, the partial current density of Ni increased dramatically which leaded to a sharp decrease of W content in the deposit. To explain their observation, they raised an overall reaction as

\[
[(\text{Ni})(\text{HWO}_4)(\text{Cit})]^{2-} + 8\text{e}_\text{M} + 3\text{H}_2\text{O} \rightarrow \text{NiW} + 7(\text{OH})^- + \text{Cit}^{3-}
\] (2.2.1)

The complexing species, \([((\text{Ni})(\text{HWO}_4)(\text{Cit}))^{2-}]\), was formed by

\[
[((\text{Ni})(\text{Cit}))^- + [(\text{HWO}_4)(\text{Cit})]^{4-} \rightarrow [(\text{Ni})(\text{HWO}_4)(\text{Cit})]^{2-} + \text{Cit}^{3-}
\] (2.2.2)

They also admitted that this complexing species has not been detected experimentally.
Younes-Metzler *et al.* [83] continued their investigation in NiW induced codeposition. In this work, they tried to provide more support to their theoretical mechanism, reactions 2.2.1 and 2.2.2, by examining bath chemistry. As in their previous work, they investigated NiW induced codeposition by varying tungstate, Ni ions, citrate, temperature and pH in similar electrolytes. Similar behaviors were observed as in their prior works. The undetected complexed species may form according to

\[
K \times c[(\text{Ni})(\text{WO}_4)(\text{Cit})(\text{H})]^{2-} = c[(\text{Ni})(\text{Cit})]^- \times c[(\text{WO}_4)(\text{Cit})(\text{H})]^{4-} \quad (2.2.3)
\]

where \( K \) is a stability constant for \([(\text{Ni})(\text{WO}_4)(\text{Cit})(\text{H})]^{2-}\), and that \( K \times c[(\text{Ni})(\text{WO}_4)(\text{Cit})(\text{H})]^{2-} \) should be a constant confirmed by the product of \( c[(\text{Ni})(\text{Cit})]^- \) and \( c[(\text{WO}_4)(\text{Cit})(\text{H})]^{4-} \). They observed the partial current density of W increased linearly with \( K \times c[(\text{Ni})(\text{WO}_4)(\text{Cit})(\text{H})]^{2-} \).

The crystalline structure of NiW was examined by Zhu *et al.* in 2002 [86]. The W content in the deposit changed the crystalline structure of electrodeposited NiW alloys from fcc Ni-type crystalline to amorphous, then back to crystalline, orthorhombic alloy. Scanning tunneling microscopy, atomic force microscopy and scanning electron microscopy were also performed to investigate the morphology of the deposits with varied W content in the deposits. They observed cracks on low W content deposits with fcc Ni-type crystalline structure. They attributed this to hydrogen embrittlement. For orthorhombic structure, the surface morphology had well-arranged fine grains. The deposits were a mixture of the two crystalline structures: crystalline (fcc) and crystalline (orthorhombic). A further work of NiW crystalline structure was conducted by Sridhar *et al.* [82]. NiW deposits electrodeposited from citrate solutions without ammonia at varied temperatures were examined by X-ray diffraction. They observed that, at temperatures of
50 – 70 °C and low current density, Ni₄W with body-centered tetragonal phase was identified.

Another work about crystalline structures of W alloys was performed by a group from Japan. [83] They examined 3 types of deposits, NiW with 16 at% W content, NiW with 20.7 at% W content and FeW with 21.6 at% W content by X-ray diffraction, small angle X-ray scattering and Extended X-Ray Absorption Fine Structure. The average crystal-grain sizes were determined by small angle X-ray scattering, 24.0 Å for NiW with 16 at% W content and 24.6 Å for NiW with 20.7 at% W content. FeW was amorphous which showed only short range order, no medium range order. They also suggested that the NiW alloys had a similar structure as Ni₄W crystal phase. For the NiW alloys, The nearest distance between Ni-Ni and Ni-W were 2.49 and 2.50 Å.

Wikiel and Osteryoung [99] examined induced codeposition of amorphous CoW by voltammetric techniques. On two substrates of glassy carbon and platinum microelectrodes, they performed cyclic voltammetry in four electrolytes, (1) ammonium citrate and boron phosphate (2) with sodium tungstate (3) with Co ions and (4) with both sodium tungstate and Co ions. The major difference between two substrates was the hydrogen evolution reactions. It was observed partial reduced W oxide was formed on glassy carbon substrate, but not on the platinum microelectrodes, in the second electrolyte of just tungstate and complex ligand. They attributed this to enhanced hydrogen evolution reactions on the platinum microelectrodes. There was an anodic peak observed on both substrates. They were due to the oxidation of metallic CoW deposits. They also performed chronoamperometric examination on both microelectrodes in the electrolyte of ammonium citrate with sodium tungstate and Co ions. On the glassy carbon electrode,
they found it was progressive nucleation and 3-dimentional growth at the potential of -0.95 and -0.97 V vs SCE, but it was instantaneous nucleation followed by 3-dimentional growth at higher potential, -1 V vs SCE. Chronoamperometry was also performed on platinum microelectrodes. Due the lower overpotential of the hydrogen evolution reaction, very different behaviors were observed, which represented the hydrogen evolution reaction, but not CoW induced codeposition. On the platinum microelectrode, they found activation energy of 39 kJ/mol for CoW induced codeposition at -1 V vs SCE by variable temperatures.
3.0 EXPERIMENTAL

3.1 Electrodeposition of Mo-Rich, MoNi Alloys from an Aqueous Electrolyte

MoNi alloys were electrodepositozed from room temperature, aqueous electrolytes containing nickel sulfate, 0.02 M, sodium citrate, 0.25 M and sodium molybdate, 0.04–0.8 M with pH 9.7, adjusted by sodium hydroxide and sulfuric acid. Vertically placed copper substrates were used as a working electrode with area of 0.533 cm². The counter electrode was a platinum mesh, and the reference electrode was Ag/AgCl. The electrodeposition setup was sketched in Figure 3.1.1. All of the deposits were produced galvanostatically, for 1 hr, by means of a Solartron, model 1287 and Zahner IM6ex. Ohmic drop was corrected by electrochemical impedance spectroscopy (EIS), model 1252A over a broad frequency range, 0.1–105 Hz.

![Figure 3.1.1: Sketch of stagnant cell.](image-url)
3.2 Induced Codeposition Behavior of Electrodeposited NiMoW Alloys

NiMoW and NiW were electrodeposited on rotating cylinder electrodes (RCE) of Cu with a diameter of 1.0 cm and a length of 1.2 cm, Figure 3.2.1. A dimensionally stable anode coated with gold was used as the counter electrode, and the reference electrode was Ag/AgCl. Cathodic current densities were varied over a wide range from 10 to 500 mA/cm\(^2\). The rotation rate was controlled with a Pine Instruments modulated speed high precision rotator. A rotating Hull cell, from Autolab, was also used when a range of current densities are desired. Figure 3.2.2 shows a sketch of the rotating Hull cell containing the working electrode rod and surrounded by the counter electrode. The working electrode was brass rod of 6 mm diameter and 8 cm length, and the counter electrode was a dimensionally stable anode coated with gold. For NiW and NiMoW electrodeposition the following electrolyte was used: 0.1 M NiSO\(_4\)·6H\(_2\)O, 0.075 M Na\(_2\)WO\(_4\)·2H\(_2\)O, 0.375 M Na\(_3\)C\(_6\)H\(_5\)O\(_7\)·2H\(_2\)O, 1 M H\(_3\)BO\(_3\), with either 0, 0.005 M or 0.075 M Na\(_2\)MoO\(_4\)·2H\(_2\)O at pH 7.0. For a comparison with the alloy, elemental Ni was also electrodeposited from a similar electrolyte which contained the same constituents as the NiMoW electrolyte, but without molybdate and tungstate.

Electrodeposition was galvanically controlled using a Solartron SI 1287 and the applied potential was corrected for ohmic drop with impedance spectroscopy using the real component intercept when frequency is high. In all cases, the electrodeposition time was 1 hr. The composition and thickness of the deposits were examined by XRF, model Kevex Omicron. The partial current densities were calculated according to Faraday’s law.
Figure 3.2.1: Sketch of rotating cylinder cell.

Figure 3.2.2: Sketch of the rotating Hull Cell.
3.3 Pulse Electrodeposition of NiMoW Alloys

Copper rotation cylinder electrodes (RCE), Figure 3.2.1, were used to maintain a comparable boundary thickness at 517 rpm, with a diameter of 1.0 cm and a length of 1.2 cm. A gold anode was used as the counter electrode, and the reference electrode was Ag/AgCl. The electrolyte contained 0.1 M NiSO$_4$·6H$_2$O, 0.075 M Na$_2$WO$_4$·2H$_2$O, 0.375 M Na$_3$C$_6$H$_5$O$_7$·2H$_2$O, 1 M H$_3$BO$_3$, 0.005 M Na$_2$MO$_4$·2H$_2$O at pH 7.0. NiMoW was electrodeposited by pulse current, generated by a PINE Instrument Company AFCBP1, triggered by a function generator, model AMEL 568. The pulse cathodic current density on times were 10 and 75 mA/cm$^2$ and the off time was zero. Frequency and duty cycle were varied. The frequency and duty cycle are defined as $f = \frac{1}{t_{on} + t_{off}}$ and duty cycle = $\frac{t_{on}}{t_{on} + t_{off}}$, respectively. In all cases, the total on time was 1 hr and electrodeposition was performed at room temperature. The deposit composition was analyzed by x-ray fluorescence (XRF), with Kevex, model Omicron XRF, and macro-scale morphology observed with an optical Zeiss microscope, model Axio Imager M1m.

3.4 Photoactive Behavior in Induced Codeposition of NiW

Three electrolytes were used for IMPS. The first one was of NiW which contained 0.375 M sodium citrate, 1 M boric acid, 0.075 M sodium tungstate, 0.15 M nickel sulfate and pH was 7. The second was of Ni contained 0.375 M sodium citrate, 1 M boric acid, 0.1 M nickel sulfate and pH was 7. The last one contained no alloy element ions and contained: 0.375 M sodium citrate, 1 M boric acid, and pH was 7. In Figure 3.4.1, the
Figure 3.4.1: Sketch of photoelectrochemical cell.

Working electrode was polycarbonate membrane of 25 mm diameter with holes of 0.4 µm sputtered 45 nm thick gold by HUMMER sputtering machine, then a thin film of Ni was electrodeposited from the Ni electrolyte for 1 hr. The reference electrode was Ag/AgCl and the counter electrode was a platinum wire. IMPS and the pretreatment before it were conducted using a Zahner IM6ex and Zahner PP210 systems. IMPS was performed in a frequency range of 500 Hz to 3000 kHz. In Figure 3.4.2, the generated UV light carried a wavelength of 365 nm. The cyclic voltammetry was conducted using a Bipotentiostat, model AFCBP1, from PINE Instrument Company in the applied potential range of -0.4 to -1.1 V vs Ag/AgCl with a sweep rate of 50 mV/s.
Figure 3.4.2: The setup of IMPS.
4.0 RESULTS AND DISCUSSION

4.1 Electrodeposition of Mo-Rich, MoNi Alloys from an Aqueous Electrolyte

As introduced in section 2.1.1, molybdenum alloys with nickel are well recognized for their superior corrosion resistance [16-20] and wear resistance [21-23] properties, and outstanding catalytic ability for the hydrogen evolution reaction [24-39, 104]. The electrodeposition of these alloys is referred to as “induced codeposition;” [105] molybdenum cannot be reduced alone from an aqueous solution, but can be fully reduced if codeposited with inducing elements, such as iron, nickel and cobalt, the iron-group metals. Similar behavior has also been observed with tungsten [105]. A consequence of this deposition behavior is that it is a challenge to achieve high Mo deposit concentration, due to the co-reduction of the iron-group ion, e.g., Ni. Typically Mo content in alloys with nickel from aqueous electrolytes has been less than 50 wt%, with electrolytes containing ammonia [59, 63, 64, 120-124]. The potential range is usually between −0.7 to −2 V vs Ag/AgCl. In 1996, Podlaha and Landolt [59] reported MoNi alloys with Mo content as high as 70 wt%, with the elimination of ammonia, and in this same vein, Younes and Gileadi [91] reported a NiW alloy with high W content, 76 wt%. In Mo or W electrolytes, ammonia addition is associated with an increase current efficiency, but at the expense of a lowered Mo or W deposit concentration [59, 63, 78, 124]. An alternative way to fabricate a high content Mo alloy is to utilize composite codeposition, incorporating Mo(s) particles in the electrolyte and capturing them in the deposit during the reduction of nickel and molybdate ions. Niedbala [125] achieved a Mo deposit composition of 79 wt% in this fashion.
As it was introduced in section 2.1.2, several mechanisms have been presented to explain the induced codeposition behavior by Ernst and Holt [113], Fukushima, et al. [67] and Chassaing et al. [64]. Inherent to both the Fukushima and Chassaing models is that there is an upper limit for Mo (or W) codeposition in an alloy. While it was possible to find deposition conditions where increasing Mo concentration in the deposit was accompanied by a drop in the current efficiency and thus hydrogen evolution, it was also possible to find the contrary situation, calling into question the decisive role of hydrogen as noted by Podlaha and Landolt [60], which was also introduced in section 2.1.2. It was noticed that if the nickel rate can be reduced or blocked, then this may be one strategy to enhance the amount of molybdenum in the deposit.

In this work, the molybdenum-nickel electrolyte, without ammonia, is reexamined as a path toward electrodepositing high Mo content alloys with nickel. The deposits are characterized for their catalytic hydrogen evolution property in sodium hydroxide. Unlike the analogous reports with tungsten, the desired alloys were obtained only at very large applied potentials, > −2 V vs Ag/AgCl. It is the first report of MoNi electrodeposited alloys exceeding the 70 wt% Mo record of 1996.

4.1.1 Deposit Composition and Thickness

Figure 4.1.1 presents the deposit (a) composition and (b) thickness results of the galvanostatic deposits without electrode or electrolyte agitation, and reduced with three different molybdate electrolyte concentrations. It is not a quiescent solution as there is considerable hydrogen evolution that provides mixing in the vicinity of the electrode. Low current densities, <100 mA/cm², did not result in a metallic deposit and appeared black, indicative of an oxide formation. The surface of the deposits at current
densities >200 mA/cm² appeared gray and these composition and thickness data are shown in Figure 4.1.1. Between 100 and 200 mA/cm² there was a transitional region where the deposits appeared black-gray. All deposits exceeded 60 wt% Mo. An increase in the molybdate ion concentration in the electrolyte increased the amount of molybdenum in the deposit at a given current density, and also shifted the region where metallic deposits were obtained to higher applied current densities. The highest value, 82 wt% Mo, was obtained in a deposit with an applied, cathodic current density of 500 mA/cm² in the 0.8 M molybdate electrolyte. Moreover, to achieve the same deposit thickness, a higher molybdate concentration electrolyte required more applied current density.
Figure 4.1.1: Galvanostatic MoNi electrodeposition on stationary Cu substrates (a) deposit concentration and (b) thickness for a 1 hr deposition time.

SEM examined the morphology of the deposits, presented in Figure 4.1.2 at two different magnifications. At a low magnification, Figure 4.1.2a, nodules, having a diameter from 0.5 to 2 μm, were uniformly distributed on the surface, with the highest population in the 1–1.5 μm diameter range. Micro-cracks were also observed on the surface, around the nodules. Inspection of the nodules at higher magnification is shown in Figure 4.1.2b. Nanoscale features were evident on the top of nodules, providing additional surface roughing.
Figure 4.1.2: SEM of a sample with 76 wt% Mo content at (a) 15 kX and (b) 150 kX.

The potential was measured during deposition, and representative potential measurements are presented in Figure 4.1.3a – c. The cathodic potential has significant fluctuations due to the hydrogen gas bubble generation, but is relatively steady after 500 s.
The current densities applied in Figures 4.1.3 (a) 500, (b) 650 and (c) 800 mA/cm\(^2\) correspond to the MoNi deposits from the 0.8 M molybdate electrolytes. More fluctuations were observed at 800 mA/cm\(^2\), compared to the 500 and 650 mA/cm\(^2\) examples, although the number of fluctuations did not always increase with applied current density. On the other hand, the amplitude of the fluctuations consistently increased with applied current density.
Figure 4.1.3: Representative potential measurements in stagnant cell at (a) 500, (b) 650 and (c) 800 mA/cm$^2$.

With an increase in the applied current density, more fluctuations was observed. There is ohmic drop as part of this measurement, and it was characterized with electrochemical impedance spectroscopy (EIS). The resulting Nyquist plot is shown in Figure 4.1.3 at two potential ranges, (a) at a potential were there was visibly no gas bubble formation at a steady state potential of $-1$ V vs. Ag/AgCl and (b) at very large applied potentials with voluminous hydrogen formation. The potential and amplitude used in Figure 4.1.4a was $-1$ V vs. Ag/AgCl and 10 mV, respectively. The ohmic resistance in Figure 4.1.4a was 7 $\Omega$. This same amplitude was used with more negative steady state potentials and a linear impedance response in current was not obtainable, attributed to the current fluctuations from hydrogen evolution observed in Figure 4.1.3. These fluctuations are at most on the order of 100 mV, thus an amplitude of only 10 mV for EIS is within this fluctuation band. Hence, at very large steady state potentials the amplitude was increased to 300 mV and the resulting spectra is presented in Figure 4.1.3. Note that the expected region for ohmic resistance is affected by the gas bubble formation, but not significantly. An inductive feature is also present, characteristic of an adsorption
process, as expected for the hydrogen evolution reaction. The ohmic drop correction is quite substantial, for example, at 500 mA/cm², the measured potential was −4.8 V with a corrected potential at the working electrode of −3 V.

![Graph](image)

Figure 4.1.4: Impedance measurement of electrolyte with 0.8 M molybdate at (a) −1 V (b) −4.5, −5 and −6 V in stagnant Cell.

4.1.2 Partial Current Densities

The current efficiencies of all the electrodeposits were less than 1%; the current efficiency of the deposit with the highest Mo content is 0.02% in 0.8 M molybdate electrolyte at 500 mA/cm². In comparison to an ammonia free nickel tungstate electrolyte,
Younes and Gileadi reported a low current efficiency, \( \sim 5\% \), accompanied with their observation of ultra high, 76 wt\% W composition. The current efficiency with Mo is lower. This difference may be attributed to the larger ratio of reluctant metal to inducing metal, \( \frac{C_{\text{Mo(IV)}}}{C_{\text{Ni(II)}}} \) of 40, compared to the ratio \( \frac{C_{\text{W(IV)}}}{C_{\text{Ni(II)}}} \) of 4, that may be contributing to a greater side reaction.

Partial current densities of both Mo, \( i_{\text{Mo}} \), and Ni, \( i_{\text{Ni}} \), were calculated by Faraday’s law, using the composition and thickness data presented in Figures 4.1.1, and are shown in Figure 4.1.5. As the molybdate concentration in the electrolyte is decreased there is a shift in the working electrode potential to less noble values, to achieve the same partial current densities (Figure 4.1.5a). Hence, a higher overpotential was required for the lower molybdate concentration. The same is true for the nickel partial current density (Figure 4.1.5b), and it is parallel to the molybdenum partial current densities. Since the amount of molybdate ions are two orders of magnitude larger than the nickel ions, according to the mechanism presented by Podlaha and Landolt \([60]\), the reaction rate of molybdenum reduction should be limited by the small amount of nickel ions and both partial current densities are expected to be parallel.

The effect of different molybdate electrolyte concentrations resulted in deposits achieved in different working potential ranges, largely dictated by the hydrogen evolution side reaction. Larger amounts of molybdate in the electrolyte lead to an increase in the side reaction rate, (Figure 4.1.5c), and confined the potential range window that could be achieved. An increase in the side reaction with molybdate electrolyte concentration has also been observed in the literature, by Beltowska-Lehman \([124]\). When the side reaction rate is most accelerated, in the 0.8 M molybdate electrolyte, both the partial current
densities of Mo and Ni are lower compared to the other electrolytes with smaller molybdate electrolyte concentration, \textit{i.e.}, 0.04 and 0.4 M molybdate. Furthermore, the nickel partial current density is decreased more than molybdenum resulting in a deposit rich in Mo. This result suggests that the working electrode surface may be partially blocked by absorbed hydrogen from the side reaction, preferentially blocking the Ni reaction rate at lower overpotentials. Also consistent with Figures 4.1.1a and 4.1.1b, an increase in electrolyte molybdate concentration resulted in a thinner deposit with more Mo(s) at the same applied current density. Thus, the factors that play an important role in MoNi deposition are: \textit{i}. the molybdate ions accelerate the side reaction with an increase in adsorbed hydrogen, \textit{ii}. the adsorbed hydrogen blocks the electrode surface competing disproportionately with metal reaction adsorbed intermediates, decreasing the rate of nickel more than molybdenum and \textit{iii}. the increase in applied current density or overpotential drives the nickel reduction more than molybdenum reduction.

![Graph showing Mo partial current density vs. potential vs. Ag/AgCl, V](image-url)
Figure 4.1.5: (a) Mo, (b) Ni and (c) side reactions partial current densities of galvanostatic MoNi electrodeposition on stationary Cu substrates, potentials corrected for ohmic drop.

4.1.3 MoNi Polarization in NaOH

Molybdenum alloys are identified by their superior hydrogen evolution kinetics. While the “best” deposit composition varies from author to author [24-39, 104]. There is a growing consensus that there is an optimum composition, and perhaps structure. To
assess the viability of the high MoNi deposits as catalysts, polarization in NaOH was examined. Figure 4.1.6 reports the (a) polarization curves compared with the copper substrate, and the resulting (b) Tafel slope and exchange current density. All open circuit potentials of MoNi deposits are less noble than the copper substrate, and have higher cathodic current densities for the hydrogen evolution reaction, as expected. A higher exchange current density, \( i_0 \), was observed for the deposits with Mo contents in the range of 65 to 69 wt.% Mo. The exchange current density values reported here are consistent and even higher than those reported in the literature [32, 126, 127], although the higher values may be attributed to the rougher surface area. Below a Mo deposit concentration of 70 wt%, the cathodic Tafel slope is between 30–45 mV/decade, and then changes over to 100 mV/decade with higher Mo deposit content. Jakšić noted that NiMo alloys follow the Volmer-Heyrovsky mechanism in base electrolytes, at high adsorbed hydrogen surface coverage, according to reaction 4.1.1 and 4.1.2.

\[
\text{M} + \text{H}_2\text{O} + \text{e} \leftrightarrow \text{MH}_{\text{ads}} + \text{OH} \quad \text{Volmer reaction} \\
\text{MH}_{\text{ads}} + \text{H}_2\text{O} + \text{e} \leftrightarrow \text{H}_2 + \text{M} + \text{OH} \quad \text{Heyrovsky reaction}
\]

(4.1.1) (4.1.2)

The Tafel slopes reported here do indeed correspond closely to the Volmer-Heyrovsky mechanism, however, with a change in hydrogen coverage when the second step (Heyrovsky step) is rate determining. For the high molybdenum deposits >70 wt% the higher cathodic Tafel slope is close to that theoretically predicted when the second adsorption step is rate determining \( ([\beta 2F/(RT2.303)])^{-1} \sim 120 \text{ mV/decade assuming a value of } \beta \text{ to be 0.5}) \) for high coverage. For deposits containing lower amounts of Mo ranging between 62–69 wt%, a lower cathodic Tafel slope can be determined theoretically if the coverage is small, with the same rate determining step.
((\beta^2 + 1)F/(RT2.303))^{-1} \sim 40 \text{ mV/decade}). If the first step (Volmer step) is rate controlling at high coverage the Tafel slope would correspond to a different value of 
\[ [F/(RT2.303)]^{-1} \sim 60 \text{ mV/decade}, \] which is much higher than the reported data for the 62–69 wt% Mo composition, and much lower than the data for Mo deposit composition >70 wt%, and thus the first step is most likely not the rate determining one. Thus differences in the Tafel slope may be due to differences in the hydrogen adsorption coverage, suggesting also, that during electrodeposition the deposit composition influences hydrogen adsorption and in turn affects the relative rates of metal reduction.
Figure 4.1.6: Catalytic behavior of MoNi electrodeposits (a) polarization curves, (b) cathodic Tafel slopes and hydrogen evolution exchange current densities.

4.2 Induced Codeposition Behavior of Electrodeposited NiMoW Alloys

As introduced in sections 2.1.1 and 2.2.1, molybdenum and tungsten alloys with nickel are well known for their outstanding corrosion resistance [17, 128, 129], wear resistance [130-132], and catalytic ability for the hydrogen evolution reaction [30, 104, 126, 127, 133, 134]. Moreover, their enhanced hardness combined with improved tribological properties (e.g., wear resistance), primarily for the W-alloys, make them ideal for microelectromechanical structures (MEMS) [11, 12] and micro-tools. To obtain these properties and applications, it is crucial to control the deposit composition and morphology. Since the electrodeposition of molybdenum and tungsten alloys are still not well understood, the conditions of electrodeposition are typically determined empirically.
It was introduced in section 2.0 that induced codeposition of molybdenum and tungsten was first identified by Brenner [105] recognizing that in aqueous solution molybdenum and tungsten ions cannot be fully reduced to a metallic state, but can be completely reduced in the presence of iron group elements, such as nickel. Experimentally, the codeposition of NiMo [59, 104, 112], CoMo [45, 122], FeMo [112, 124], NiW [84, 104, 124], CoW [115, 135], and FeW [72, 115], has been widely examined in a variety of aqueous electrolytes. In many of these electrolytes ammonium hydroxide is a key component to achieve high current efficiencies in excess of 60%, although with relatively low amounts of the reluctant metal (i.e., Mo or W) in the deposit. Vasauskas et al. [136] has noted that ammonia species provides a large buffer capacity at high pH that may contribute to the high efficiency. Decreasing the amount of ammonia in the electrolyte can be used as a strategy to increase Mo [59] and W [87] in deposits when codeposited with Ni, albeit at low current efficiency ≤ 10%. The addition of ammonium hydroxide to aqueous solutions can yield appreciable aqueous ammonia depending on the pH, which can be problematic in a plating line as the ammonia readily volatilizes, and can be oxidized at the anode [137], thus its concentration is not easy to maintain. Chronic exposure to ammonia can irritate the eyes, nose and upper respiratory tract [138]. CoW alloys having up to 51 wt% W and current efficiencies of 50% have been reported by Weston et al. [71] from ammonia free electrolytes containing gluconate and similar results have been achieved in citrate-boric acid electrolytes at neutral pH for CoW [139, 140]. No ammonia free aqueous electrolytes with efficiencies surpassing 50% have been reported for Mo alloys.
It was introduced in sections 2.1.2 and 2.2.2 that the mechanism of induced codeposition is still not well defined. Some key features for the Mo alloy system have been captured by models introduced by Fukushima et al. [67], Chassaing et al. [64], and Podlaha and Landolt [58-60]. A common adsorption mechanism that has been adopted for the iron-group elements is one where the adsorbed species promotes the reduction of the metal ion [141-143],

$$\text{Ni}(\text{II}) + e^- \rightarrow \text{Ni}(\text{I})_{\text{ads}} \quad (4.2.1)$$

$$\text{Ni}(\text{I})_{\text{ads}} + \text{Ni}(\text{II}) + 2e^- \rightarrow \text{Ni(s)} + \text{Ni}(\text{I})_{\text{ads}} \quad (4.2.2)$$

A similar approach has also been presented by Chassaing and Wiart [144] to describe Ni(II) reduction with Zn(II), where a mixed intermediate, $$(\text{NiZn})_{\text{ads}}^+$$, is believed to catalyze the discharge of Ni$^{+2}$ ions.

In section 4.1, it was observed that the partial current density of Ni can be inhibited with a large co-reducing hydrogen side reaction rate, attributed to adsorbed hydrogen species, and following a Volmer-Heyrovsky [32] mechanism according to reactions 4.1.1 and 4.1.2, with the second step rate determining. Brenner [105] has suggested that there is an analogous behavior of Mo induced codeposition that can also hold for W induced codeposition. Eliaz and Gileadi [47, 78] proposed a mechanism for W induced codeposition where deposition may originate from mixed-metal complexed species rather than adsorbed species. While there is some evidence that a NiMo adsorbed species can indeed exist, observed via in situ Raman spectroscopy [52, 57], the alternative complexed species have not yet been experimentally observed.

There is currently not a general consensus on how these alloys codeposit and in particular the nature of the inducing species. Thus the control of the deposit composition
and subsequent structure leading to the desired properties are still difficult to predict \textit{a priori}. Here, Mo and W are induced together with Ni to examine the induced codeposition behavior. There are a few reports of the electrodeposition of NiMoW, though not for the purpose of examining induced codeposition. Zhu and Yao [145] investigated the electrodeposition of NiMoW in a citrate bath and showed that the crystalline structure is influenced by the deposit composition. They also compared the morphology of NiMo and NiMoW and observed cracks in the NiMo deposits when the Mo content was higher than 40 at \%. With the addition of W in NiMoW alloys with similar Mo content, no cracks were observed. Cesiulis et al. [146] investigated the electrodeposition of NiMoW alloys in a pyrophosphate bath and deposit morphology. A small addition of molybdate to a NiW electrolyte eliminated macro-cracks observed in NiW, when the W content in the deposits was less than 5 \textasciitilde 6 at.\%. But if the W content in the deposits was higher than this, cracks were observed.

NiMoW alloys are best known as catalytic precursors for creating a transition metal sulfide that is used for the removal of heteroatoms (N, S, O) in the presence of large amounts of hydrogen in hydrodesulphurization of organic molecules such as thiophene, benzo thiophene and dibenzo thiophene [147-150]. In this context the addition of Mo to NiW is advantageous because it promotes an amorphous structure that when treated at high temperature with H_{2}S/H_{2} results in a NiMoWS active catalyst. Electrodeposited NiMoW was also considered as a promising catalyst candidate for the hydrogen evolution reaction by Raj et al. [39, 151]

Here, NiMoW was electrodeposited in citrate-boric acid electrolytes onto rotating cylinder electrodes with varied molybdate concentration, and the partial current densities
of each metal reduction determined. The reaction orders, with respect to molybdate concentration, were compared to an adsorption model that includes either a nickel ion species or a nickel adsorbed species as the inducing agent for molybdate and tungstate reduction. Both Mo and W induced codepositions are compared together in one electrolyte in order to observe if the nickel inducing agent preferentially helps to reduce one element over the other. It is the first report of examining the reaction orders of this system, and to identify the coupled nature of the reduction of molybdate and tungstate in the presence of a nickel inducing agent.

4.2.1 Results

Figure 4.2.1 presents the deposit composition of NiMoW and NiW alloys at a constant rotation rate of 517 rpm in the turbulent flow regime for an RCE, Figure 3.2.1. In Figure 4.2.1a, the NiMoW alloy results are electrodeposited from the 0.075 M MoO$_4^{2-}$ electrolyte with equimolar WO$_4^{2-}$. Despite, the same amount of MoO$_4^{2-}$ and WO$_4^{2-}$ in the electrolyte there is significantly more Mo in the deposit, (∼65 wt.% Mo, ∼30 wt.%Ni, ∼5 wt.% W). Also, the Mo, W and Ni composition was nearly constant throughout the whole cathodic current density range from 50 to 450 mA/cm$^2$. Below 50 mA/cm$^2$, no metallic deposits were observed. When the concentration of MoO$_4^{2-}$ was reduced to 0.005 M (Figure 4.2.1b), the Mo amount in the deposit decreased and the amount of Ni and W consequently increased. With an increase of applied current density, the composition changed: Mo and Ni content in the deposits slightly increased with a significant drop in the W amount. A similar behavior was also observed in the electrodeposition of NiW alloys (Figure 4.2.1c) there is a large drop in the W content in the deposits decreasing from ∼50 wt.% to less than 10 wt.% with applied current density. It is a more dramatic
decrease than in the electrolyte containing 0.005 M MoO$_4^{-2}$. A decrease in the amount of W at high current densities in a NiW system has been previously observed by others, such as Younes et al. [86] and Ibrahim et al. [135].
Figure 4.2.1: Compositions of NiMoW and NiW alloys electrodeposited in electrolytes of (a) 0.075, (b) 0.005 and (c) 0 M molybdate.

Figure 4.2.2: Efficiency of NiMoW and NiW and Ni electrodeposition.

The current efficiency is shown in Figure 4.2.2. At cathodic current densities larger than 200 mA/cm$^2$, water reduction dominates and efficiency is on the order of 1%. At cathodic current densities between 50 and 200 mA/cm$^2$ there are larger differences in
the efficiency between the three electrolytes. The largest efficiency occurs when there is no MoO$_4^{2-}$. At 10 mA/cm$^2$, and with the addition of 0.005 M molybdate the current efficiency is one order of magnitude lower than with no molybdate in electrolyte. A further increase in molybdate concentration to 0.075 M resulted in no deposit generated at 10 mA/cm$^2$. Deposits were only obtained when the applied cathodic current density was 50 mA/cm$^2$ or larger from this electrolyte. All deposits from the 0.075 M electrolyte had very low current efficiencies $\sim 1\%$. 

![Graph (a)](image1.png)

![Graph (b)](image2.png)
Figure 4.2.3: Partial current densities of (a) Mo, (b) Ni, (c) W and (d) side reactions for the electrodeposition of NiMoW, NiW and Ni.

The partial current densities are shown in Figure 4.2.3 for the galvanostatic deposition from the three electrolytes, determined from the composition and thickness measured by XRF, and plotted versus the steady state potential corrected for ohmic drop. The Mo partial current density, in Figure 4.2.3a, is relatively insensitive to potential. An increase in the molybdate concentration in the electrolyte doesn’t increase the Mo partial
current density, but decreases it. At low overpotential, (e.g. −1.6 V vs Ag/AgCl) the reaction order with respect to molybdate was \[ \frac{\partial \log(i_{Ni})}{\partial \log(C_{MoO_4^{2-}})} = -0.7 \]. At large overpotentials, mass transport effects are expected to dominate and thus an increase in \(\text{MoO}_4^{2-}\) should increase the partial current density, not decrease it. Thus, kinetic effects may dominate and species may be hindered from reaching the surface to react.

Both the Ni partial current density, Figure 4.2.3b, and the W partial current density, Figure 4.2.3c decrease significantly when Mo is codeposited. For example, at a potential of −1.6 V vs Ag/AgCl the change of the log \(i_{Ni}\) with the log of the concentration of molybdate, \[ \frac{\partial \log(i_{Ni})}{\partial \log(C_{MoO_4^{2-}})} = -1 \] and that for the partial current density of W, \[ \frac{\partial \log(i_{W})}{\partial \log(C_{MoO_4^{2-}})} = -1.5 \], in other words an apparent reaction order that is negative with molybdate for both Ni and W. Introducing more molybdate inhibits Ni and W reduction rates. When Ni is electrodeposited alone, superimposed on Figure 4.2.3b, Ni reduction behaves kinetically controlled, with an increase in the partial current density with potential.

The side reaction partial current density, Figure 4.2.3d, shows a difference in slope when \(\text{MoO}_4^{2-}\) is present in the electrolyte, decreasing with higher amounts of molybdate. Hence, the lowering of the current efficiency is due to the metal reduction rates being inhibited. In section 4.1, it was suggested that adsorbed hydrogen can affect the electrodeposition of NiMo alloys by limiting the available surface area on the working electrode. Note that the hydrogen evolution side reaction rate can be also affected by the composition of the deposits. For example, Jaksic et al. [32] examined the
hydrogen evolution reaction kinetics on NiMo electrodes of varied Mo content and showed that the Mo content in the electrodes is a crucial factor in determining the catalytic property. The composition of NiW is as important as NiMo to catalyze the hydrogen evolution reaction [152]. Additionally, an argument for the enhanced catalytic ability of both NiW and NiMo rests in Trasatti’s [153] classic volcano-type curve showing the dependence of the logarithm of the hydrogen evolution exchange current density on the intermediate transition metal-hydrogen bonding strengths. Interpolating from their data collection [153] elemental Ni, has a M-H bond strength of 47 kcal/mol, and is on one side of this plot, exhibiting a weak chemisorption of hydrogen, and for both Mo and W, their M-H bond strengths are about 75 kcal/mol, on the other side of the plot with a strong bonding energy promoting high adsorbed hydrogen, so that the combined NiMoW alloy, may serve to optimize the hydrogen bonding being neither too strong, nor too weak, and thus a strong function of the deposit composition. As the sum of Mo and
Figure 4.2.4: Rotation rate dependence of the partial current densities of (a) Ni, (b) W and (c) Mo and (d) deposit composition of alloys deposited from the NiMoW electrolyte containing 0.005 M molybdate, and (e) elemental Ni, at 50 mA/cm$^2$.

W content increases in the deposits, with more MoO$_4^{2-}$ in the electrolyte, the hydrogen desorption step may become more difficult, resulting in a higher fractional amount of adsorbed hydrogen which may block the metal reduction reactions. In this limit, the
hydrogen evolution reaction is also expected to be lower. For example, when the amount of Mo and W in the deposit is largest the lower is the hydrogen side reaction, at large negative potentials, in the 0.075 M MoO$_4^{-2}$ electrolyte. Compared to the other two electrolytes, the hydrogen desorption rate becomes the rate determining step. When both Mo and W are not present and there is only elemental deposition of Ni, it is observed that the hydrogen side reaction rate is considerably more facile than NiMoW and NiW and representative of the electrosorption step (reaction 4.1.1).

In Figure 4.2.4, the partial current densities at different electrode rotation rates during Ni and NiMoW electrodeposition from the 0.005 M molybdate electrolyte is presented at an applied cathodic current density of 50 mA/cm$^2$. The rotation rate on the x-axis is plotted to the 0.7 power in accordance with the Eisenberg equation [154],

$$\delta = 99.62d^{-0.4}v^{0.344}D_{lim}^{0.356}S^{-0.7}$$

(4.2.3)

The nickel reduction rate in NiMoW electrodeposition is shown in (Fig 4.2.4a). There is an observed increase in the nickel partial current density from 517 to 1392 rpm and then it remains relatively constant at higher rotation rate. However, an inset of the data at higher rotation rate shows that the partial current density of Ni slightly increases with rotation rate. The W reduction rate is, Figure 4.2.4b, is not affected by increasing rotation rate when the rotation rate exceeds 1392 rpm, and follows the same shape as Ni. The Mo reduction rate, Figure 4.2.4c, does increase when rotation rate is increased, but a linear regression line (the square of the correlation coefficient is 0.9) of Mo partial current density at varied rotation rate shows a non-zero intercept, 0.93, suggesting a mixed kinetic-transport control. The change of Mo partial current density is accompanied by the same magnitude of change in the Ni partial current density, which, in Figure
4.2.4d, results in an alloy composition that is not significantly affected by rotation rate. In contrast, the deposit composition changes appreciably with the applied current density and MoO$_4^{-2}$ concentration. Hence, mass transport can affect the reaction, but kinetics play a more important role under the experimental conditions considered here. When Ni is electrodeposited alone in the electrolyte eliminating tungstate and molybdate, Figure 4.2.4e, the Ni reduction rate is two times higher compared to the case when it is electrodeposited as an alloy, suggesting an inhibitory effect during alloy codeposition.

A rotating Hull cell was also employed to examine the effect of temperature on the NiMoW electrodeposition in the electrolyte of 0.005 M molybdate. To achieve the same boundary layer thickness as the rotating cylinder electrodes, the rotation rate of the rotating Hull cell was 717 rpm according to Eisenberg’s equation, 4.2.3. Electrolyte temperatures of 30, 45 and 60 °C were examined at an average current density of 20 mA/cm$^2$. Photographs of the deposits are shown in Figure 4.2.5. It is clear that the electrolyte temperature decreased the range of local current densities, where a metallic deposit could be formed. At the temperature of 30 °C, a metallic deposit can be formed when the local current density was $> \sim 6$ mA/cm$^2$, 0.3 (white number along side of the working electrode) times the average current density. However, when temperature was increased to 45 °C, a metallic deposit only can be formed at the local current density of $> \sim 10$ mA/cm$^2$, 0.5 times the average current density. Finally at temperature of 60 °C, the local current density needed to be $> \sim 30$ mA/cm$^2$ to achieve a metallic deposit.
Figure 4.2.5: NiMoW electrodeposited at variable temperatures on rotating Hull Cell at average current density of 20 mA/cm².

The numbers in Figure 4.2.5 are the dimensionless ratios of the local current density to the average, applied current density and are determined assuming a primary current distribution. A primary current distribution assumes that the reaction is much faster than ohmic limitations that direct current flow. To confirm that the electrodeposition was under primary current distribution, a polarization curve was conducted at those temperatures, shown in Figure 4.2.6. The conductivities of the electrolyte at variable temperatures were measured by conductivity meter: 61 ms at 30 °C,
70 ms at 45 °C and 82.5 at 60°C. According to \( Wa = \frac{\partial E}{\partial t} \frac{L}{\kappa} = \frac{R_{ci}}{R_{\Omega}} \), the Wagner number was calculated and listed in Figure 4.2.5. It is clear that the Wagner numbers of electrolytes at variable temperatures were close to 0, which indicates that the electrodeposition was under primary current distribution. The current resistance was mainly attributed to ohmic resistance, thus the numbers given in Figure 4.2.5 are a good estimation of the local applied current densities.

Figure 4.2.6: Polarization curves of variable electrolyte temperatures in the electrodeposition electrolyte.
Figure 4.2.7: Polarization curves of side reactions.

For a further understanding of the temperature effect, the polarization curves of side reactions were examined in the electrolyte of no alloy elements. It was observed that temperature significantly enhanced the side reaction, which also explained why temperature decreased the current density range of electrodeposition. It is due to the side reaction being accelerated by temperature inhibiting the reduction of alloy elements. By examining the deposits by energy dispersive X-ray spectroscopy (EDS), the temperature didn’t significantly influence the composition, Table 3, e.g., at estimated local current density of 60 mA/cm², the composition was about 19 wt. % Mo, 34 wt. % Ni, 47 wt. % W.
Table 3: Compositions of deposits electrodeposited on rotating Hull cell.

<table>
<thead>
<tr>
<th>Estimated local current density, mA/cm²</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Compositions, wt. %</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>Ni</td>
</tr>
<tr>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>30</td>
<td>12</td>
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<td>50</td>
<td>16</td>
</tr>
<tr>
<td>60</td>
<td>19</td>
</tr>
</tbody>
</table>

4.2.2 Mechanistic Evaluation

Common mechanisms that have been used to capture the behavior of Ni electrodeposition with alloys includes an adsorbed intermediate, as given in reactions 2.1.11 – 2.1.13, where the first step has been cited as the rate determining step. Thus, the rate will depend on the available surface area that is not occupied by adsorbed intermediates, \(1- \sum \theta\), and the logarithm of the partial current density of Ni can be written as

\[
\log\left(\frac{i_{Ni}}{i_{Ni}}\right) = \log\left(2Fk_{Ni,I}C_{Ni(II)}\right) + \log\left(1 - \sum \theta\right) - \frac{\beta_{Ni,FE}}{2.303RT}
\]  

(4.2.4)

where the fractional adsorption terms of molybdenum, \(\theta_{Mo}\), and hydrogen, \(\theta_{H}\), are a function of the amount of codepositing molybdenum from molybdate ions. Thus the changes in the partial current density of nickel with molybdate ions can be represented by
the following expression, and from the experimental data, this term has a negative reaction order

$$\frac{\partial \log (i_{Ni})}{\partial \log (C_{MoO_4^2}^{-2})} = \frac{\partial \log \left(1 - \sum_{j} \theta_{j}\right)}{\partial \log (C_{MoO_4^2}^{-2})} = -1$$

(4.2.5)

which is consistent with a blocking effect from adsorbed species, in the absence of mass transport.

A reaction order expression can also be derived for the partial current density of Mo from the Podlaha-Landolt mechanism, reactions 2.1.12 and 2.1.13. Assuming only a kinetic control, with the first step rate controlling, the expression is

$$\log (i_{Mo}) = \log (6Fk_{Mo,1}C_{Ni(t)}) + \log \left(1 - \sum_{j} \theta_{j}\right) + \log \left(C_{MoO_4^2}^{-2}\right) - \frac{\beta_{Mo,1}2FE}{2.303RT}$$

(4.2.6)

and the corresponding change in the logarithm of the Mo partial current density with the logarithm of the concentration of molybdate as

$$\frac{\partial \log (i_{Mo})}{\partial \log (C_{MoO_4^2}^{-2})} = \frac{\partial \log \left(1 - \sum_{j} \theta_{j}\right)}{\partial \log (C_{MoO_4^2}^{-2})} + 1$$

(4.2.7)

Substituting the reaction order obtained for the Ni partial current density, which defines

$$\log \frac{1}{\sum_{j} \theta_{j}} \log (C_{MoO_4^2}^{-2}) = 1$$

results in a kinetic equation for the Mo partial current density that should not change with the addition of molybdate,

$$\frac{\partial \log (i_{Mo})}{\partial \log (C_{MoO_4^2}^{-2})} = -1 + 1 = 0$$

which clearly is not in agreement with what was observed in this study. Similarly, if we utilize the Podlaha-Landolt model to represent the W partial current density...
\[
\log (i_w) = \log \left(6Fk_{w,2}C_{\text{Ni(II)}C_{\text{WO}_4^2}}\right) + \log \left(1 - \sum \theta_i\right) - \frac{\beta_{w,1}2FE}{2.303RT} \quad (4.2.8)
\]

the logarithm of the W partial current density with the logarithm of the molybdate concentration is the same expression as that found for Ni, and equals -1,

\[
\frac{\partial \log (i_w)}{\partial \log \left(C_{\text{MoO}_4^2}\right)} = \frac{\partial \log \left(1 - \sum \theta_i\right)}{\partial \log \left(C_{\text{MoO}_4^2}\right)} = -1 \quad (4.2.9)
\]

also not close to what is experimentally observed (~-1.5). Therefore modification is needed to the Podlaha-Landolt mechanism to better predict the experiment data.

If it is assumed that the inducing species are the adsorbed Ni(I) intermediate rather than the soluble Ni(II) species, whether complexed or not with ligand “L”, the first step of the reduction reaction for Mo and W, reaction 2.1.12 and 2.1.13 are modified accordingly,

\[
\text{MoO}_4^{2-} + \text{NiL(I)_{ads}} + 2\text{H}_2\text{O} + 2e^- \rightarrow \left[\text{NiL}^{2-}\text{MoO}_2\right]_{\text{ads}} + 4\text{OH}^- \quad \text{RDS} \quad (4.2.10)
\]

\[
\left[\text{NiL}^{2-}\text{MoO}_2\right]_{\text{ads}} + 2\text{H}_2\text{O} + 4e^- \leftrightarrow \text{Mo(s)} + \text{NiL(I)_{ads}} + 4\text{OH}^- \quad (4.2.11)
\]

and in the same manner for tungstate reduction,

\[
\text{WO}_4^{2-} + \text{NiL(I)_{ads}} + 2\text{H}_2\text{O} + 2e^- \rightarrow \left[\text{NiL}^{2-}\text{WO}_2\right]_{\text{ads}} + 4\text{OH}^- \quad \text{RDS} \quad (4.2.12)
\]

\[
\left[\text{NiL}^{2-}\text{WO}_2\right]_{\text{ads}} + 2\text{H}_2\text{O} + 4e^- \leftrightarrow \text{W(s)} + \text{NiL(I)_{ads}} + 4\text{OH}^- \quad (4.2.13)
\]

Casting the partial current densities of the Mo and W in terms of the reacting species in the first step, assuming it is a rate determining step, yields in the absence of mass transport, respectively,

\[
\log (i_{\text{Mo}}) = \log \left(6Fk_{\text{Mo,2}}\right) + \log \left(\theta_{\text{Ni}}\right) + \log \left(C_{\text{MoO}_4^2}\right) - \frac{\beta_{\text{Mo,1}}2FE}{2.303RT} \quad (4.2.14)
\]
\[
\log(i_w) = \log(6Fk_{W,1}C_{WO_2}^{-}) + \log(\theta_{Ni}) - \frac{\beta_{W,1}2FE}{2.303RT}
\]  \hspace{1cm} (4.2.15)

The two partial current densities for Mo and W are now coupled through the adsorbed Ni intermediate, and the Ni intermediate competes for free surface sites primarily with hydrogen, so these rates are indirectly related to hydrogen adsorption. Hence,

\[
\frac{\partial \log(i_{Mo})}{\partial \log(C_{MoO_2}^{-})} = \frac{\partial \log(\theta_{Ni})}{\partial \log(C_{MoO_2}^{-})} + 1
\]  \hspace{1cm} (4.2.16)

\[
\frac{\partial \log(i_w)}{\partial \log(C_{MoO_2}^{-})} = \frac{\partial \log(\theta_{Ni})}{\partial \log(C_{MoO_2}^{-})}
\]  \hspace{1cm} (4.2.17)

Experimentally there is a change of the logarithm of the W partial current density with the logarithm of molybdate concentration of -1.5, thus substituting

\[
\frac{\partial \log(\theta_{Ni})}{\partial \log(C_{MoO_2}^{-})} = -1.5
\]  into

\[
\frac{\partial \log(i_{Mo})}{\partial \log(C_{MoO_2}^{-})}
\]  gives a more reasonable decrease in the Mo partial current density,

\[
\frac{\partial \log(i_{Mo})}{\partial \log(C_{MoO_2}^{-})} = -1.5 + 1 = -0.5
\]  , close to the experimentally observed value.

At low molybdate concentration, the Mo partial current density has a mass transport component, and the kinetic expression can be modified accordingly, to reflect changes in the surface concentration of molybdate. The derivative of the logarithm of the Mo partial current density with the logarithm of concentration in equation 4.2.17 has an additional term.
\[
\frac{\partial \log \left( \left[ i_{Mo} \right] \right)}{\partial \log \left( C_{MoO_4^{2-}} \right)} = \frac{\partial \log \left( \theta_{Ni} \right)}{\partial \log \left( C_{MoO_4^{2-}} \right)} + 1 + \frac{\partial \log \left( \frac{C_{MoO_4^{2-}}^s}{C_{MoO_4^{2-}}^b} \right)}{\partial \log \left( C_{MoO_4^{2-}} \right)} \quad (4.2.18)
\]

The last term can be approximated by assuming a convective-diffusive transport using a Nernst boundary layer assumption, where \( \delta \) is the mass transport boundary layer with a linear concentration gradient. As the potential becomes more negative introducing a transport effect, \( C_{MoO_4^{2-}}^s < C_{MoO_4^{2-}}^b \), then

\[
\frac{C_{MoO_4^{2-}}^s}{C_{MoO_4^{2-}}^b} \approx \frac{D_{MoO_4^{2-}}}{\delta} \frac{\beta_{Mo \cdot Ni \cdot FE}}{RT} \quad \text{and} \quad \frac{\partial \log \left( \left[ i_{Mo} \right] \right)}{\partial \log \left( C_{MoO_4^{2-}} \right)} = 1.
\]

In other words, mass transport effects increase the Mo partial current density, as expected. When there is a mixed control, as in the data presented here, the influence of mass transport opposes the inhibiting effect of the absorption of co-reacting species, such as hydrogen.

The side reaction is dominated by the hydrogen evolution reaction and follows the Volmer-Heyrovsky mechanism, 4.1.1 and 4.1.2, with the second step, 4.1.2, rate determining step [32]. Hence, the partial current density of the side reaction can be represented as:

\[
\log \left( \left[ i_{side} \right] \right) = \log \left( 2Fk_{H,c} \right) + \log \left( \theta_H \right) - \frac{\beta_{H,H}FE}{2.303RT} \quad (4.2.19)
\]

where the fractional coverage of hydrogen adsorption, \( \theta_H \) can be approximated from the first step assuming a quasi-equilibrium approach,

\[
\theta_H = \frac{k_{la}a_M(1 - \theta_{Ni} - \theta_{Mo} - \theta_W)\exp \left( -\frac{F}{RT}E \right)}{k_{la}C_{OH} + k_{la}a_M \exp \left( -\frac{F}{RT}E \right)} \quad (4.2.20)
\]
with $a_M$ representing the activity of the solid phase. At potentials more negative to -1.6 V vs Ag/AgCl, the change of the slope of $\log\left|i_{\text{side}}\right|$ with potential during electrodeposition, Figure 4.2.3(d), can be attributed to the saturated amount of adsorbed hydrogen. Similarly, during the catalysis of hydrogen in the basic electrolyte, the apparent Tafel slope change with deposit composition can result from a change in $\theta_H$ due to the activity differences between deposits.

![Diagram](image)

**Figure 4.2.8:** Schematic of adsorbed intermediates occurring during the electrodeposition of NiMoW, NiWMo and NiW.

The adsorbed hydrogen can also affect the composition of the deposits by limiting each metal reduction rate. Figures 4.2.1 and 4.2.3 illustrate that the metal content and the metal partial current densities are not a function of potential with a large amount of molybdate in the electrolyte. Taking the molybdate out of the electrolyte increases the amount and rate of W but there is a pronounced affect with potential. Figure 4.2.8 is a schematic that summarizes these observations. The changes in the metal reduction rate may be reflected in the amount of adsorbed species at the surface, which, in turn, is dictated by the solid state composition. With a large amount of molybdate in the
electrolyte, NiMoW in Figure 4.2.5, the composition of the alloy remains constant despite a decrease in the hydrogen side reaction rate, particularly at potentials $E < -1.6 \text{ V vs Ag/AgCl}$, which is suspected of being accompanied with a stronger binding energy for hydrogen adsorption. Thus, the fractional adsorption amount must not change considerably with potential to keep the partial current densities of all metals unchanged with potential, as reflected in the schematic. Lowering the amount of molybdate, or eliminating it in the electrolyte, NiWMo and NiW in Figure 5, does indeed result in a higher W partial current density, with more W in the deposit. However, there is a decrease in the W partial current density with potential. The decrease in the W partial current density can be attributed to an increase in the amount of adsorbed hydrogen, $\theta_H$. A remaining question is why there is more Mo in the deposit compared to W when there is an equimolar amount of each ion in the electrolyte? If the present model governs, then this answer resides in the ability of the Mo-intermediate to compete more effectively with the W-intermediate at the electrode surface, hence, $\theta_{Mo} > \theta_W$, which is also a function of the solid state composition of the metal, and the amount of adsorbed nickel. Furthermore, this work suggests that the reason why Mo and W cannot be deposited from aqueous electrolytes alone is not that it accelerates the side reaction, but that it promotes hydrogen adsorption and it is this adsorbed hydrogen intermediate that blocks further reduction. The codeposition of Ni with either Mo or W, or both, helps to reduce the hydrogen binding energy of the hydrogen intermediate and thus allows for adsorption of other species permitting the reduction of Mo and W.
4.2.3 X-ray Photoelectron Spectroscopy

All the deposits electrodeposited here appeared metallic, although it is known that a native oxide should form in air on the deposit surface, which contributes to the outstanding corrosion resistance of these alloys. X-ray photoelectron spectroscopy (XPS) was performed on selective deposits for further understanding of the native oxide and to ensure complete reduction of the elements in the bulk portion of the deposits. In Figure 4.2.9, XPS was conducted on NiMoW electrodeposited from the equal molar tungstate and molybdate electrolyte at -75 mA/cm² with/without argon gas etching. The spectra was labeled for peaks of interest. The C peak is expected to be due to the citrate in the electrolyte which was included in the deposit. The O peak is attributed to the oxides on the deposits surface. Before etching, on the surface of the deposit, there is a layer of oxides. After etching, it was observed that the peaks of alloy elements became more observable. In Figure 4.2.10, two positions were chosen on the surface of NiMoW deposit, details of alloy elemental peaks of Ni, Mo and W are present. In Figure 4.2.10a, peaks of Mo were identified according to the binding energy from literature [155-159]. On the surface molybdenum is present in the following forms: Mo, MoO₃ and MoO₂. In Figure 4.2.10b, only the peak of Ni 2p3/2 was identified from the background [160], which indicates the amount of Ni on the surface of the deposit was very little, which indicates that the oxides are primarily due to molybdenum and tungsten species. It was also confirmed by Obradovic et al. [118] Two forms of W were observed in Figure 4.2.10c, which are WO₃ and W [161, 162].
Figure 4.2.9: XPS survey on NiMoW deposit with/without argon gas etching.
Figure 4.2.10: XPS on two positions on the surface of NiMoW deposit for (a) Mo, (b) Ni and (c) W.
(a) Mo 3d\(\frac{3}{2}\) and Mo 3d\(\frac{5}{2}\) peaks for 30 sec etch and 6 sec etch.

(b) Ni 2p\(\frac{1}{2}\) and Ni 2p\(\frac{3}{2}\) peaks for 30 sec etch and 6 sec etch.
After argon gas etching, Figure 4.2.11a and b, the oxides layer was removed, and very sharp peaks of Mo and Ni were observed, which indicates that Mo and Ni were fully reduced during NiMoW electrodeposition. However, Figure 4.2.11c, both WO$_3$ and W peaks were present: WO$_3$ 4f7/2 at 35.6 eV, WO$_3$ 4f5/2 at 37.7 eV, W 4f7/2 at 31.6 eV and W 4f5/2 at 31.6 eV. This indicates that tungsten oxide penetrates further within the deposit compared to molybdenum, or that the tungstate may be partially reduced. In Figure 4.2.1a, the deposit electrodeposited from the equal mole molybdate and tungstate electrolyte contained very little W, ~5 wt%. In the contrast, the majority of deposit was Ni and Mo, which overlap the peak of Mo and Ni from the electrolyte.
As a comparison, XPS was also performed on NiW electrodeposited from the NiW electrolyte at 100 mA/cm², Figure 4.2.12. It was observed that on the top surface, there were mainly oxides and C coming from the citrate, which was identical to the NiMoW deposit, shown in Figure 4.2.13a. On the surface of NiW, there is no Ni peak observed. Figure 4.2.13b, both WO₃ and W were observed. Comparing with 4.2.10c, the peaks of W were larger than WO₃, which could be due to the much larger W content in the NiW deposit than NiMoW deposit. Figure 4.2.14, after 6 and 30 sec argon gas etching, very sharp peaks of Ni and W were observed, which indicates NiW was fully reduced. In Figure 4.2.14b, WO₃ 4f5/2 peak was also observed attributing the same reason as in Figure 4.2.11c.
Figure 4.2.13: XPS on two positions of NiW deposit surface for (a) Ni and (b) W.
Figure 4.2.14: XPS on argon gas etched NiW deposit for (a) Ni and (b) W.
4.3 Pulse Electrodeposition of NiMoW Alloys

4.3.1 Effect of Pulsing Parameters on Deposit Compositions

In Figure 4.3.1, the (a) Mo wt % and (b) W wt % measured in the deposit over a wide pulse frequency range, frequency is the inverse of the sum of t_{off} and t_{on}, and a duty cycle of ½, duty cycle is the ratio of t_{on} over the sum of t_{off} and t_{on}, is presented and compared to its corresponding dc composition. Although there is considerably less MoO$_4^{2-}$ than WO$_4^{2-}$ in the electrolyte, the deposit composition does not reflect the MoO$_4^{2-}$:WO$_4^{2-}$ ion electrolyte ratio in the deposits, with a preferential deposition of Mo. There is no significant difference between the composition of deposits pulse and dc electrodeposited at a cathodic current density of 75 mA/cm$^2$ over a large frequency range. However, when the pulse cathodic current density is decreased to 10 mA/cm$^2$, the Mo content in the deposit decreased, and W increased, compared to the dc case.
Figure 4.3.1: Deposit composition of (a) Mo and (b) W pulse electrodeposited at a duty cycle of 1/2 and variable frequency; dc deposit composition shown as line on left.

Since only the lower current density (10 mA/cm\(^2\)) influenced the deposit composition when pulsed deposited, the effect of the duty cycle was further examined. The compositions of these deposits are present in Figure 4.3.2. The Mo and W content in
Figure 4.3.2: Deposit composition of (a) Mo, (b) W and (c) Ni in the deposit pulse electrodeposited at pulse current density of 10 mA/cm² and variable duty cycle and frequency, dc deposit composition shown as line on left.

the deposit, shown in Figure 4.3.2 (a) and (b), are significantly affected by the duty cycle. In Figure 4.3.2 (a), a larger duty cycle decreases the Mo content in the deposits, while in Figure 4.3.2 (b), it increases the W content and, in Figure 4.3.2 (c), doesn’t affect the Ni content significantly. A longer off time leads to more Mo and less W content in the deposit and doesn’t significantly affect the Ni content in the deposits. Moreover, the larger the duty cycle the deposit composition became less dependent on the frequency.
Since Ni induces both Mo and W the pulse deposition is able to tune the ratio of Mo:W and shift a preferential deposition for Mo (under dc) to W.

4.3.2 Morphology

Optical images of three pulse deposit surfaces are presented in Figure 4.3.3. All three deposits have the same on time per period, 10 ms, with different off times, having duty cycles of (a) 1/4, (b) 1/2 and (c) 4/5. In Figure 4.3.3, as the duty cycle increases the

Figure 4.3.3: Optical images of deposits electrodeposited by pulse with duty cycles of (a) 1/4, (b) 1/2 and (c) 4/5, 10 mA/cm² pulse current density, 10 ms on time.
Figure 4.3.4: SEM images, magnification of 10 k, of deposits electrodeposited by pulse with duty cycles of (a) 1/4, (b) 1/2 and (c) 4/5, 10 mA/cm$^2$ pulse current density, 10 ms on time.
cracks on the deposits become more numerous, in other words, the shorter the off time the more cracks. When the duty cycle is 1/4, Figure 4.3.3 (a), no observable cracks presents at this scale.

Scanning electron microscope (SEM) was used to examine the morphology of the deposits at higher magnifications of 10 to 100 k in Figure 3.3.4 – 3.3.6. It was confirmed that the higher duty cycle increased the crack density on the deposits. Figure 3.3.4a, there was no observable crack at this scale when the duty cycle was ¼. When the duty cycle was increased to ½, few cracks were observed. At the duty cycle of 4/5, more cracks on the surface of deposits were formed. Furthermore, Figure 3.3.5a revealed that there were also cracks on the deposit electrodeposited with duty of ¼, which were much finer than the cracks on the other deposits. It also showed that there were also nanometer scale holes. Figure 3.3.6, at magnification of 100 k, showed that the surface of the deposits electrodeposited with duty cycle of 4/5 and 1/2 were full of nano scale pits, which might be generated between grain boundaries.

4.3.3 Adsorption and Desorption during Pulse Electrodeposition

Figure 4.3.7 presents the measured potentials of pulse electrodeposition with variable \( t_{on} \) and \( t_{off} \) at pulse current density of 10 mA/cm\(^2\). It is of interest that, when \( t_{on} \) was short, 10 ms, \( t_{off} \) can significantly changes the potential of the pulse. The difference between \( t_{off} \) of 2.5 and 30 ms was 0.6 V. This difference was reduced by longer \( t_{on} \). When \( t_{on} \) was 100 ms, this difference was only about 0.1 V between \( t_{off} \) of 25 and 300 ms. After \( t_{on} \) was increased to 1 s, no observable difference between any \( t_{off} \). This could indicate that the coverage of adsorbed intermediates was different at \( t_{on} \) of 10 ms. More adsorbed intermediates formed during \( t_{on} \) were desorbed during longer \( t_{off} \). When the frequency
Figure 4.3.5: SEM images, magnification of 60 k, of deposits electrodeposited by pulse with duty cycles of (a) 1/4, (b) 1/2 and (c) 4/5, 10 mA/cm² pulse current density, 10 ms on time.
Figure 4.3.6: SEM images, magnification of 100 k, of deposits electrodeposited by pulse with duty cycles of (a) 4/5 and (b) 1/2, 10 mA/cm$^2$ pulse current density, 10 ms on time.
Figure 4.3.7: Measured potentials of NiMoW electrodeposition with varied $t_{on}$ and $t_{off}$ frequency at pulse current density of 10 mA/cm$^2$. 
was low, for all the duty cycles, all the adsorbed intermediates could desorb, which eliminated the potential difference during $t_{on}$.

Adopting an adsorption reaction mechanism approach, similar to that of Podlaha and Landolt [60], adsorbed intermediates of Mo, W, Ni and H form during the electrodeposition of NiMoW. Hence, during the 1$^{st}$ pulse on time, Mo, W, Ni and H intermediates are adsorbed on the working electrode (See Figure 4.3.8). In the following off time, all types of adsorbed intermediates desorb from the working electrode, but to be consistent with observed deposit composition, more W intermediates desorb than Mo intermediates. It is also consistent with the observation that the longer the off time the less W content in the deposit and more Mo is present. Since some area is left open by the desorbed intermediates, during the 2$^{nd}$ on time, they are refilled by the intermediates which are similar to the 1$^{st}$ on time. Since, longer off times can lead to more desorption of intermediates, including H, it can also help to decrease cracks in the deposits due to less adsorbed hydrogen.

![Figure 4.3.8: Schematic of intermediates adsorption and desorption during the pulse electrodeposition of NiMoW.](image)

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4.4 Photoactive Behavior in Induced Codeposition

4.4.1 Intermediates in Induced Codeposition of NiW

There were several mechanisms raised to describe the induced codeposition of molybdenum and tungsten alloys, although there is no general agreement due to a lack of evidence of intermediate species that participate in the proposed mechanisms. The mechanisms presented by Chassaing et al. [64] and Podlaha and Landolt [58, 60] proposed intermediate species that may contained partially reduced metal oxides at the electrode surface, while Younes et al. [87] included reactants that where complexed species in the electrolyte. Since the Mo(VI) or W(VI), which can’t be fully reduced in one step, the investigation on the intermediate in the induced codeposition appears especially important. Moreover, it is essential that in order for it to be detected the technique used needs to be conducted in situ with electrodeposition.

The adsorbed intermediates suggested by Chassaing, et al., [64] Podlaha and Landolt [60], and our previous work in Chapter 4.2 contain W (or Mo) oxide and Ni oxide, thus, it is expected to be a semiconductor. Since WO$_2$ and NiO are p-type semiconductors [163], a similar semiconducting material may be formed as an adsorbed intermediate. If an intermediate is in fact present, it may be affected by UV light if its band gap energy is less than the energy UV light delivers. UV irradiation includes wavelengths that can range between 400 – 100 nm (3.1-12.4 eV). The band gap of NiO is 3.25 eV [164]. The band gap can also be influenced by size; for example, in a recent work of Watanabe et al., [165] they suggested that the size of WO$_3$ quantum dots can affect the band energy, changing from 2.6 eV, for the bulk, to 3.7 eV, for quantum dot size of one nanometer. The band gap energy of NiO also can be changed [166]. Patil and
Kadam found the thickness of NiO thin films can decrease the band gap energy from 3.58 to 3.4 eV from thin (0.028 µm) to thick (0.23 µm) films. Shaposhnikov et al. [167] modeled the electronic properties of WO₂ by first-principles calculations and found that WO₂ had metal like band structure when in a stable monoclinic phase at room-temperature, while WO₂ is a semiconductor with a band gap of ~0.6 eV, while in a high-temperature metastable orthorhombic phase.

In order to provide more insight of the induced codeposition mechanism and the intermediates formed during the induced codeposition, intensity modulated photocurrent spectroscopy is used that can generate a response in current to UV irradiation during deposition if the requisite semiconductor is present and adsorbed to the surface of the working electrode. The UV light used in this work is monochromatic, having a wavelength of 365 nm corresponding to 3.4 eV from the relation \( E = \frac{hc}{\lambda} \), where \( h \) is Plank’s constant, \( 4.1 \times 10^{-15} \text{ eV} \cdot \text{s} \), \( c \) is the speed of light, \( 3 \times 10^8 \text{ m/s} \) and \( \lambda \) is the wavelength of the UV light. If the intermediates have a band gap larger than 3.4 eV, no response will be observed.

4.4.2 Intensity Modulated Photocurrent Spectroscopy (IMPS)

Intensity modulated photocurrent spectroscopy (IMPS) is used in photoelectrochemistry to investigate the kinetics of photoelectrochemical reactions at the semiconductor | electrolyte interface and the semiconductor itself. It is widely used in solar cell research [168-171] and characterizing electrical properties of semiconductors [172-174]. Additionally, IMPS has been used to investigate the passivation of iron [175] and hydrogen evolution reactions on semiconductors [176, 177]. In this technique, the complex ratio of photocurrent to the intensity of light is measured over a wide range of
the light intensity, modulated in a sinusoidal fashion. If it is plotted in a Nyquist plot, it usually presents as one semicircle in the 1st quadrant for n-type semiconductors and in 3rd quadrant for p-type semiconductors. When the frequency is varied over many magnitudes from low to high, the IMPS semicircle will start at the intercept of the real component axis, where this intercept is close to or at the zero point, then will reach a point, where the absolute value of the imaginary component has the largest value. Eventually, it will come back to the real component axis to complete a semicircular shape at the other intercept that is far from the zero point. It can also form two semicircles, when the depletion layer capacitance is large and charge transfer is fast [178].

In the work of Oekermann et al., [179] they investigated the charge transfer and recombination kinetics at the electrodes of phthalocyaninatozinc(II), hexadecafluorophthalocyaninatozinc(II) and N,N’-dimethyl perylene tetracarboxylic acid diimide by IMPS. In this work, they listed three key parameters in IMPS. At the low-frequency limit, I₁, is the intercept of a semicircle on the real component axis, X-axis, at the low frequency end. When there is only recombination, I₁ should be zero. A high-frequency limit, I₂, represents the flux of minority carriers. The third important parameter is the frequency of the highest imaginary part, f_max. When there is only recombination, f_max will represent time constants of recombination. Muñoz et al. [180] examined photoelectrochemical reduction of nitrate on p-Si coated with metallic Re thin films by IMPS, the real and imaginary component were represented by the following:

\[
\text{Re}\left(\frac{i_{\text{photo}}}{\text{photo flux}}\right) = \frac{C_{\text{SC}}}{C} \frac{\omega^2 + \frac{C_{\text{SC}}}{C} k_1 (k_1 + k_2)}{(k_1 + k_2)^2 + \omega^2}
\] (4.4.1)
\[
\text{Im} \left( \frac{i_{\text{photo flux}}}{i_{\text{photo flux}}} \right) = \frac{C}{C_{\text{SC}}} \frac{\alpha\left(1 - \frac{C_{\text{SC}}}{C} \right)k_1 + k_2}{(k_1 + k_2)^2 + \omega^2}
\]

(4.4.2)

where, \( C_{\text{sc}} \) is the semiconductor space-charge capacitance and \( C \) is the total interface capacitance defined as:

\[
\frac{1}{C} = \frac{1}{C_{\text{SC}}} + \frac{1}{C_{\text{H}}}
\]

(4.4.3)

\( C_{\text{H}} \) is the Helmholtz capacitance. The two rate constants, \( k_1 \) and \( k_2 \), were for the direct charge transfer from the semiconductor to the interface and an electron-hole pair recombination at the interface, respectively. Therefore, the frequency of the highest imaginary part, \( f_{\text{max}} \), can be calculated as

\[
f_{\text{max}} = \frac{\omega_{\text{max}}}{2\pi} = \frac{k_1 + k_2}{2\pi}.
\]

When \( \omega = 0 \),

\[
\text{Re} \left( \frac{i_{\text{photo flux}}}{i_{\text{photo flux}}} \right) = \frac{k_1}{k_1 + k_2}, \quad \text{and when } \omega \gg k_1 + k_2, \quad \text{Re} \left( \frac{i_{\text{photo flux}}}{i_{\text{photo flux}}} \right) = \frac{C}{C_{\text{SC}}}.
\]

They are sketched in Figure 4.4.1.

IMPS also can be used to investigate photoelectrochemical hydrogen evolution at p-InP [177]. The rate constants of recombination and charge transfer derived by IMPS were supported by photoelectrochemical impedance spectroscopy (PEIS). In their work, the photoelectrochemical hydrogen evolution was investigated in 1 M sulfuric acid solution. The rate constants of charge transfer and recombination, the ratio of charge transfer rate constants over the sum of the charge transfer and recombination rate constants and the capacitance of the depletion layer are an analog of IMPS and PEIS in the bias potential range of -0.35 to -0.5 V vs SEC. Oskam et al. [173] investigated the electrical properties of n-type (III) Si in aqueous \( \text{K}_4\text{Fe(CN)}_6 \) solution. They observed that
a perfect semicircle in IMPS of this system, which indicated that the surface recombination was controlled by a single time constant process. They also examined the relation between $f_{\text{max}}$ and the applied potential at three different intensities of light through an applied potential range of 0 to 0.6 V vs SCE. It was observed that when the applied potential is more positive, the dependence of $f_{\text{max}}$ on the applied potential was weak. When the applied potential became more negative, $f_{\text{max}}$ became constant and not dependent on the applied potential at all. The third region, where the applied potential is the most negative, there was a linear relation between $\lg(f_{\text{max}})$ and applied potential. The recombination time constant is depend on the applied potential, which indicates at a positive enough potential the partial recombination took place.

A noteworthy work was conducted by Hickey and Riley [181], where a tin oxide electrode coated by (3-mercaptopropyl)trimethoxysilane (MPTMS) and then modified by
CdS nanoparticle was investigated by IMPS. The CdS nanoparticles formed a submonolayer on the electrode. The rate constants of holes and electrons on this modified electrode were obtained by interpreting the IMPS spectra with an equivalent circuit. This work also shows that IMPS can enable an examination of photoactive species that is attached to an electrode, even if the layer of this photoactive species is as thin as a monolayer.

In this work, it is the first time IMPS is applied to investigate induced codeposition of NiW. Since the intermediates formed during the process of NiW electrodeposition might have semiconductor properties, which could enable us to examine the induced codeposition in situ. This is essential to understand the reaction mechanism of induced codeposition and broaden the technique of investigation on the intermediates that is adsorbed and complexed with ligand that is citrate in this case.

**4.4.3 Results and Discussion**

In Figure 4.4.2, cyclic voltammetry (CV) was applied for NiW and Ni. It was observed that at a given overpotential, the electrodeposition rate of pure Ni is much lower than NiW. And no significant mass transport peak was observation in the range of -0.4 to -1.1 V vs Ag/AgCl for both Ni and NiW electrodeposition.

In Figure 4.4.3, IMPS was performed in the electrolyte of NiW, where the electrodeposition potential was maintained at -0.95 V vs Ag/AgCl, which is enough to form deposits. Before IMPS, pretreatment was conducted, which was maintained at the
Figure 4.4.2: CV of NiW and pure Ni in potential range of -0.4 V to -1.1 V vs Ag/AgCl with a sweep rate of 50 mV/s.

same potential as the potential used in the IMPS experiment, in order to reach steady state deposition, and thus a steady state amount of adsorbed intermediate concentration. The pretreatment time was varied from 0 to 60 min in Figure 4.4.3. IMPS spectra are well reproduced as evident from the similar response of the Nyquist plots. The data show that a pre-treatment time of 10 min is sufficiently long to reach steady state. The values of the frequency at the minimum or maximum of the semi-circle, $f_{\text{max}}$ were between 77 and 97 kHz. It also shows that at the high frequency, the response became noisy, and not linear, and it starts to lose the shape of a semicircle. Hence, some IMPS spectra looks like two semicircles, but it might be due to the noisy response in the high frequency end, *e.g.* Figure 4.4.3 (c). It is significant that the low-frequency intercept is always at the origin, which indicates that recombination is the dominate process of the current attributed to the light response, *i.e.*, photocurrent [178, 179].
Figure 4.4.3: IMPS at -0.95 V vs Ag/AgCl in NiW electrolyte with pretreat time 0 to 60 min.

In Figure 4.4.4, the IMPS spectra of NiW at varied applied potentials from -0.85 to -1.05 V vs Ag/AgCl is presented, with a 10 min pretreatment at the applied potential. It is clear that with a change in working electrode potential the low frequency intercept that stayed at the origin. However it did influence the $f_{\text{max}}$ and the high frequency intercept, in
other words, the size of semicircles. For a better understanding of how potential affected the IMPS spectra, the model of Muñoz et al., Equation 4.4.1 and 4.4.2, were applied to interpret this group of data. Since the low frequency intercept, \( \text{Re}(\frac{i_{\text{photo}}}{\text{photo flux}}) = \frac{k_1}{k_1 + k_2} \) at \( \omega = 0 \), at the origin point through this range of applied potentials, \( k_1 \) is therefore \( \sim 0 \). This indicates only electron-hole pair recombination occurs [178-180]. Hence, \( f_{\text{max}} = \frac{\omega_{\text{max}}}{2\pi} = \frac{k_2}{2\pi} \), \( k_2 \) can be reached by \( f_{\text{max}} \). To fit the data, the ratio of \( \frac{C}{C_{\text{SC}}} \) is adjusted.

\( \frac{C}{C_{\text{SC}}} \) and \( f_{\text{max}} \) used for the theoretical fits are present in Figure 4.4.5. It is clear that \( \frac{C}{C_{\text{SC}}} \) and \( f_{\text{max}} \) reach a maximum at applied potential of -0.9 V vs Ag/AgCl. This could indicate a switching of rate determining step. At \( \leq -0.90 \) V vs Ag/AgCl, the rate determining step was the desorption step, as the mechanism suggested in section 4.2.2, reaction 4.2.13 for W reduction. When applied potential was > -0.9 V vs Ag/AgCl, the rate determining step was switched to the adsorption step, reaction 4.2.12, as it was suggested in section 4.2.2.

\( \frac{C}{C_{\text{SC}}} \) maintains at very small scale, \( 10^{-5} \) to \( 10^{-6} \), which indicates the total interface capacitance, \( C \), is close to the Helmholtz capacitance, \( C_{\text{H}} \). The composition of deposits electrodeposited for 10 min are plotted in Figure 4.4.6. It is observed that W content in the deposits gradually increase with applied potential.
\[ \text{Im} \left( \frac{i_{\text{photo}}}{\text{photo flux}} \right), \mu \text{AW}^{-1} \text{m}^2 \]

\[ \text{Re} \left( \frac{i_{\text{photo}}}{\text{photo flux}} \right), \mu \text{AW}^{-1} \text{m}^2 \]
Figure 4.4.4: IMPS spectra (O) and theoretical fits (—) of NiW at applied potentials of -0.85 to -1.05 V vs Ag/AgCl.

Figure 4.4.5: $f_{\text{max}}$ and $C/C_{\text{sc}}$ used for the IMPS theoretical fits of NiW.
Figure 4.4.6: Compositions of deposits electrodeposited for 10 min at varied applied potentials of -0.85 to -1.05 V vs Ag/AgCl.

As a comparison, IMPS was also performed on the electrodeposition of pure Ni by taking out tungstate from the NiW electrolyte and maintaining the concentration of the other species. IMPS was conducted at variable potential and plotted in Figure 4.4.7. At the potentials of < -0.9 V vs Ag/AgCl, no observable deposit was formed after 30 min electrodeposition. In Figure 4.4.1, it also showed that the Ni reduction started at a potential of ~ -0.9 V vs Ag/AgCl. When potential reached to -0.9 V vs Ag/AgCl, a deposit of Ni was obtained. Hence IMPS was only conducted at potentials ≥ -0.9 V vs Ag/AgCl. There was a pretreatment conducted before IMPS, which is maintained at the same potential of IMPS for 10 min. It was observed that varied potentials didn’t significantly change the high frequency intercept and $f_{\text{max}}$. The low frequency intercept was 0 just as in the IMPS of NiW. The same theoretical model of Muñoz et al. [180] is used to interpret the plots as for NiW. The parameters of $f_{\text{max}}$ and $\frac{C}{C_{\text{SC}}}$ are plotted in
Figure 4.4.8. It is observed that the applied potential decreased $f_{\text{max}}$, and $\frac{C}{C_{\text{SC}}}$ was stable at about $1.5 \times 10^{-6}$. Comparing NiW and pure Ni, it is clear that, at a given applied potential, $f_{\text{max}}$ and $\frac{C}{C_{\text{SC}}}$ of NiW are about one magnitude higher than Ni. It indicates inducing tungstate into the electrolyte significantly changes the electrical properties of adsorbed intermediates formed during the electrodeposition. This change of electrical properties could be due to different chemical composition of the adsorbed intermediates, e.g. Ni(I)$_{\text{ads}}$ for pure Ni electrodeposition and [Ni(I)LWO$_2$]$^{2-}$, suggested in Chapter 4.2, for NiW electrodeposition. For both Ni and NiW the value of $\frac{C}{C_{\text{SC}}}$ are very small, which indicates that the total interface capacitance is mainly of Helmholtz capacitance.
(b) \(-0.95\) V

(c) \(-1\) V
Figure 4.4.7: IMPS (O) and theoretical fits (—) of pure Ni electrodeposition at variable applied potentials.

Figure 4.4.8: $f_{\text{max}}$ and $C/C_{\text{sc}}$ used for the IMPS theoretical fits of pure Ni.

To confirm the IMPS spectra of NiW is due to the adsorbed intermediates, IMPS on NiW deposits was conducted in the electrolyte of no alloy element ions at the potential of -0.6 V, which is close to OCP and generated anodic current of 24 μA, and -0.4 V vs Ag/AgCl.
Ag/AgCl, which is positive enough to generate an anodic current of 747 µA at the working electrode, where an oxide layer was formed. A 10 min pretreatment at the applied potential was also performed before IMPS. The results are presented in Figure 4.4.9. It is clear that at -0.6 V vs Ag/AgCl, no significant semicircle was observed and the majority of points stayed around the origin, though in the first quadrant. This indicates that on the surface of the NiW deposit, there were very little oxide or adsorbed intermediates, thus no semicircle impedance response was detected beyond the background noise. When the applied potential was moved positively to -0.4 V, a semicircle in IMPS response developed, where $f_{\text{max}}$ is 24.5 kHz. This indicates that when the potential is positive enough, a layer of oxide was generated, which resulted in a semicircle in IMPS. The same theoretical model as used in other IMPS was applied here, which provided $\frac{C}{C_{\text{sc}}}$ of $8.5 \times 10^{-7}$. Comparing $f_{\text{max}}$ and $\frac{C}{C_{\text{sc}}}$ with the IMPS of NiW of more cathodic applied potential, $f_{\text{max}}$ is the same as at -0.85 V vs Ag/AgCl, but is much smaller than the rest and $\frac{C}{C_{\text{sc}}}$ is much smaller than all the applied potential of cathodic currents. This indicates that the response of IMPS at the applied potential where a cathodic current can be generated was due to the adsorbed intermediates. When the applied potential was moved more positive than the OCP, the adsorbed intermediates were eliminated, and hence, the IMPS response disappeared. At the same time, a layer of oxide was formed. When the applied potential was moved more positively, oxide was formed, which produced the IMPS response again.
Figure 4.4.9: IMPS on NiW substrates in the electrolyte of no alloy element ions at applied potential of (a) -0.6 and (b) -0.4 V vs Ag/AgCl.
|Im(\textit{i}_{\text{photo}}/\text{photo flux})|, \mu\text{AW}^{-1}\text{m}^2

|Re(\textit{i}_{\text{photo}}/\text{photo flux})|, \mu\text{AW}^{-1}\text{m}^2

(a) -0.75 V

(b) -0.85 V

500 Hz

31 kHz

153 kHz
Figure 4.4.10: IMPS (O) and theoretical fits (—) in MoNi electrolyte at varied applied potentials.
Figure 4.4.11: IMPS (O) and theoretical fits (—) in molybdate electrolyte at varied applied potentials.

In Figure 4.4.10, IMPS was also applied in the electrolyte of NiMo, where the tungstate in the NiW electrolyte was replaced by molybdate at the same concentration. In the potential range of -0.75 to -0.95 V vs Ag/AgCl, no deposit was observed after 30 min electrodeposition. At the potential > -0.95 V vs Ag/AgCl, IMPS was not applied due to
the noisy response of hydrogen bubbles. Hence, IMPS was used to examine a region where it is molybdate ions are only partially reduced. It is of interest that Ni deposits were observed at -0.95 and -0.9 V vs Ag/AgCl, when pure Ni was electrodeposited, Figure 4.4.7a-b, however, after introducing molybdate to the electrolyte, no deposit was observed. In Figure 4.4.11, the IMPS response is shown using an electrolyte of Mo, where Ni ions were removed from the electrolyte of NiMo. It was observed that, in the potential range of -0.75 V to -0.95 V vs Ag/AgCl, the spectra had a similar size and shape as in the electrolyte of NiMo, at a given potential, which indicated that similar partially reduced products were formed. This partially reduced product could be partial reduced molybdate, which covered the surface of working electrolyte in the electrolyte of NiMo and inhibited the reduction of Ni. It also confirmed the observation in section 4.2.

4.5 Examination of adsorbed hydrogen intermediates

In Chapters 2.1 and 2.2, it was introduced that the side reaction of the induced codeposition of Mo and W is mainly the hydrogen evolution reaction. The mechanism of the hydrogen evolution reaction follows a Volmer-Heyrovsky reaction mechanism [32]. In section, 4.1 and 4.2, it was observed that the intermediates formed by hydrogen evolution reaction competed with Mo, W and Ni reduction for the available area on the working electrode. Hence, it is essential to understand the coverage of the adsorbed intermediate of hydrogen evolution reaction on the substrate of Mo and W alloys with Ni.

In this section, 3 substrates were examined, NiMoW (28 wt. % Mo, 36 wt. % Ni and 36 wt. % W), NiW (34 wt. % W and 66 wt. % Ni) and pure Ni. The NiMoW and NiW had a close W content in the deposits. Chronoamperometric techniques were applied in the electrolyte of taking out all alloy elements to examine the side reactions. In
Figure 4.5.1, the potential was first held at a constant potential $E_1$ for 5 min, then switched to $E_2$, which was close to OCP, but more negative, at $t_0$, where current started to be measured. The values of $E_1$ were varied and the value of $E_2$ remained at -0.65 V vs Ag/AgCl. The adsorbed intermediate from the hydrogen evolution reaction was formed and reached steady state at $E_1$ after 5 min. After the potential dropped to $E_2$, -0.65 V vs Ag/AgCl, an anodic current was generated due to desorption of the adsorbed intermediates.

Figure 4.5.1: Scheme of Chronoamperometry.
Figure 4.5.2, the current measurement started at \(t_0\) as the 0 point. It was observed that the anodic current of the NiMoW substrate was the largest at a given potential, and the pure Ni substrate had the smallest anodic current. On the NiMoW substrate, at a given time before the anodic current reached 0, the applied potential, \(E_1\), increased the anodic current at \(E_2\) until \(E_1\) was -2.5 V vs Ag/AgCl where the anodic current at \(E_2\) became saturated. This could indicate that the fractional coverage of adsorbed hydrogen intermediates became 1, at \(E_1\) of -2.5 V vs Ag/AgCl. On the substrate of NiW, the applied potential, \(E_1\), increased the anodic current at \(E_2\) until \(E_1\) was -2.25 V vs Ag/AgCl where the anodic current at \(E_2\) reached a maximum. On the substrate of pure Ni, the applied potential, \(E_1\), gradually increased the anodic current at \(E_2\) throughout the \(E_1\) range of -0.8 to -3 V vs Ag/AgCl.

For a better understanding, Figure 4.5.3, the charge was integrated from the anodic current in Figure 4.5.2 and \(E_1\) was corrected for the ohmic drop. In corrected \(E_1\) range of -0.8 to -2 V, at a given corrected \(E_1\), the charge of the anodic current on the NiMoW substrate of was the largest. It could indicate that there was more adsorbed hydrogen intermediates than occurring with the other two substrates. Also note that the charge of the double layer was not corrected in this plot. For all substrates, corrected \(E_1\) increased the total charge of the anodic current, \(q\), when \(E_1\) was < -1.6 V vs Ag/AgCl, and \(q\) reached a maximum here. This could attribute to \(\theta_H\) reached to 1 at this potential.
Figure 4.5.2: Anodic current density of variable substrates, (a) NiMoW, (b) NiW and (c) pure Ni.

Figure 4.5.3: Charges of anodic current on variable substrates.
5.0 CONCLUSIONS

The highest Mo content in a MoNi alloy, 82 wt%, fabricated by electrodeposition in an aqueous electrolyte was reported. The composition was affected by the amount of molybdate in the electrolyte despite the low concentration of nickel ions. Molybdate in the electrolyte enhanced the side reaction that generated considerable amounts of hydrogen, lowering the partial current densities of both Mo and Ni, but with $i_{Ni}$ decreased more than $i_{Mo}$. As a consequence of the low current efficiency with copious hydrogen evolution, the deposits were cracked on the microscale and had rough surface morphology. The deposits were catalytically active toward hydrogen evolution in sodium hydroxide. Distinct changes in Tafel slope with Mo wt% was attributed to the change in hydrogen adsorption in a Volmer-Heyrovsky mechanism with the second step rate determining. The catalytic examination is consistent with the electrodeposition results in that the coverage of hydrogen adsorption is influenced by the composition of the alloy and affects the relative rate of metal reduction.

NiMoW was electrodeposited from aqueous electrolytes at room temperature. More Mo is deposited than W in an equimolar solution with Ni, thus, there is a preferential induced codeposition of Mo compared to W. The metal partial current densities decrease with added molybdate in the electrolyte. The current efficiency decreases with molybdate addition to the electrolyte and the side reaction exhibits a change of slope over the potential range investigated. During NiMoW electrodeposition, the metal reduction partial current densities are influenced by the adsorbed hydrogen species which are affected by the deposit composition. The Podlaha-Landolt model was expanded to include the role of the nickel and hydrogen adsorbed intermediates.
Consistent with the measured reaction orders reported here, the nickel adsorbed intermediate species is the most probable species that induces both Mo and W. The lowering of the metal partial current densities with added molybdate was attributed to a blocking effect by adsorbed hydrogen. The observation that Mo reduction is favored over W reduction is described by the ability of the molybdate-nickel intermediate to adsorb more readily than the tungstate-nickel intermediate.

Induced codeposition of NiMoW alloys was for the first time investigated by pulse electrodeposition. Results show that the deposit composition can be affected significantly by varying duty cycle, and to a lesser extent, frequency. It was observed that the longer off time during pulse electrodeposition leads to more Mo and less W content in the deposit, when the on time is the same. This is attributed to more W intermediates desorbed than Mo intermediates during the off time, and a longer off time enhances this difference. Smaller duty cycles, in other words longer off times, lead also to fewer macro-cracks, possibly due to more desorption of adsorbed hydrogen.

IMPS analysis was used to investigate in Ni and NiW electrodeposition. Photoactive adsorbed intermediates that have a semiconductor behavior were detected. The IMPS spectra were interpreted by a theoretical model suggested by Muñoz et al. [180]. It was found that, for both pure Ni and NiW electrodeposition, the electron-hole pair recombination dominated the response and was an indication of the intermediates and total interface capacitance was mainly of Helmholtz capacitance. By comparing the IMPS spectra of Ni and NiW, NiW had about one magnitude larger \( f_{\text{max}} \) and \( \frac{C}{C_{\text{SC}}} \) than Ni. This could indicate different adsorbed species. It is confirmed by Chapter 4.2 that
introducing tungstate into the Ni electrodeposition electrolyte can generate a different adsorbed complex species.

In this work, the composition range of Mo and W alloys electrodeposited from aqueous solution was extended. The induced codeposition of Mo and W was comprehensively investigated by galvanostatic and pulse electrodeposition in varied boric-citrate electrolytes. The understanding of Mo and W induced codeposition was improved by suggesting a new reaction mechanism and an adsorbed intermediate. It was the first time ever that IMPS was applied to *in situ* investigate induced codeposition for the adsorbed intermediate which is essential to this system.
6.0 RECOMMENDATIONS

i. Including Co and Fe into the adsorption model: An adsorption mechanism of Mo and W induced codeposition with Ni was suggested, and the role of Ni was identified as a catalyst for Mo and W reduction in the form of Ni(I)\(_{\text{ads}}\). However, Co and Fe are also considered good inducing elements for Mo and W induced codeposition, so it is of great interest to investigate whether an identical adsorption model can apply to Mo and W induced codeposition with Co and Fe. In this work, Mo ion reduction was favored over W ion reduction when NiMoW was electrodeposited in an equal molar molybdate and tungstate electrolyte. If Ni ions are replaced by Co or Fe ions, will Mo reduction still be the dominating process over W? This is another interesting point of examining Mo and W induced codeposition with Co or Fe, which helps us understand more about induced codeposition of Mo and W.

ii. Applications and properties of Mo rich MoNi and NiMoW alloys: Catalytic properties of hydrogen evolution reactions were examined here. However, working as a catalyst is only one of many potential applications which Mo rich MoNi and NiMoW alloys are obtain. Examining the tribology, hardness and corrosion resistance of Mo rich MoNi and NiMoW alloys can enrich the database of material science and the options for industry. For example, the corrosion resistance of NiMoW can be examined by a polarization curve to understand the formation of the passivation layer which is essential for the corrosion properties. Variable thickness of the passivation layer can also affect the hardness. Hence, the balance point and profile between corrosion resistance and hardness are essential for industry.
iii. Material science: It will be of interest to examine the solid state of NiMoW by XRD to correlate the structure with the deposition conditions and resulting corrosion resistance or hydrogen catalyst properties. XRD can show whether the deposit is amorphous or crystalline, and if crystalline, provide the grain size that can be affected by the deposition parameters. XPS is another great tool to examine NiMoW, which is useful to investigate the surface valence state, composition and oxide formation. With the help of argon etching, depth profiling XPS can also provide insight on the deposit surface layer and help to explain the nature of the superior hydrogen catalytic properties and corrosion resistance.

iv. Further work of IMPS: This work showed the potential of IMPS used for investigation on the adsorbed intermediates which are photoactive. This is a brand new application of IMPS, so further work is recommended here to build a standard procedure and mathematic model for the application of IMPS on metal electrodeposition, where a photoactive intermediate is expected. This will enable investigation in situ, and provide not only a complement to expensive in situ Raman technique for identifying the presence of intermediates, but can also be used to characterize the intermediates electronic behavior (e.g., electron-hole recombination time constants). In the case of induced codeposition of Mo and W, the next step should be to build a mathematic relation between the IMPS spectra and the coverage of adsorbed intermediates, which is essential to improve the current model.
7.0 REFERENCES


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