Use of a Mixed Formaldehyde and Sodium Hypophosphite Reducing Agent Bath in the Electroless Synthesis of Cu-Ni-Mo-P Electro-catalyst Active for Glycerol Oxidation

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A new electroless bath was formulated in which two reducing agents - NaH_2PO_2 and formaldehyde – acted synchronously for the synthesis of electroless Cu-Ni-Mo-P/graphite electro-catalyst. The bath was operated at a pH of 10.2 and temperature of 80^oC. Baths containing only sodium hypophosphite or formaldehyde reducing agents but with the same amounts of other bath constituents were used as controls in the deposition process. The deposits were characterized using SEM, EDX and XRD. Preliminary investigations conducted on oxidations of formaldehyde and glycerol show that the catalyst is an effective electro-catalyst as prepared, and that variations in the metallic composition of the electro-catalyst affect its electro catalytic activity.

1. INTRODUCTION

Biofuels are the fastest growing segment of the renewable energy market, with annual global production projected to reach 4.6 million barrels of oil equivalent (mboe/d) in 2040 from 1.3 mboe/d in 2012 (IEA)[1]. Biodiesel, a common biofuel, is usually produced by the transesterification of vegetable oils and fats, a process that produces 1kg of glycerol for every 10 kg of biodiesel made. Very few commercial processes using this glycerol have emerged. Notably, Solvay has patented the Epicerol technology, and built plants to produce epichlorohydrin in Europe, Thailand (2009) and China (2014)[2]. Considerable research interest has been focused on what to do with this material, which is mostly disposed of as waste and therefore has associated disposal costs [3]. One promising area is its use as the fuel in direct liquid fuel cells. This is because glycerol has a relatively high energy density

of 18 MJ/kg, compared to hydrogen (120 MJ/kg) and methanol (22 MJ/kg) [4, 5]. Also, direct glycerol fuel cells can be used to co-generate electricity and fine chemicals, through selective electrolytic oxidations at the fuel cell anode [6].

Currently, catalysts for glycerol fuel cell anodes are gold (Au) ($360.00/g) and platinum (Pt) ($1,950.00/g) composites. Since catalysts can account for as much as 55-86% of the entire raw material cost of running a chemical plant annually [7], a right balance between efficiency and cost can lead to substantial savings. Primary research in fuel cell electro-catalysis has tended to focus on the development of catalysts with minimal noble metal component that are capable of catalyzing the alcohol oxidation reactions efficiently [8]. The inclusion of copper (Cu)($0.85/g) and nickel (Ni)($4.34/g) in catalyst alloys for alcohol oxidation improves the catalytic ability [9 -10], though there is no consensus yet as to the ratios of these metals that make the optimal oxidation catalyst. Their use as the principal metals in alcohol oxidation electro-catalyst therefore merits further investigation.

The choice of the synthesis method for the Cu/Ni alloys is important, since synthesis methods affect the microscopic morphology of the catalyst, and the catalytic activity towards the reaction of interest. Cu/Ni deposits can be prepared by different methods, some of which are sol gel techniques [11], atomic layer deposition [12] sputtering[13], wetness impregnation, co-precipitation and electroless methods[14]. Electroless deposition as a synthesis method offers advantages of ability to plate on complex geometries with a re-useable bath which is easier to control. In this method, auto catalytic reactions are set up on prepared surfaces (the support material) from solutions containing the metal ions to be reduced. As a technique, it has been successfully deployed in deposition on plates of regular geometry, where it is relatively easy to monitor the progression of deposition, a challenge that becomes apparent when making catalyst powders. Hence, the electroless deposition method has not been widely used in the preparation of catalysts.

Electroless deposition is a mature technique; Brenner patented the technology for the deposition of several metals, including copper and nickel [15]. A typical electroless plating bath is an aqueous solution containing metal ion precursors of the metals to be deposited, stabilizers, reducing agents, pH adjusters and chelating agents. Electroless Ni has been commercially produced for use in corrosion prevention in process equipment, plastics, turbine parts and electronics, to mention but a few [16]. Electroless copper has also been produced by the electronics industry because of copper's unique conducting properties[17].   To plate Cu, a formaldehyde bath is used at pH of 12, while Ni could be plated in both acidic (pH 5)[18] or alkaline (pH 9-10) hypophosphite baths. To electrolessly co-deposit nickel and copper onto one substrate in catalytically relevant amounts presents challenges that are absent when a single metal is being plated: First, the bath has to contain constituents that can adequately chelate Cu and Ni, and sustain the stability of the electroless bath. Furthermore, the reducing agent has to be capable of reducing both metals; both the pH and temperatures have to be optimized for a co-deposition process. Successful electroless deposition of Cu-Ni-P has been carried out in acid hypophosphite baths [14, 18]. However, very low amounts of Cu ((2-4%)[18]) are typically deposited with Ni in such acidic conditions. It is therefore of interest to explore an electroless bath formulation for Cu-Ni-Mo-P for which higher copper ion concentrations can be used without inhibition to the deposition process.

Processing conditions, nature of support and bath additives can further enhance the properties of the deposited catalysts. Mo can provide desirable mechanical properties – strength and thermal stability for example - to deposits; phosphorus, in trace amounts is known to improve the activity of catalysts by increasing their acidity [19]. This is so despite the fact that high phosphorus content results in amorphous deposits -an indication of non-crystallinity. Hence the inclusion of Mo and P in Cu/Ni based catalysts can improve the range of conditions under which they can be used.

In this paper, supported quaternary catalyst containing copper, nickel, molybdenum and phosphorus alloys have been prepared through electroless deposition in a mixed reducing agent bath. Cyclic voltammograms have been used to probe the catalytic ability of the synthesized CuNiMoP electrocatalysts towards glycerol electro-oxidation.

2. EXPERIMENTAL

2.1 Corrosion potentials of Ni and Cu in mixed reducing agent

The corrosion potentials of both Ni and Cu were determined in mixed and unmixed solutions of formaldehyde and NaH_2PO_2. 10 ml formaldehyde solution (as supplied) was used to make up 250 ml aqueous formaldehyde solution.
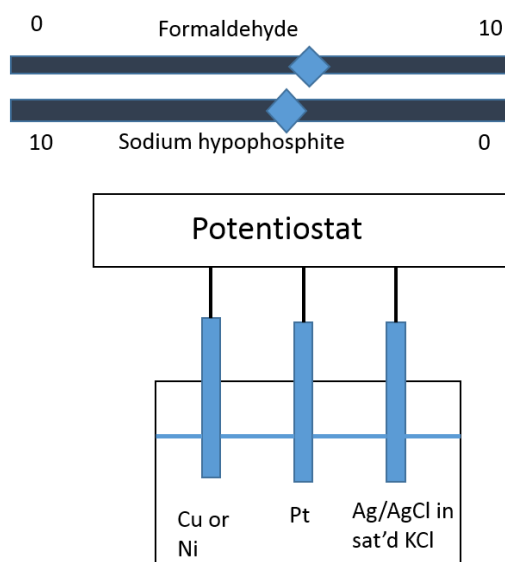
Figure 1. Schematic diagram of the experimental set-up for the determination of the corrosion potentials of Ni and Cu under different pH conditions

Volumes of this solution ranging from 0 ml to 10 ml, and 0.114 M NaH_2PO_2 (volume varying from 10 ml to 0 ml) were mixed to make up 10 ml of electrolytes for a three electrode cell system consisting of Ni working electrode, Pt counter electrode and Ag/AgCl in saturated KCl as reference electrode. The cell was connected to a Solartron S1 1287 Electrochemical Interface potentiostat, and

the open circuit potentials monitored. The same procedure was also followed when Cu was substituted as the working electrode. NaOH was used to adjust the pH of the electrolyte. Figure 1 is a schematic of the experimental set-up.

2.2 Electroless plating using bath formulations based on the results of study of Cu and Ni corrosion potentials

Based on the results of corrosion study of both Cu and Ni, a mixed-reducing agent bath was formulated with the compositions given in Table 1.

Table 1. Bath composition of mixed formaldehyde and sodium hypophosphite reducing agent bath

Material (250 ml plating bath)	Amount (g)
$NiSO_4.6H_2O$	3.36
$CuSO_4.5H_2O$	0.06 – 3.04
$NaMoO_4$	1
$NaH_2PO_2.H_2O$	1.35
K-Na-tartrate	2.5
Gluconic acid potassium salt	4.75
Sodium citrate	2
Formaldehyde (ml)	10
pH	10.2

The temperature was brought to 80^oC and NaOH was used to adjust the pH to within 10.2 ± 0.3. The substrate, Pd catalyzed alumina or Pd catalyzed graphite, was introduced and the bath was continuously stirred. Effervescence was observed, and the bath gradually darkened, both indicating that plating was occurring. Plating was carried out for different lengths of time, at the end of which the reaction was quenched by immersing the reactor in ice. The catalyst was filtered out of solution, washed twice in DI water and once in anhydrous methanol. It was then dried for 24 hours at 60 ^oC before being subjected to further testing and characterization.

For the single reducing agent baths, the same procedures and conditions were adopted. All bath constituents except the other reducing agent remained as constituted in Table 1 - i.e. the hypophosphite bath contained no formaldehyde, and the formaldehyde bath contained no hypophosphite.

2.3 Characterization of Cu-Ni-Mo-P deposits

Zeiss 1540 XB Cross Beam Scanning Electron Microscope (SEM) was used to examine the changes in surface morphology of the prepared Cu-Ni-Mo-P thin film oxides as a function of time. XRD was used to study the crystallinity of the deposited material, while EDS was used to determine the elemental compositions of different samples. The XRD data was taken with a Siemens D500 x-ray diffractometer with nickel filtered Cu Kα radiation (λ=1.540 A) and a graphite diffracted beam monochromator.

2.4 Electrode preparation

To prepare the electrodes used for the cyclic voltammograms and polarizations, 0.305 cm diameter, 99.9995% (metals basis) Alfa Aesar graphite rods were used as substrates for the electroless deposition process. They were first polished, and sonicated for 5 minutes before being dried at 60 ^{o}C for one hour; all other processing conditions also remained as described in section 2.2 above.

3. RESULTS AND DISCUSSION

3.1 Reducing agent study

The reducing agent study was undertaken to understand the corrosion behavior of copper and nickel, the principal metals in the catalyst. To be co-deposited, their deposition potentials have to be made as close as possible to each other. At 25°C, Ni has a standard electrode potential of -0.25V vs SHE while Cu has +0.33V vs SHE. The implication is that in an unmodified electroless bath operated in neutral conditions, Cu will be less cathodic than Ni (as confirmed from Figure 2), and so Ni will be preferentially deposited.
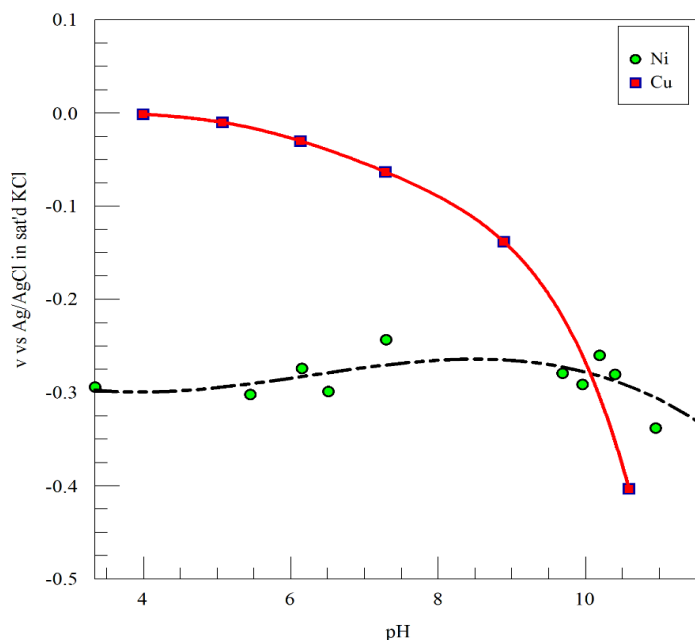
**Figure 2**. Open circuit behavior of Cu and Ni with respect to changes in pH

To be co-deposited, their potentials have to be made as close as possible. The inclusion of complexing agents in the electroless bath has been used to vary deposition potentials[18].. The approach we adopted was to monitor the corrosion behavior of Cu^{2+} and Ni^{2+} ions in aqueous formaldehyde and sodium hypophosphite environments with respect to changes in pH. We hypothesized that there was a pH window in which they would both be sufficiently cathodic for co-deposition.

Various mixtures of reducing agents, as described in experimental set up above, were used to test the corrosion potentials of Ni and Cu. These potentials were tabulated and studied; the results indicated that with a mixture of 6 ml of the prepared formaldehyde solution and 4 ml 0.114 M sodium hypophosphite, the corrosion potentials were sufficiently close together to merit further investigation. Figure 2 shows plots of the corrosion potentials of Cu and Ni in a 6 ml formaldehyde solution and 4 ml hypophosphite solution mixture over a pH range of 4-11. When the pH is below 7, Ni is much more cathodic than Cu. Further, as the mixed reducing agent bath pH becomes more basic, the corrosion potential of copper changes more rapidly than that of nickel. At pH greater than 10, there is a sharp drop in the corrosion potential of copper. The graphs coincided when pH was about 10.2. This confirmed that our initial hypothesis was right; both reducing agents are active within this window making it possible for the co-deposition of both metals. Outside this window, only one reducing agent is active for one metal. This is observed for the hypophosphite bath which is active for the deposition of nickel in pH <10 although the co-deposition of copper can only occur when the copper ion concentration is below a certain level in such a bath, as will be shown later. This formed the basis for all subsequent experiments that were carried out at pH of 10-11, using a mixture of reducing agents.

The essential information that was obtained from these preliminary experiments on the mixed reducing agent study was that a mixture of formaldehyde and hypophosphite reducing agents can provide a stable bath that could co-deposit the metal ions of interest at a pH of 10.2.

3.2 SEM and XRD Characterizations

The deposits were characterized with SEM and XRD to identify any changes in the morphology that arise from the preparation methods.
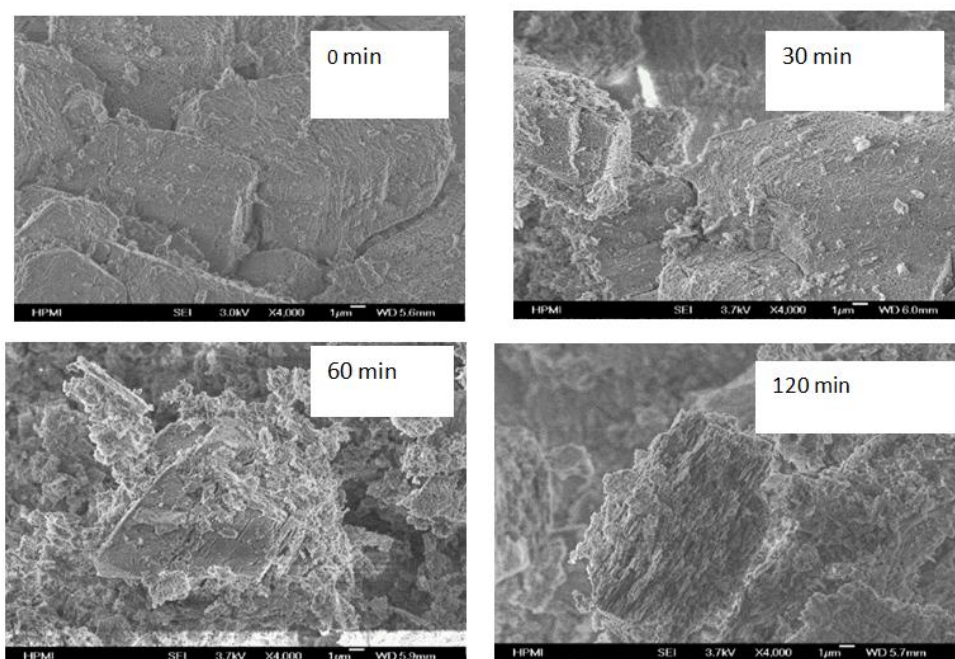
Figure 3. SEM images of CuNiMoP from mixed reducing agent bath

Figure 3 shows SEM images of the plated material; changes in morphology can be seen with increase in electroless plating time. Before the electroless deposition, the surface of the alumina is relatively free, with minute deposits of Pd that was used to catalyze it. After 30 minutes of plating, deposition is visible, and the sharp edges seen in the un-plated alumina are disappearing. This phenomenon becomes much more pronounced in the 60 minute sample. After 120 minutes, the entire alumina surface has become covered. Thus, there is a remarkable difference in morphology between the un-plated and plated samples. Analysis of the deposit composition shows that the Cu/Ni ratio decreases with plating time suggesting that copper tends to plate out faster in the bath.

The crystallinity of the material deposited on the surface was also investigated using XRD. Figure 4 shows several identified diffraction peaks that are characteristic of Ni, Cu and their oxides. The sharpness of these peaks is evidence of crystallinity of the deposits.
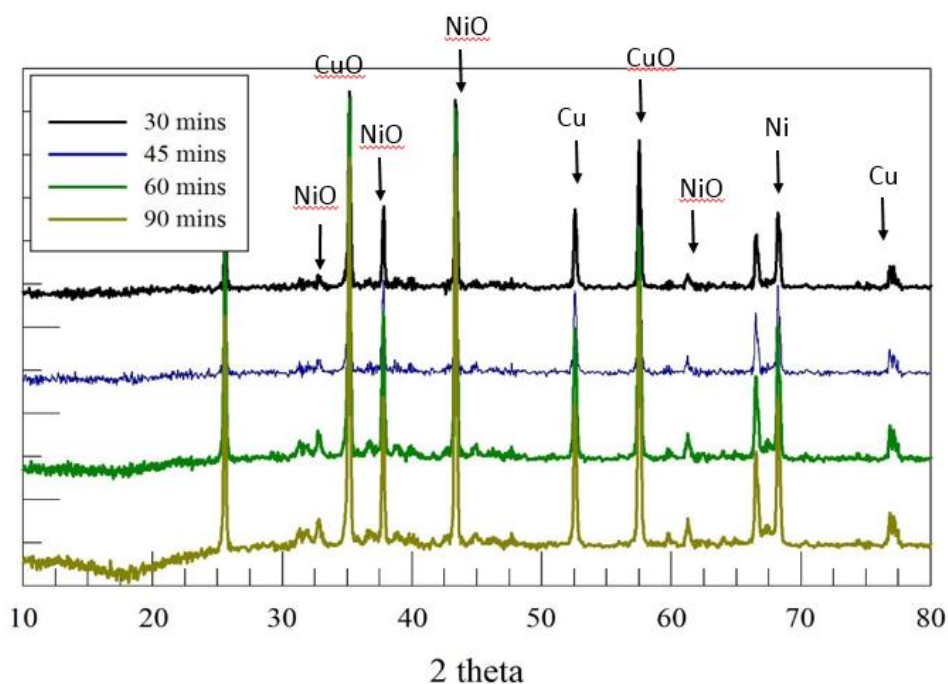

Figure 4. XRD of samples plated with reducing agent mixtures containing the ratio 6 ml formaldehyde per 4 ml sodium hypophosphite solution

The presence of elemental material implies that the catalyst may be used as prepared for glycerol electro-oxidation.

3.3 Effect of concentration Cu^{2+} ions in the electroless bath

To study the effect of concentration of Cu^{2+} ions on the plating bath and electroless deposits, the amount of copper sulfate in the bath was varied while keeping all other components constant. In all instances, the bath remained productive and stable.

Figure 5 compares the plated material loading (wt. %) as a function of Cu^{2+}/Ni^{2+} molar ratio in the electroless bath. In the mixed reducing agent bath (formaldehyde + sodium hypophosphite), the plated material loading is not limited by Cu^{2+} ion concentration in the bath, and thus the bath continues to yield copper rich deposits, even when Cu^{2+}/Ni^{2+} ratio approaches 1.0.
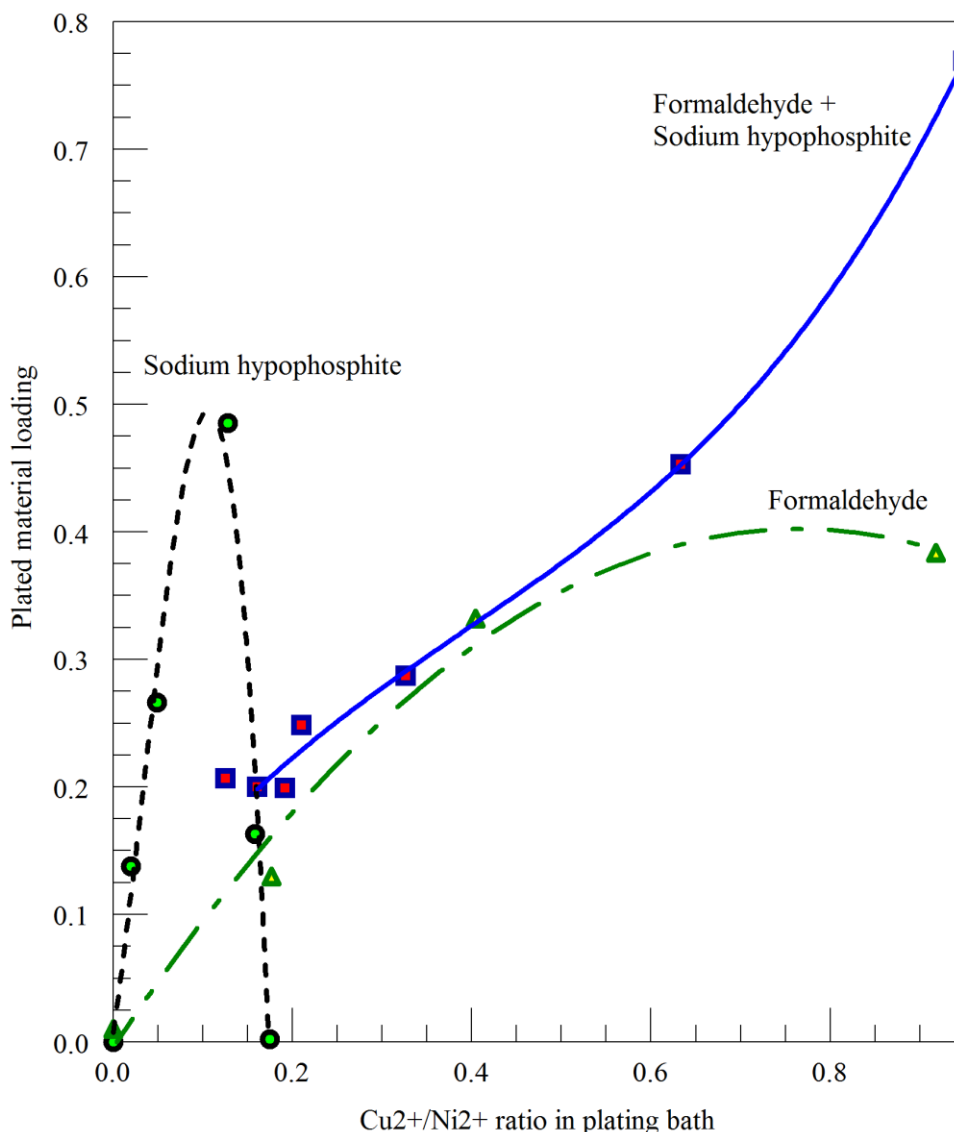
Figure 5. Material deposited on substrate surface (wt %) as a function of Cu/Ni ratio in bath for mixed reducing agent, hypophosphite and formaldehyde baths

This contrasts with the results for the single reducing agent baths (sodium hypophosphite) and (formaldehyde). For the pure hypophosphite bath, beyond a Cu^{2+}/Ni^{2+} ratio of 0.17, the bath fails to plate further materials. It seems that at higher copper concentration in the bath, copper appears to constitute a catalyst poison and lower the bath activity until it stops plating. For the single reducing agent formaldehyde bath, much lower material loadings were obtained with a maximum loading of about 48 wt. % . This bath also suffers the disadvantage that Cu begins to precipitate at Cu^{2+}/Ni^{2+} ratio

>0.4. Also, as expected, low amounts of Ni were co-deposited in this bath. However, with the mixed reducing agent bath, the alkaline bath is stable even with high Cu^{2+}/Ni^{2+} ratios (0.08 -1.0), in contrast to hypophosphite only (in alkaline bath (0.02-0.17) (this work) and acidic baths (0-0.02)[18]).

Ni-Cu-P deposits have been prepared electrolessly[18, 20] under acidic hypophosphite conditions, the inclusion of copper in these deposits serving to enhance color, corrosion and thermal properties. The amounts of copper in these deposits varied from (2-3%)[18, 20] to (0-66%)[21]. To achieve the higher copper content Ni/Cu alloys, various avenues have been explored: for instance, organic sulfur compounds are included as complexing agents [21, 22] or addition of trace amounts potassium ferrocyanide [23]. In this work, the focus has been on increasing the copper content of the electroless bath by the introduction of a second reducing agent, formaldehyde. Figure 5 shows that as much as 76% copper can be obtained in the electroless deposits (within the Cu/Ni ion ratios used in this work).

Our results confirm that Cu will not be deposited from a hypophosphite alone bath, as copper does not oxidize hypophosphite.
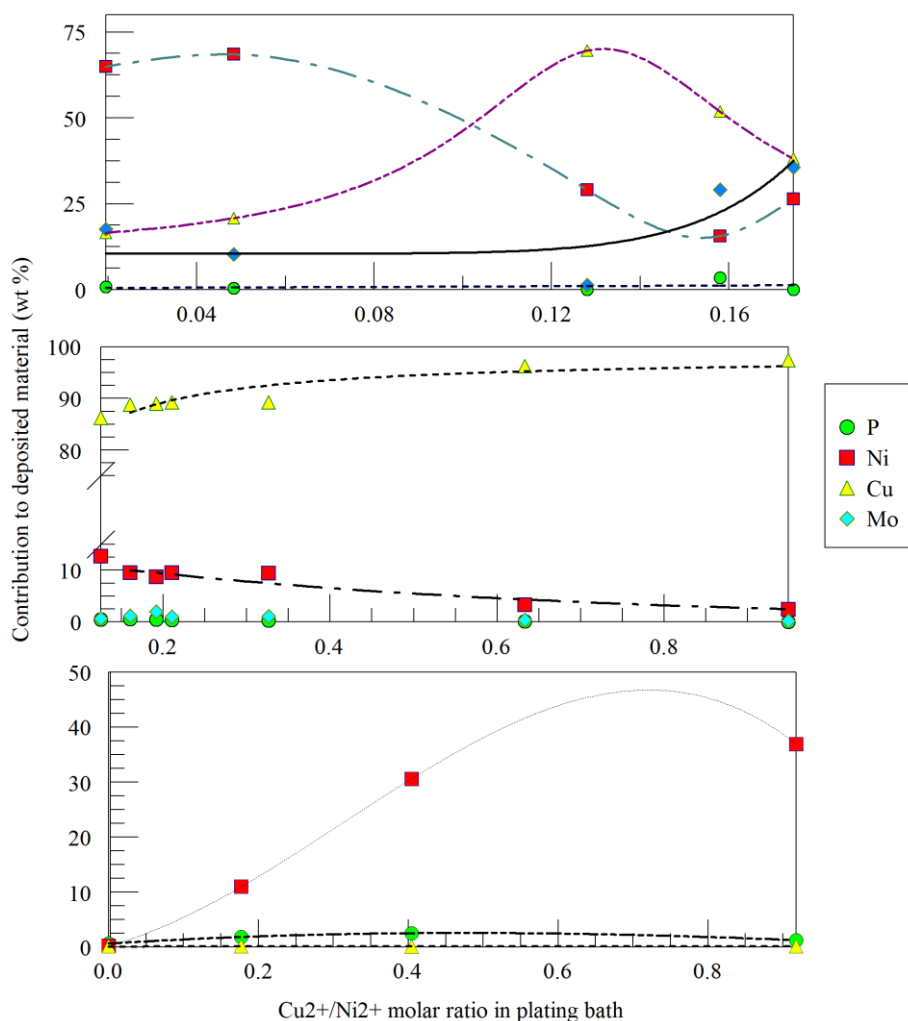
Figure 6. Element contribution to the total material deposited from a mixed reducing agent, sodium hypophosphite and formaldehyde baths

However, there is evidence that including nickel ions in a copper hypophosphite bath will promote copper deposition as nickel will first be deposited and then act as nucleation sites for copper deposition [20]. This suggests that two mechanisms are in effect for copper deposition in a mixed-reducing agent bath:- the nickel-promoted copper deposition from hypophosphite, and the copper deposited from the formaldehyde oxidation. These two re-enforcing mechanisms account for the high copper contents of the deposits. Hence, this is an important finding and evidence supporting the concept of a mixed reducing agent plating bath.

Elemental composition of the deposits was determined with EDX. Figure 6 shows the elemental composition of the deposited material for the three different baths. For the mixed reducing agent bath, copper rich deposits were obtained (85-95.8 wt. %), with Ni contents varying from 14.6 wt. % to about 4.18 wt. %. Much lower amounts of Mo and P were detected in the deposit. The deposition behavior of Mo does not seem to follow any clear cut pattern and suggests that the mechanism of its inclusion in the catalyst is different from the other three. There is a definite pattern to the deposition of Cu, Ni and P: as the copper content of the deposit increases, the Ni and P contents decrease. This is in excellent agreement with the results of Touir et al[18] who investigated CuNiP deposits on steel plates at a pH of 5; the Cu^{2+}/Ni^{2+} ratio was within the range $(0 - 0.02)$; they however give no information on the total material loading obtained with this acidic bath for better comparison with this work's $20 - 76$ wt. %. Hence, electroless plating with mixed reducing agent is not substrate specific and this is currently being investigated.

CuNiMoP deposition in the hypophosphite only bath appears to be principally governed by Cu^{2+}/Ni^{2+} ratios in the plating bath. Below a Cu^{2+}/Ni^{2+} ratio of 0.1, the bath preferentially deposited Ni; from 0.1-0.16 molar ratio, more Cu was deposited than Ni. At a ratio of 0.1, equal amounts of Cu and Ni were deposited. As the Cu^{2+}/Ni^{2+} molar ratio increased, the amount of Ni in the deposit fell from a maximum of 70 wt.% at 0.05 Cu^{2+}/Ni^{2+} molar ratio to < 20 wt. % beyond 0.17. For Cu, as the Cu^{2+}/Ni^{2+} molar ratio increased, the amount of copper in the deposit rose from an initial 16 wt. % to a maximum of 70 wt. % at about 0.15. The behaviors of Mo and P in the pure hypophosphite bath are similar to what was described in the mixed reducing agent bath above.

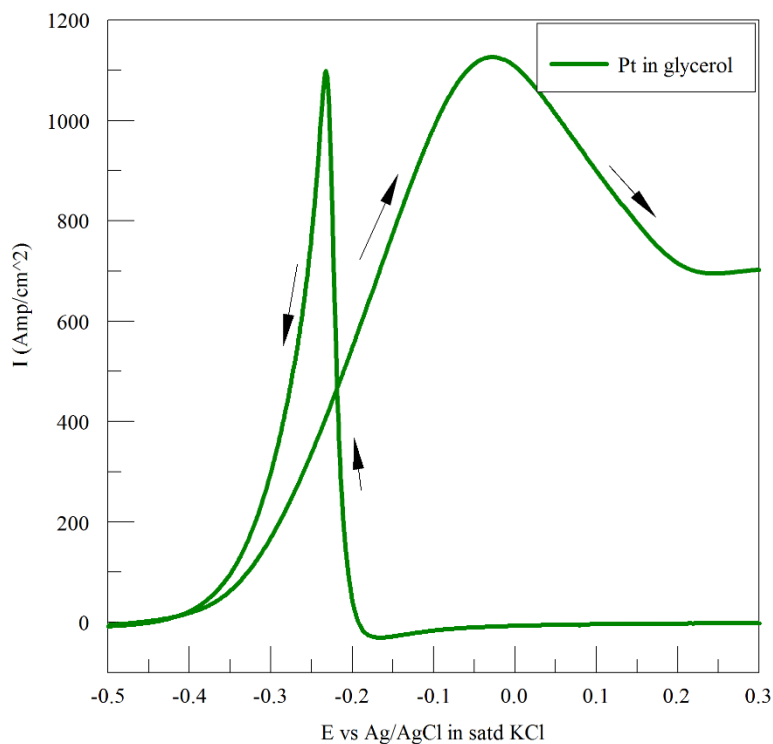*3.4 Electrocatalytic activity of Cu-Ni-MO-P catalyst for alcohol and aldehyde oxidization*

This work is part of on-going effort towards the development of non-precious metal anode material for a glycerol fuel cell. Cyclic voltammograms obtained for formaldehyde (Figure 7) and glycerol (Figure 8) showed that the catalyst is active for their electro-oxidation as prepared. Double oxidation peaks, characteristic of alcohol and aldehyde oxidations were observed for both reactants. This is in agreement with Enyo et al, who found that high Cu content Cu/Ni alloys could oxidize formaldehyde [24]. The activity of the CuNiMoP /graphite was also compared with those of graphite (Figure 8), and Pt (Figure 9). Similar oxidation behavior was obtained with both Pt and CuNiMoP qualitatively from the cyclic voltamograms. Graphite on the other hand showed no activity for glycerol electro-oxidation. This is evidence that the oxidation peaks observed with CuNiMoP/graphite had no discernable contribution from the graphite support.
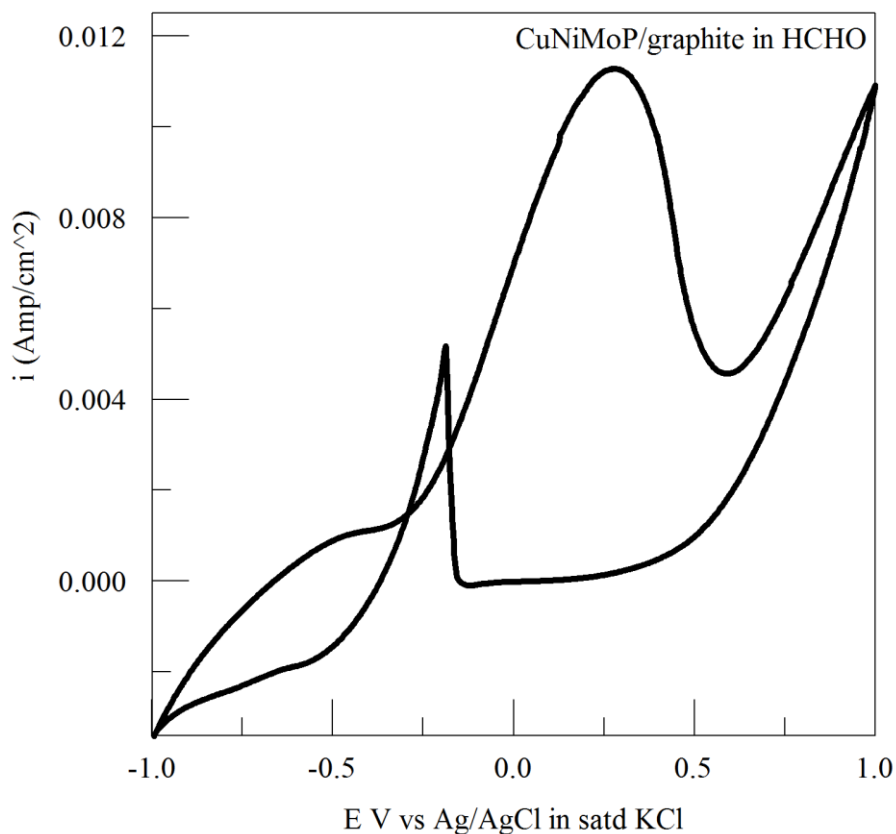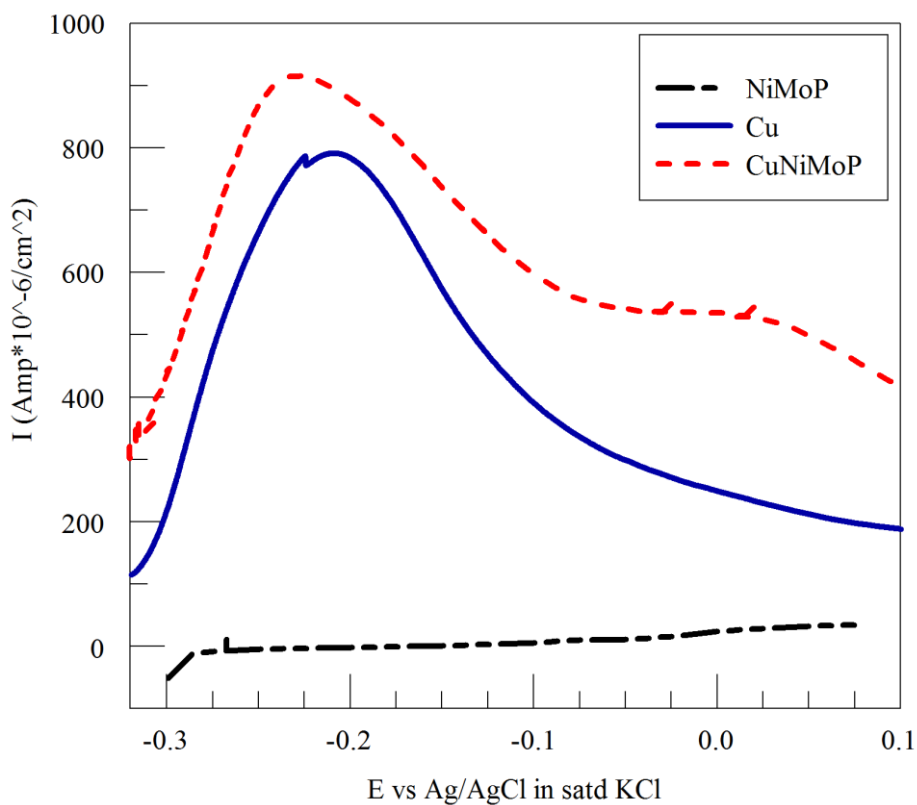
Figure 7. Cyclic voltammetric (CV) oxidation of formaldehyde (0.1 M formaldehyde + NaOH)
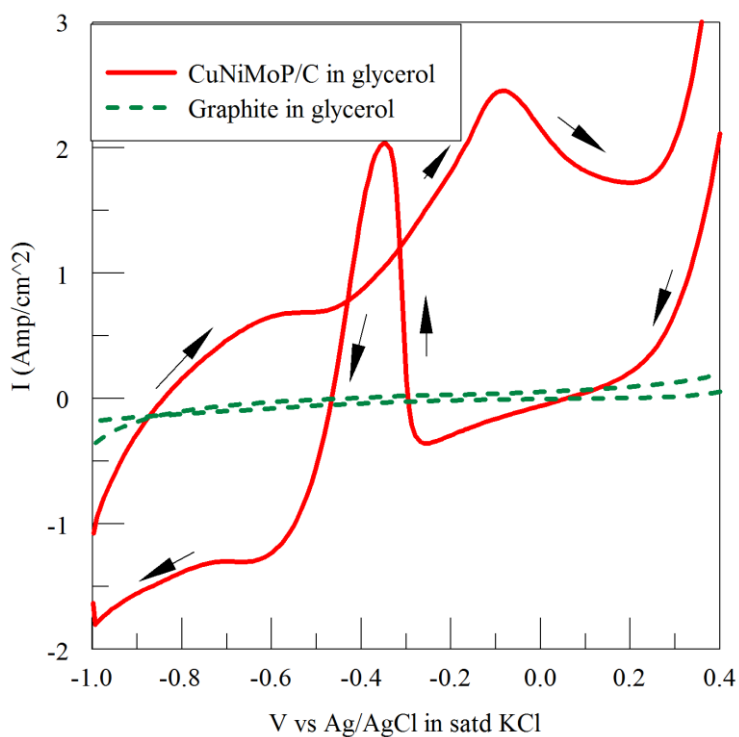

Figure 8. Cyclic voltammogram (CV) showing oxidation of glycerol (0.1 M glycerol + NaOH) on CuNiMoP/graphite electrode

Figure 9. Cyclic voltammogram (CV) oxidation of glycerol (0.1 M glycerol + NaOH) on Pt at 25 ^{o}C and atmospheric pressure (scan rate: 25 mV/s).

Figure 10. A comparison of the electrocatalytic activity of Cu, NiMoP and CuNiMoP electrocatalysts in 4M glycerol + NaOH, scan rate 0.5mV/s .
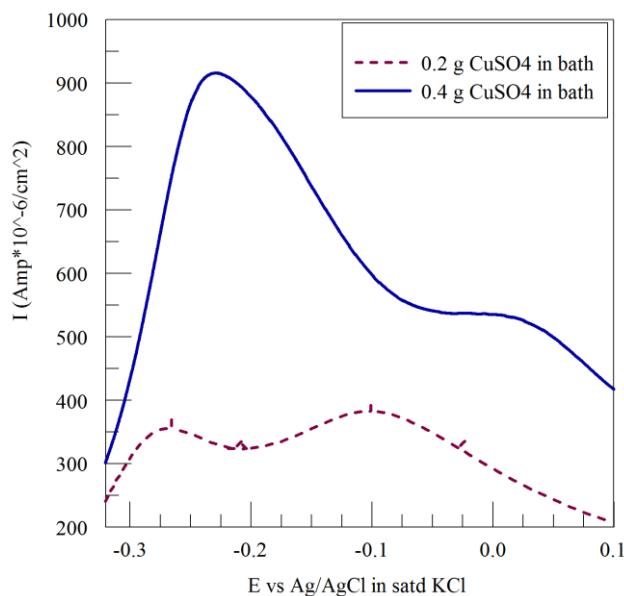
Figure 11. Polarization curves for electrocatalyst prepared from 0.2g and 0.4 g CuSO4 in electroless bath showing effect of deposit composition on polarization curves for 4M glycerol + NaOH, scan rate 0.5mV/s.

The multi-metallic CuNiMoP catalyst activity towards electro-oxidation of glycerol is compared with those of Cu and NiMoP in Fig. 10. The polarization data in the figure show that electroless NiMoP catalyst had limited activity towards glycerol electro-oxidation. Electroless Cu electrocatalyst activity towards glycerol electrooxidation is comparable to the CuNiMoP as indicated in the figure 11. Despite Ni alone not being strongly active for glycerol oxidation, the result suggests some enhancement or synergy of Cu performance with co-deposited Ni. It is known that Ni is able to passivate exposed metal surfaces in a mechanism similar to that of chromium; Cu-Ni alloys containing about 20% Ni are corrosion resistant to the concentrations of caustic soda encountered during these electrolytic oxidations [18].

These characteristics may result in a more stable catalyst under electrolysis conditions. Although the Pt, Cu and CuNiMoP electro-catalysts are active for glycerol oxidation, effort towards identifying the oxidation products and elucidating a mechanism for the reactions is beyond the goal of present contribution.

4. CONCLUSIONS

Electroless Cu-Ni-Mo-P deposits were prepared using a mixed reducing agent bath that contained both sodium hypophosphite and formaldehyde. The approach used in the development of the synthesis method may be applied to synthesize metal alloys from the same electroless bath. In this work particularly, the resulting bath is capable of yielding high plated material loading with high Cu and low phosphorus contents. It is able to co-deposit both copper and nickel, far in excess of the amount that could be deposited in either hypophosphite or formaldehyde baths under the same bath

conditions. The high Cu concentration in both the bath and deposits is a compelling argument for the use of a mixed reducing agent. Preliminary results show that the deposited catalyst was active for glycerol electro-oxidization.

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