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Short Communication

A Nickel(II) N′-(2-hydroxybenzylidene)morpholine-4-carbothiohydrazide Electrocatalyst for Hydrogen Evolution Reaction

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In this study, a nickel(II) N′-(2-hydroxybenzylidene)morpholine-4-carbothiohydrazide complex has been evaluated as an electrocatalyst for the hydrogen evolution reaction (HER) in the presence of 0.2 M $[NBu_4][BF_4]$, and deaerated DMF. The cyclic voltammetry shows two reduction peaks at -0.95 V and -1.34 V corresponding to the reduction of the couples Ni^{2+}/Ni^{+1} and Ni^{1+}/Ni respectively and the two oxidation peaks appeared at 0.68 V and 1.04 V. Additionally, the hydrogen evolution reaction was investigated using a known concentration of acetic acid. The second reduction peak was shifted to approximately 57 V relative to the free acetic acid reduction peak. The maximum activity was recorded in the presence of 31.5 equivalents of acetic acid and reached the current saturation at 235 µA.

Keywords: Semicarbazone, Hydrogen evolution reaction, Nickel complexes, Electrocatalysis

1. INTRODUCTION

Although carbon dioxide (CO_2) is a significantly important gas for many organisms including plants, animals, and some types of bacteria, other investigations have now demonstrated that CO_2 is the primary greenhouse gas of fossil fuel combustion.[1-3] The estimation of CO_2 concentration in the atmosphere was referred to reasonable rates previously exemplified by approximately 230 ppm relative to the current rates that have incredible growth of CO_2 concentration. The dramatic increase in CO_2 concentration is estimated to be about 30% more with approximately 370 ppm. It has been demonstrated that global climate changes require a sustainable level of CO_2 concentration below 550 ppm maximum.[1] The global climate changes have inspired efforts to mitigate the dependence on fossil fuels as a primary source of energy. The guiding paradigm required for any effective energy production system is to create or develop a novel methodology that can supplement and eventually replace fossil fuels by taking into consideration the economic sides and environmental aspects. Despite significant efforts now being devoted to replacing fossil fuels and evolving alternative energy sources, sustainable and renewable energy scientists believe that the dependence on the current energy source will remain a dominant energy source beyond 2050.[4]

Many renewable and sustainable energy technologies are attractive targets for replacing fossil fuels. These technologies which include, but are not limited to, solar cells, wind, nuclear energy, etc., are limited due to concerns about the environmental and cost aspects.[5] The hydrogen-based energy offers an exciting opportunity for the development of CO_2-free energy sources. Hydrogen gas can be produced from various sources including, conventional electrolysis, bacterial biomass, photolytic process, and catalytic decomposition of hydrocarbons exemplified by methane gas. Currently, the most popular source of hydrogen-based energy (approximately 500 billion Nm^3 yearly) is produced using conventional fuels.[1] The Hydrogen Evolution Reaction (HER) offers an excellent alternative technique to produce hydrogen-based energy with free CO_2 emission that is advantageous for global warming potential (GWP). Previously, platinum has been used as an electrocatalyst for the electrochemical reduction of protons. However, its high cost and reproducibility are vital drawbacks.[6-10]

Numerous transition metal complexes with a large π-system such as metalloporphyrins that have great catalytical, photophysical and electrochemical properties become interesting study in recent years.[11-13] Among these transition metals, the hydrogen evolution reaction for thiosemicarbazones that are popular in many biological applications such as antitumor agents,[14] anticonvulsants[15], and herbicides,[16] and are precisely used as selective agents [17-18] have been investigated previously due to their stability and reactivity. A few review articles report the electrochemical properties using a potentiometric method that considered a significant and accurate technique. Interestingly, the technique is extensively applied for the study of ionic equilibria in solutions.[19-23] Here we report the performance of Nickel(II) N′-(2-hydroxybenzylidene)morpholine-4-carbothiohydrazide complex Ni(HL)Cl as electrocatalysts for proton reduction into hydrogen.

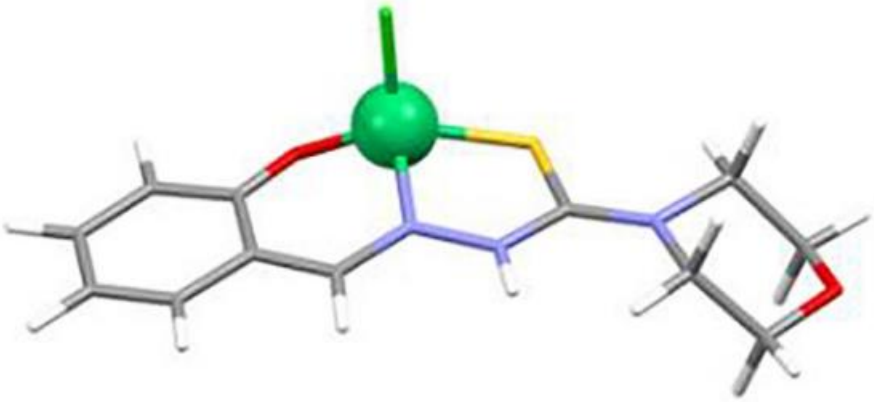

Figure 1. The structure of Nickel(II) N′-(2-hydroxybenzylidene)morpholine-4-carbothiohydrazide where gray is carbon, red is oxygen, pale blue is nitrogen, yellow is chloride, and green is nickel

2. MATERIALS AND METHODS

All reagents and solvents were acquired from Sigma-Aldrich and used without further purification.

2.1 Synthesis of N′-(2-hydroxybenzylidene)morpholine-4-carbothiohydrazide ligand (H_2L)

H_2L ligand was synthesized by the mixing of 1.37 mL salicylaldehyde (12.40 mmol) and 2.00 g of 4-morpholinethio-semicarbazide (12.40 mmol) in 30 mL of ethanol in the presence of a few drops of concentrated sulfuric acid (H_2SO_4). Then, the mixture was refluxed for approximately 2 h. The yellowish-white precipitate was washed with cold ethanol two times and dried under a vacuum overnight

2.2 Synthesis of Nickel(II) N′-(2-hydroxybenzylidene)morpholine-4-carbothiohydrazide Electrocatalyst Ni(HL)Cl

Similarly, the complex of nickel(II) n′-(2-hydroxybenzylidene)morpholine-4-carbothiohydrazide electrocatalyst (Ni(HL)Cl) has been prepared based on a previously reported procedure.[24] 0.65 g (5 mmol) of nickel chloride hexahydrate ($NiCl_2.6H_2O$) was dissolved in 50 mL of ethanol. Then, 1.33 g of the thiosemicarbazone ligand (5 mmol) was dissolved into 20 mL of ethanol. The nickel solution then was added slowly to the ligand solution. The mixture was slowly mixed and refluxed for approximately 8 h at 80 °C. The product was washed with cold ethanol and diethyl ether two times and dried under a vacuum overnight.

2.3 Electrochemical Measurements

The electrochemical measurements of Ni(HL)Cl were performed using the cyclic voltammetry technique (CV) at room temperature. CV instrument was operated in three electrodes, the glassy carbon working electrode, the platinum counter electrode, and Ag/AgCl reference electrode. The electrode potential is monitored on ±100 mV s^{-1}. The E_{OCP} has a scan rate of 1.0 mV s^{-1}. Potentiostat (Autolab PGSTAT 128N) electrochemical cell was used for processing and NOVA 1.10 software was utilized for analysis.

3. RESULTS AND DISCUSSION

The structure of the Ni(HL)Cl complex (figure 1) has unique features such as stability and reactivity due to the chelation effect and the aromaticity of the complex. In Ni(HL)Cl, N, O, and S donor atoms are coordinated to the metal center forming tetrahedral geometry with a torsion angle with regard to the planned median of the complex of 9°. The planarity of the Ni(HL)Cl complex is weak with low symmetry. The complex is electron-rich and can enhance the electronic and electrochemical features.

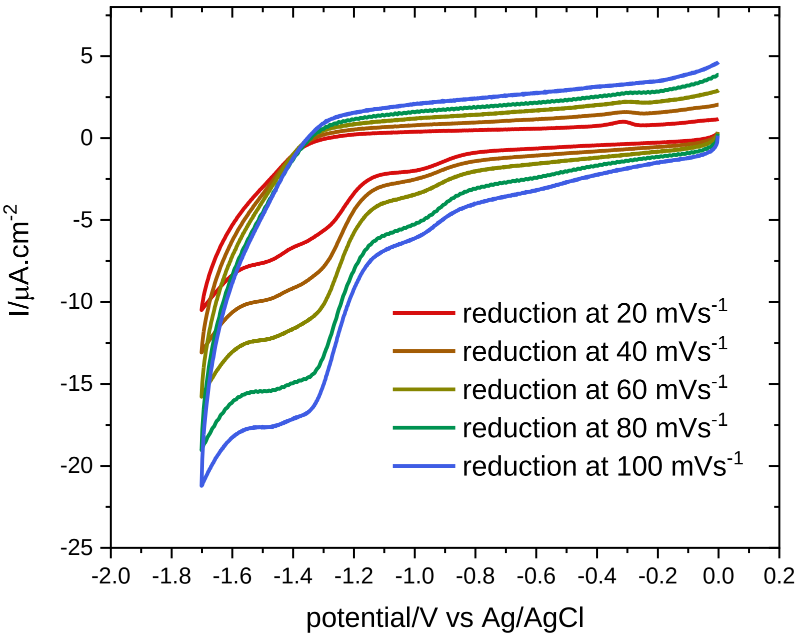

Figure 1. The cyclic voltammetry result displays the reduction of Ni(HL)Cl in 0.2 M $[NBu_4][BF_4]$ DMF-solution at different scan rate; 20, 40, 60, 80 and 100 mVs^{-1}.

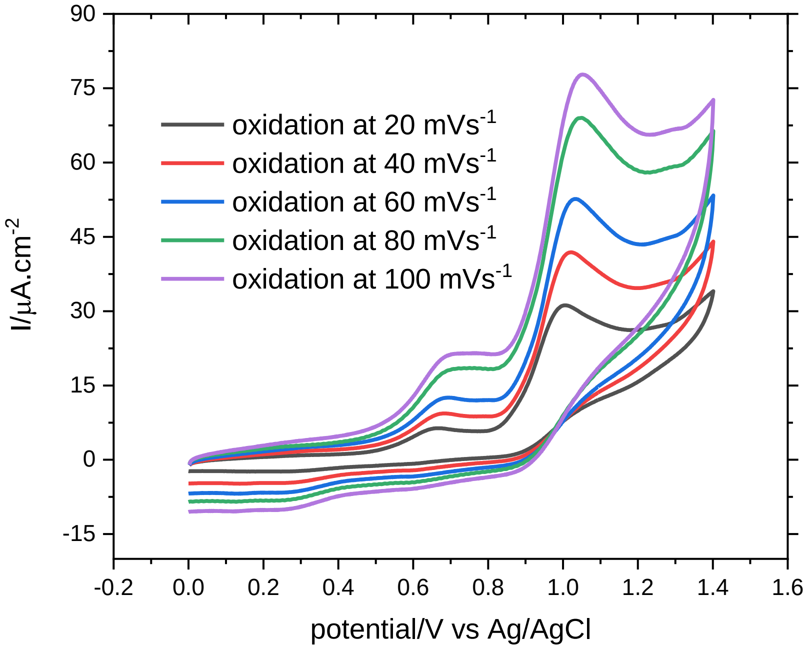

Figure 3. The cyclic voltammetry result displays the oxidation of Ni(HL)Cl in 0.2 M $[NBu_4][BF_4]$ DMF-solution at different scan rate; 20, 40, 60, 80 and 100 mVs^{-1}.

For cycle voltammetry, the Ni(HL)Cl displays two reduction peaks at -0.95 V and -1.34 V corresponding to the reduction of the couples Ni^{2+}/Ni^{+1} and Ni^{1+}/Ni respectively. Interestingly, the oxidation peaks were retarded and displayed peaks at 0.68 V and 1.04 V due to the presence of resistivity. Both oxidation and reduction experiment was carried out in the presence of 0.2 M tetrabutylammonium tetrafluoroborate, $[NBu_4][BF_4]$, and 1.13 mM of the complex using DMF as solvent under nitrogen gas to deaerate oxygen. The result of the two experiments is shown in Figures 2 and 3. In Figure 5, it has been determined that the current reduction peaks of nickel complexes vary linearly with the square root of the scan rate due to non-complicated mass transfer control.

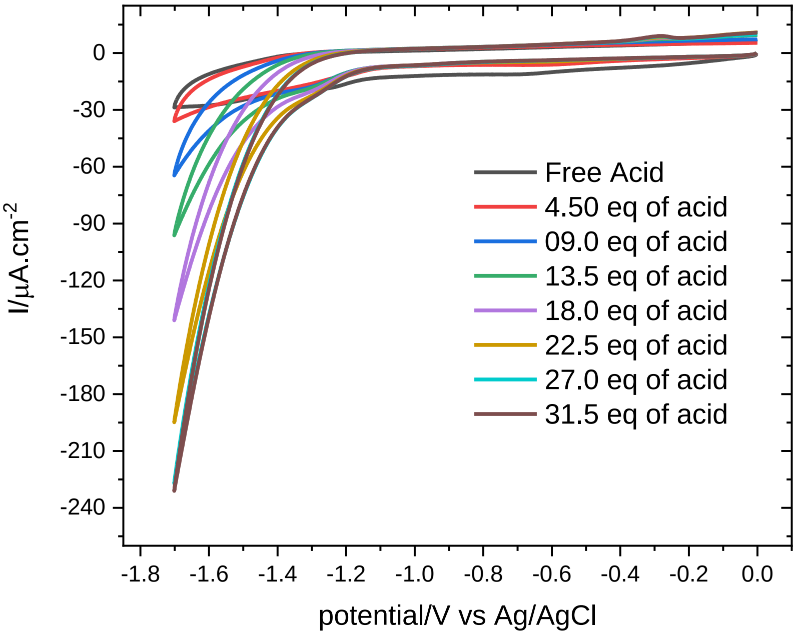

Figure 4. The cyclic voltammetry result displays the reduction of Ni(HL)Cl in DMF containing 0.2 M $[NBu_4][BF_4]$ at a different acidic acid equivalent; 4.5 eq, 9 eq, 13.5 eq, 18 eq, 22.5 eq, 27 eq and 31.5 eq.

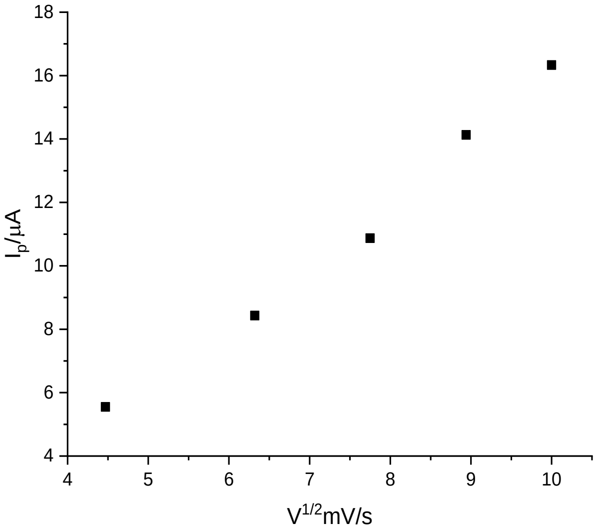

Figure 5. The relationship between the current reduction peaks of NI(HL)Cl in DMF containing 0.2 M $[NBu_4][BF_4]$ versus the root square of different scan rate

For hydrogen evaluation reaction (HER) experiments, the acetic acid (CH_3COOH) was selected to be used as a proton source for proton reduction into molecular hydrogen, and Ni(HL)Cl complex was examined as an electrocatalyst. Interestingly, the second reduction peak was observed at -1.28 V with a clear shift of approximately 570 mV relative to the free acetic acid reduction peak at 1.85 V. Notably, as the acid equivalents number increased as the current (I) increased. The sequence of acid equivalent was increased by 4.5 equivalent. The maximum activity was recorded at 31.5 equivalent of acetic acid and reach saturation at 235 µA. The reduction of proton at a different acidic acid equivalent is shown in Figure. 4.

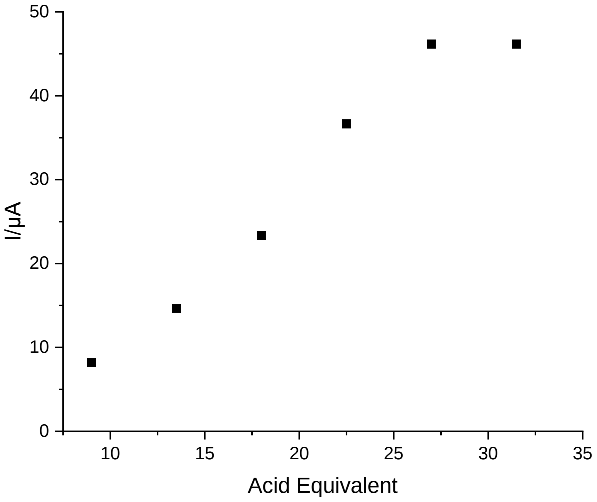

Figure 6. The relationship between the current reduction peaks of NI(HL)Cl in DMF containing 0.2 M $[NBu_4][BF_4]$ versus different acid equivalent

It has been determined previously that the variation of the voltage vs current is proportional to the square root of different scan rates based on the following equation.

$$I_{cap} = A \cdot Cf \cdot v$$

Where A is the surface area of the electrode, v is the scan rate and, Cf is the capacitance. For Ni(HL)Cl electrocatalyst, a linear dependence was observed when the current was plotted versus the square root of different scan rates ranging from 20 mV to 100 mV with a 20 mV interval of voltage as illustrated in Figure. 5. Additionally, the current density or I_{pc} was plotted against different CH_3COOH equivalent at reduction potentials of -1.28 V as displayed in Figure. 6. A linear dependence was observed with the addition of CH_3COOH equivalent before the saturation due to the production of hydrogen.

The use of semicarbazone ligands in hydrogen evolution reactions is promising and can be used as novel organocatalysts[25,26] which have been growing increasingly[27,28] for example, the electrocatalytic activities of 2,2'dipyridylamine were investigated and displayed an excellent activity in acidic polymer electrolytes.[26] Also, polyethylene terephthalate was examined to generate the molecule of hydrogen as the ligand is significant in many applications such as waste reforming reactions.[29] A previous study was reported by Violeta and co-workers for two iron semicarbazone complexes; $Fe(H\text{-}PLTSC)(PLTSC)]_4H_2O$ and $[Fe(H_2\text{-}PLSC)Cl_2(H_2O)]Cl$ in DMF containing 0.2 M tetrabutylammonium tetrafluoroborate $[NBu_4][BF_4]$.[25] Pyridoxal semicarbazone ligands and their Fe(III) complexes were investigated as electrocatalysts for hydrogen evolution reactions. The results illustrate a redox shift for about 350 and 550 mV respectively. Additionally, the highest electrocatalytic activities have been observed at the second equivalent of acetic acid at 45 µA and 35 µA respectively with four times higher than the acid-free for both ligands. Similarly, the nickel complex displays a further redox shift and more electrocatalytic activities relative to the cobalt complexes as summarized in Table1. The cyclic voltammetry experiment of [Co(PLSC)(SO_4)(H_2O)$_2$] and [Co(PLITSC-H)(PLITSC-2H)]CH_3OH have been performed using DMF as a solvent and containing 0.2 M tetrabutylammonium tetrafluoroborate [NBu_4][BF_4]. The proton reduction occurred at -1.58 V and -1.28 V respectively with a shift of 270 mV and 500 mV relative to the free acid.[30] Additionally, the electrocatalytic performance of the nickel complexes has been shown greater potential shift relative to the copper complex [31] as summarized in Table 1.

Table 1. The Potential shift and the highest electrocatalytic activities of different Semicarbazone compounds

Semicarbazone	Potential (V)	Potential shift (mV)	The highest electrocatalytic activities (μA)	Reference
Ni(HL)Cl	-1.28	570	235	This work
[Fe(H-PLTSC)(PLTSC)]4H_2O	-1.40	350	45	[25]
[Fe(H_2-PLSC)Cl_2(H_2O)]Cl	-1.20	550	35	[25]
[Co(PLSC)(SO_4)(H_2O)$_2$]	-1.58	270	110	[26]
[Co(PLITSC-H)(PLITSC-2H)]CH_3OH	-1.28	500	130	[26]
[Cu(PLSC)Cl_2]	-1.53	320	1100	[27]

In this experiment, Ni(HL)Cl has been used as an electrocatalyst to enhance the production of hydrogen. The postulated mechanism of hydrogen evolution reaction (HER) using Ni(HL)Cl as an electrocatalyst is shown in Figure 7. The started Ni^{2+} could accept two electrons and reduced to law valent $Ni^{(0)}$. The electrocatalyst pathway begins with linking hydrogen to the Ni^{2+} metal of the carbothiohydrazide which results in breaking the hydrogen bond to recreate the Ni(HL)Cl starting material thus completing the catalytic cycle.

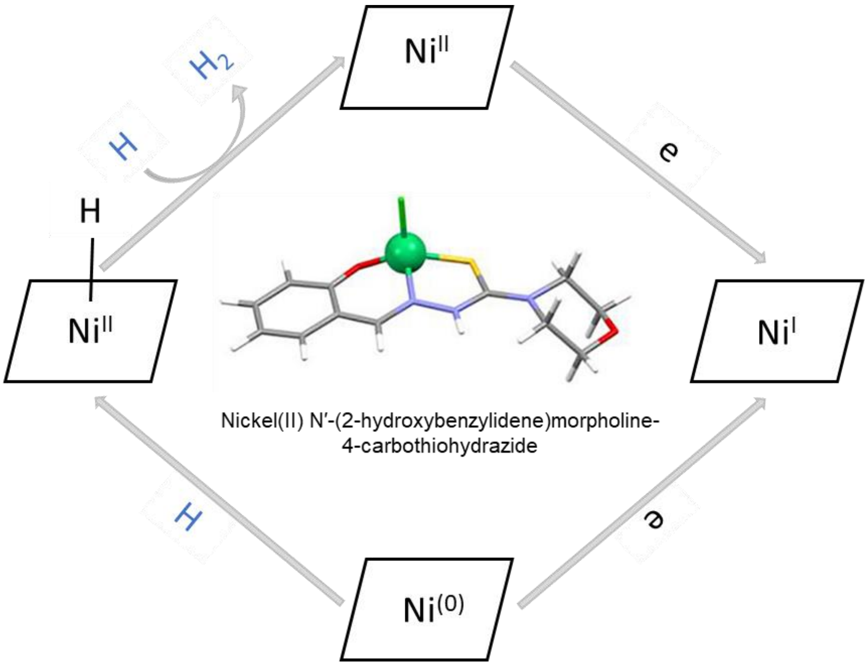

Figure 7. The electrocatalyst mechanism for the hydrogen evolution reaction

4. CONCLUSIONS

The cyclic voltammetry of Ni(HL)Cl complex illustrates a good electrocatalytic activity for proton reduction into molecular hydrogen due to its great stability which can be attributed to the presence of S-N chelating ligands with the metal center as well as the large electron density within the aromatic ring. [31] It can be concluded that the use of transition metals with chelating ligands such as Ni(HL)Cl enhances the HER process giving rise to high electrocatalytic activities. Consequently, transition metals with semicarbazone ligand can be considered novel organocatalysts.[26] The cyclic voltammetry result of a torsional Ni(HL)Cl tetrahedron presented the ability of the complex to enhance the electrocatalyst reduction of different CH_3COOH equivalent at reduction potentials of -1.28 V with a clear shift of approximately 570 mV towards the positive potentials and produce the molecular hydrogen through the hydrogen evaluation reaction. It has been noted that the current density increased linearly with the addition of CH_3COOH equivalent leading to a conclusion that a conversion of the acid into molecular hydrogen has been performed successfully.

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