Short Communication

Hydrogen Evolution Reaction Activity of A Nickel(II) N(4)-morpholinyl isatin-3-thiosemicarbazone Electrocatalyst

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Remarkably, Hydrogen production is an eco-friendly energy source and renewable energy mitigating the addiction to fossil fuels. Hydrogen can be produced directly by water photoelectrolysis using appropriate electrocatalysis in a process known as hydrogen evolution reaction (HER). The use of an appropriate electrocatalyst rich in delocalized electron density can increase the efficiency of the hydrogen evolution reaction exemplified by Nickel(II) N(4)-morpholinyl isatin-3-thiosemicarbazone complex. We herein determine the ability and the efficiency of the electrocatalyst to produce the hydrogen gas taking the advantage of the strong π-system delocalized around the ring.

1. INTRODUCTION

Recently, energy demand has been sharply increasing because of the continuous growth of the world population and rapid economic development. As a result, greenhouse gases are introduced into the atmosphere, threatening the environment. Although the emission of greenhouse gases (GHG) exemplified by the emissions of carbon, sulfur, and nitrogen oxides are a real concern to the environment as already well-known due to fossil-fuel-based energy addiction e.g., coal, natural gas, and petroleum products.[1–3] The efforts to develop renewable and sustainable energy are still continuous. Unfortunately, there are many obstacles due to several factors such as safety, cost, as well as efficiency.[4,5]

Hydrogen production is considered as a great alternative pathway not only to mitigate the use of fossil fuels but also to alleviate the impact of greenhouse gases on the environment.[6,7] Remarkably, enormous progress has been done in power stations, space technologies, and automobiles using hydrogen-based energy.[8,9] Hydrogen gas can be produced utilizing several techniques such as the photolytic process, water electrolysis, bacterial biomass, the catalytic decomposition of methane, and the photoelectrochemical route (PEC).[10–12] In PEC, hydrogen can be produced directly by water photoelectrolysis using appropriate electrocatalysis. Interestingly, the anode and cathode in the electrochemical cell carry out the hydrogen evolution reaction (HER) [13–16] which is considered as a great platform to develop a green hydrogen-based energy cable to mitigate the emissions of harmful gases and generate CO-free hydrogen energy. In HER, the electrocatalyst plays a vital role in the conversion of the hydrogen atom to the molecule of hydrogen.[17-20]

It has been determined that the ligand containing C, N, O, or S donor atoms can stabilize the organometallic complex such as amines, hydrazones, imidazoles, thioureas, and thiosemicarbazones (HL) which have become an interesting electrocatalyst due to the strong stability of these complexes raising from the strong interactions between the transition metal and the S and N atoms.[21] Recently, Nemours studies have investigated the use of thiosemicarbazone as catalysis with various transition metals such as RuHL, PdHL, CuHL, and ReHL.[21-24] We herein investigate the utilization of A Nickel(II) N(4)-morpholinyl isatin-3-thiosemicarbazone complex as a potential electrocatalyst to produce hydrogen molecules taking the advantage of the great structural features of the nickel thiosemicarbazone complex (NiHL) exemplified by the large π-system delocalized around the ring. The structure of nickel thiosemicarbazone is displayed in Figure 1.
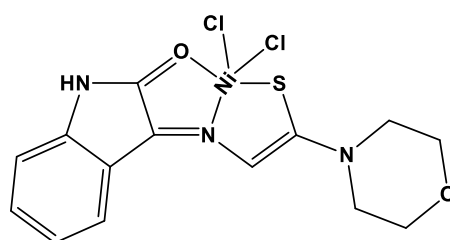

Figure 1. The structure of Nickel(II) N(4)-morpholinyl isatin-3-thiosemicarbazone complex

2. MATERIALS AND METHODS

2.1. Materials

Solvents and all other starting materials were procured from local suppliers, Saudi Arabia and utilized as received. Chemicals such as morpholine, sodium hydroxide, carbon disulfide, sodium chloroacetate, hydrazine monohydrate, nickel(II) chloride hexahydrate, ethanol, hydrochloric acid, acetic acid etc., were purchased from Merck and Sigma-Aldrich. Deionized water was used throughout the experiment. All analytical data supported the structure of the synthesized complex and agreed with the data from the literature.

2.2 Synthesis of N(4)-morpholinyl isatin-3-thiosemicarbazone ligand (HL)

The aforementioned thiosemicarbazone was synthesized as previously reported. [25] Generally, (1:1:1) molar ratios of morpholine, sodium hydroxide, and carbon disulfide were added to the sodium chloroacetate and stirred for approximately 20 min at room temperature. Then, 40 mL of conc. HCl was added dropwise to the yellow solution to yield S-carboxymethyl morphenyldithiocarbamate as a white precipitate. Then, 0.1 mol of the latter was dissolved in 50 mL of hydrazine monohydrate and refluxed for about 20 min. 50 mL of water was added to the resulting mixture, and the yellow precipitate of the ligand was filtered out and then washed three times with cold water.

2.3 Synthesis of Nickel(II) N(4)-morpholinyl isatin-3-thiosemicarbazone (NiHL)

The nickel(II) complex has been synthesized as described previously [25] by adding a 1:1 molar ratio of nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) and the organic ligand (HL) to 30 mL of ethanol. The reaction was refluxed for 2h, and then the solution was left to evaporate slowly on a hot plate (~35 °C) to yield crystals, which were collected and washed multiple times with diethyl ether.

2.4 Electrochemical Measurements

The cyclic voltammetry technique (CV) was used to determine the hydrogen evolution reaction (HER) in the presence of 0.2 M Tetrabutylammonium tetrafluoroborate ($[NBu_4][BF_4]$) as the supporting electrolyte and deaerated DMF at various acetic acid concentrations. The cyclic voltammetry standard cell contains three electrodes as follows silver/silver chloride reference electrode, the auxiliary electrode e.g., platinum (Pt), and glassy carbon as operating (CPE) (0.07 cm^2). The cyclic voltammetry technique is monitored by using Potentiostat (Autolab PGSTAT 128N) and processed using NOVA 1.10 software.

3. RESULTS AND DISCUSSION

The low symmetry square pyramid nickel thiosemicarbazone (NiHL) complex has great structural features and behaves as a neutral tridentate sulfur-containing counterpart making two five-membered rings towards the nickel metal center. Interestingly, the nickel thiosemicarbazone complex has a free pair of electrons on the oxygen, and the sulfur forms a strong covalent bond with the nickel metal. The linkage between the metal center and the sulfur-containing counterpart donor increases the stability. Furthermore, the large aromaticity enhances the reactivity making the nickel thiosemicarbazone an elective candidate for electrochemical applications, including HER. Metal moiety plays a significant role in electrocatalysis reactions and is considered as one of the main factors that enhance the proton reduction reaction of hydrogen atoms to hydrogen gas in HER; besides other factors such as the proton donor, the formation energy of the activated complex from proton donor, and the availability of the active sites. [26]

The cyclic voltammetry experiments (CV) for NiHL complex containing 0.2 M $[NBu_4][BF_4]$ in deaerated DMF solvent, and 1.10 mM of the electrocatalysis display two reduction peaks at $E_p^{red} = $ -1.11

and -1.34 V corresponding to Ni$^+$/Ni and Ni^{2+}/Ni$^+$, respectively. The reduction data of the NiHL complex are illustrated in Figure 2. The peaks are retareded due to the resistivity of NiHL complex as determined in the oxidation peaks at E_p^{ox} =0.93 and 1.29 V. The oxidation data of the NiHL complex are illustrated in Figure 3. The cyclic voltammetry was investigated at different scan rates (v) ranging from 20 to 100 mVs^{-1} g to determine the alteration in the redox reaction with the capacity current (C_f) and known electrode surface area (A) based on Dylla equation ($I_{cap} = A \cdot C_f \cdot v$) [26, 27]
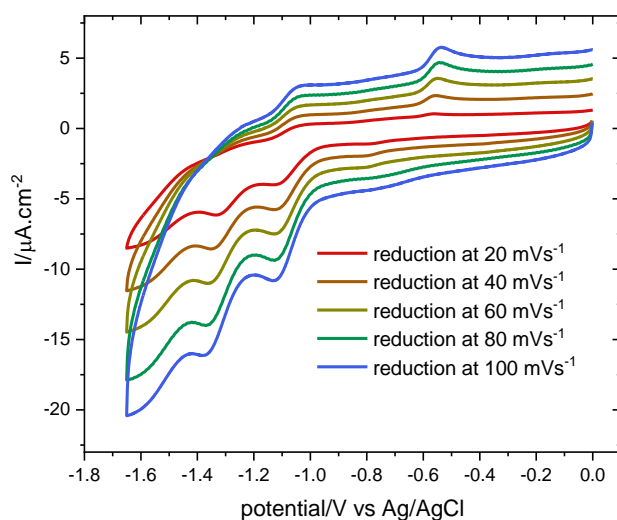

Figure 1. Cyclic voltammogram of NiHL reduction containing 0.2 M [NBu$_4$][BF$_4$] in DMF solvent at various scan rates of 20 to 100 mVs^{-1}.

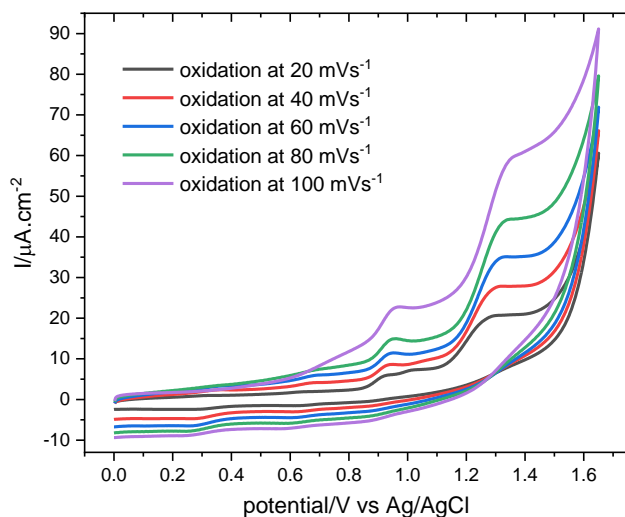**Figure 3.** Cyclic voltammogram of NiHL oxidation containing 0.2 M [NBu$_4$][BF$_4$] dissolved in DMF solvent at various scan rates 20 to 100 mVs^{-1}.
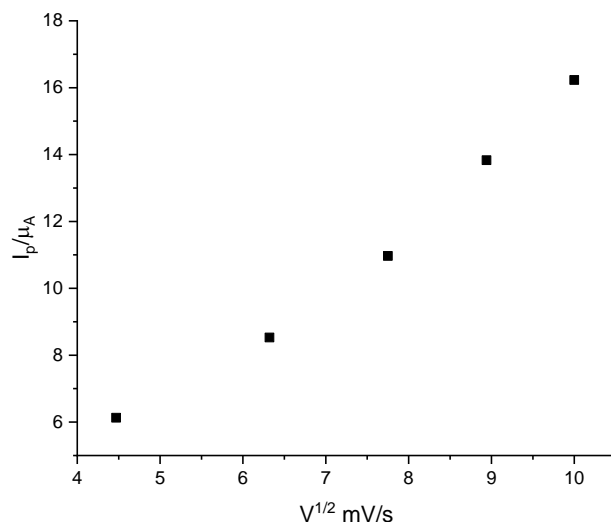
Figure 4. Dependence of the square root of the scan rate ($V^{1/2}$) at various scan rates 20 to 100 mVs^{-1} on the current reduction peaks of NiHL in DMF containing 0.2 M [NBu$_4$][BF$_4$]

Figure 4 represents the proportionality of the current reduction peaks to the square root values of scan rates. Notably, the current peak raises linearly with the square root of the scan rate at a constant analyte concentration, which indicates a diffusion-controlled process on the electrode's surface. To investigate the performance of (NiHL) complex for hydrogen evolution reaction (HER), the hydrogen production using (NiHL) as an electrocatalyst containing 0.2 M [NBu$_4$][BF$_4$] dissolved in DMF solvent was performed at various acid concentrations ranging from 4.5 to 36.0 equivalents (relative to the mole number of the catalyst) see Figure 5.

For hydrogen evolution reaction experiments, the direct reduction of free-catalyst was observed at − 1.85 V under the same conditions. Interestingly, the addition of NiHL electrocatalyst shifts the second potential wave to approximately 550 mV at − 1.30 V. It has been determined that the peak current increases linearly with the addition of acetic acid until reaching saturation at 55 µA and 36 equivalents of the acid due to the formation of hydrogen molecules (H$_2$) see Figure 6.
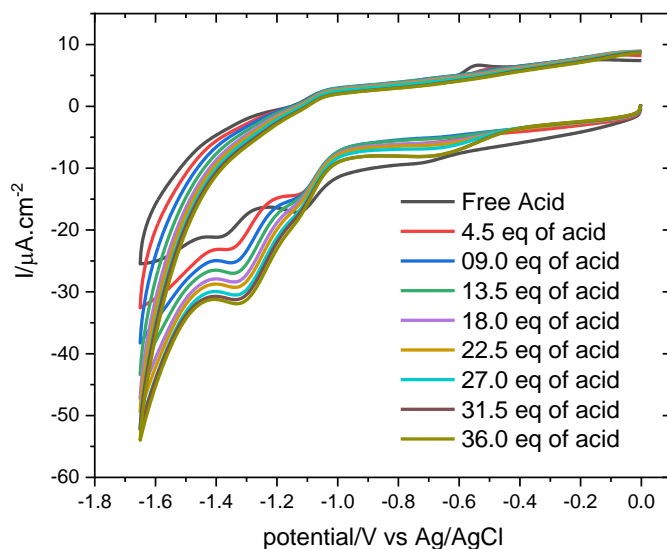
Figure 5. The CV of NiHL containing 0.2 M [NBu$_4$][BF$_3$] in DMF solvent at various acid equivalents ranging from 4.5 - 36 eq.

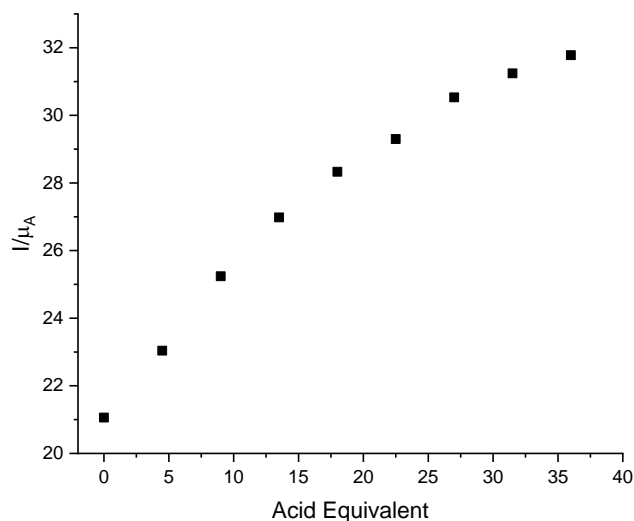**Figure 6.** The effect of the acetic acid conc. on I/μA for the Ni(I)/Ni(0) reduction wave at various acetic acid equivalents

The Ni(II)-based coordination complexes have been used as electrocatalysis in the hydrogen evolution reaction experiments. The potential wave and electrocatalytic activities of Ni(II)-based coordination complexes have encouraged many researchers to investigate the electrocatalytic activities of these complexes [26]. Previously, Ni-hangman porphyrin was investigated in similar conditions and showed a potential shift for about 5 mV only at – 1.76 V. Another Ni- pentafluorophenyls porphyrin was investigated and displayed similar results. The second potential wave of Ni- pentafluorophenyls porphyrin was recorded at – 1.72 V with a tiny shift for about 5 mV. However, the use of Ni- based on 1,10- phenanthroline ligand showed a much greater potential shift for about 370 mV at – 1.48 V [28].

Comparing these results to the nickel thiosemicarbazone electrocatalyst, the NiHL complex illustrates a greater potential shift. The proton reduction occurs at – 1.30 V with a shift of 550 mV relative to the free acid as displayed in Table 1.

Table 1. The Potential wave shifts for various Ni(II)-based coordination complexes

Ni(II)-based coordination complexes	Potential (V)	Potential shift (mV)	Reference
Ni-hangman porphyrin	− 1.76	90	[25]
Ni-pentafluorophenyls porphyrin	− 1.72	130	[25]
Ni-phenanthroline	− 1.48	370	[25]
Ni-thiosemicarbazone	− 1.30	550	This work
Ni-thiacalix[4]arene-based electrocatalyst	-1.33	520	[26]
Ni-1,10- phenanthroline	-1.48	370	[29]

Moll *et al.* synthesized a nickel(II) coordination complex based on thiacalix[4]arene and applied it for electrocatalytic performance. Cyclic voltammetry, which measures redox couples, identifies the coordination complex as having two reduction peaks at 0.57 and 1.33V with a shift in the second reduction peak for about 520 mV corresponding to the two redox couples Ni^{2+}/Ni^+ and Ni^+/Ni, respectively. The NiHL complex illustrates slightly greater potential as compared with the Ni-thiacalix[4]arene. The highest peak current was observed to be at 67 µA. The maximum activity of the complex is slightly greater than the NiHL complex. From the results, we can conclude that the complex has similar electrocatalytic activity as compared to the NiHL complex. In another study, hydrogen evolution reaction (HER) was carried out using a complex based on Ni-1,10- phenanthroline and had comparable outcomes [29]. The application of Ni-based 1,10-phenanthroline ligand was examined and demonstrated a substantially higher potential shift for approximately 370 mV at - 1.48 V. Overall, in comparison to other well-known nickel(II)-based phenanthroline derivatives, the investigated nickel(II) complex NiHL produced better electrocatalytic findings due to the complex structure's hydrophobic interior and the presence of cavitands point [29].

According to the previous work, the suggested mechanism of hydrogen evolution reaction using nickel thiosemicarbazone as an electrocatalyst in similar conditions, the redox reaction has occurred in four consecutive steps involving the reduction NiHL form Ni(+2)→ Ni(+1) and Ni(+1)→ Ni(0) by accepting two electrons. Then, the hydrogen atom attaches to the nickel thiosemicarbazone complex causing oxidation of the metal center from Ni^0→ Ni^{2+}. Finally, another hydrogen atom is involved in the reaction forming a molecular of hydrogen and recreating the nickel thiosemicarbazone starting material as shown in the scheme. 1
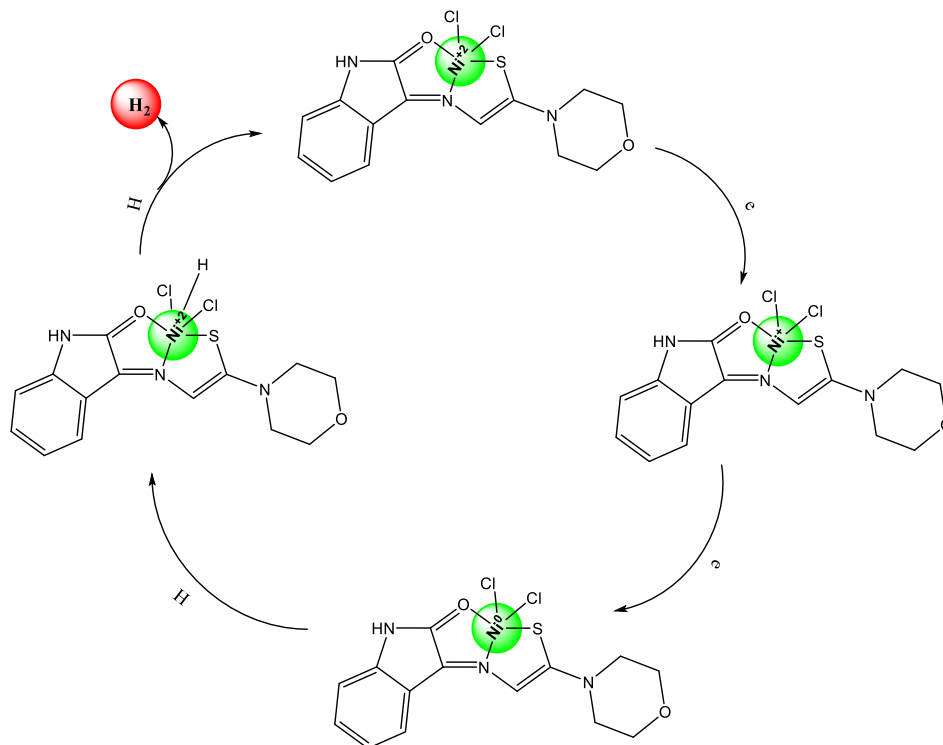
Scheme 1. The suggested mechanism for HER using NiHL as an electrocatalyst.

4. CONCLUSIONS

The utilization of the nickel thiosemicarbazone complex as an electrocatalyst in the HER process displayed an excellent result due to the great delocalization of electron clouds around the ring of thiosemicarbazone. NiHL electrocatalyst has a strong potential shift (~550 mV) at − 1.30 V. Notably, a linear relationship was observed between the peak current with acetic acid equivalents. Recording the saturation at 55 µA with 36 eq. of the acetic acid implies the production of hydrogen gas. The nickel thiosemicarbazone electrocatalyst shows a strong potential shift relative to the other Ni-based electrocatalyst such as Ni-hangman porphyrin, Ni-pentafluorophenyls porphyrin, and Ni-phenanthroline. Finally, the postulated mechanism of HER using the nickel thiosemicarbazone electrocatalyst displayed a reversible redox reaction.

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