Electrocatalytic Activity of (Bis(salicylaldehyde)ethylenediamino)Ni(II) Complex for CO_2 Reduction

M. C. R. Peiris and M. Y. Udugala-Ganehenege

Abstract—**Environmental pollution caused by increased emission of CO_2 is one of the biggest global issues in the 21st century. Among the several other methods to reduce CO_2 in the atmosphere, utilization of CO_2 by electrocatalytic reduction to get chemical species such as oxalic or formic acid has received a considerable attention at present. Related to this issue, our research team mainly focuses on the synthesis of efficient electrocatalysts to bind and reduce CO_2. The work reported herein describes the electrocatalytic reduction of CO_2 by (bis(salicylaldehyde)ethylenediamino)Ni(II)([Ni(Salen)]) complex. Cyclic voltametric studies, carried out in DMF using tetraethylhexaflouro phosphate (TEHFP) as the electrolyte, at a glassy carbon electrode revealed that [(Ni^{2+}Salen)/ (Ni^{+}Salen)] reduction takes place at -1.8 V and the reduced form of the [Ni(Salen)] complex is capable of catalyzing CO_2 reduction around -1.8 V. The efficiency of the reduction process in terms of i (CO_2) / i (N_2) ratio is 1.10. The peak-to-peak separation ΔE_p of 200 ± 2 mV is much bigger than the expected value for an electrochemically reversible process (57) mV that involves one electron transfer. The large ΔE_p is an indicative of the involvement of multi-electron reduction process.**

Index Terms—**Catalytic reduction, nickel complexes, schiff base complexes.**

I. INTRODUCTION

Transition metal macrocyclic Schiff base complexes are popular among the other metal complexes due to their many chemical applications. Electrocatalytic utilization of small molecules by transition metal macrocyclic complexes have become a popular research area. Research studies using [Ni(Salen)] have been carried out for the reduction of small molecules such as O_2 [1]. However, no such studies are reported for CO_2 reduction. It has been reported that Schiff base complexes similar to [Ni(Salen)] convert CO_2 into useful products [2]-[12] such as oxalate or formate [2]-[5]. The work reported herein presents a modified procedure to synthesize [Ni(Salen)] and its catalytic activity for the reduction of CO_2 in DMF at room temperature.

II. METHOD AND MATERIALS

The reported [Ni(Salen)] complex was synthesised by modifying the literature procedure [1]. Nickel acetate (10 mmol, 2.539 g) was dissolved in hot ethanol (25 mL). Salicylaldehyde (20 mmol, 2.12 mL) and ethylenediamine (10 mmol, 0.670 mL) were added to it and the resultant solution was refluxed for 1 hour. The solution was filtered through a sintered glass funnel and orange crystalline product was isolated. The isolated product was washed several times with hot methanol and dried in a desiccator for 24 hours before performing the analysis. Expected structure and light microscopic figure of the product are given in Fig. 1 A) and Fig. 1 B).

Cyclic voltammetry (CV) was recorded from -2 to +2 V potential window under N_2 atmosphere. Then, CO_2 gas was passed through the solution for 15 minutes in a closed system. After the solution is saturated with CO_2, while keeping the CO_2 atmosphere just above the solution, CV was recorded. Reversibility of the [Ni(Salen)] complex for CO_2 reduction was studied by purging N_2 back to the system and running the CV. UV-Visible spectra were recorded before and after studying electrochemistry.

UV-Visible absorption spectra were obtained from a UV-1800 double beam spectrophotometer manufactured by the SHIMADZ co-operation. X-Ray Fluorescence (XRF) data were collected from a 400 MHz Bru kev DRX 400 spectrometer with a 5 mm broadband inverse probe and z-quadients. IR spectra were determined from a FT-IR model 400 spectrometer for dry KBr pellets. Electrocatalytic studies were carried out using an electrochemical workstation (AUTOLAB).

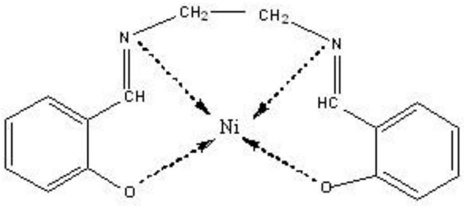

Fig. 1 A). Expected structure for the synthesised Ni(Salen) complex.

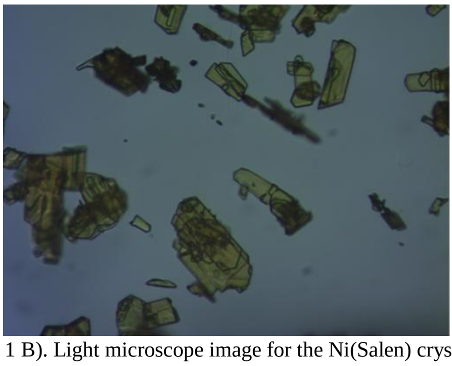

Fig. 1 B). Light microscope image for the Ni(Salen) crystals.

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III. RESULTS AND DISCUSSION

FT-IR, UV-Visible data of [Ni(Salen)] complexes are shown in Fig. 2 and Fig. 3 respectively. The comparison of the FT-IR data for synthesised and reported complex is given in Table I. Observed data are consistent with the reported data [1]. XRF data confirm that [Ni(Salen)] complex contains 100% of Ni and absence of other elements as impurities. The CV for the synthesised complex shows a reduction and an oxidation band at -1.82 and -1.62 V respectively.

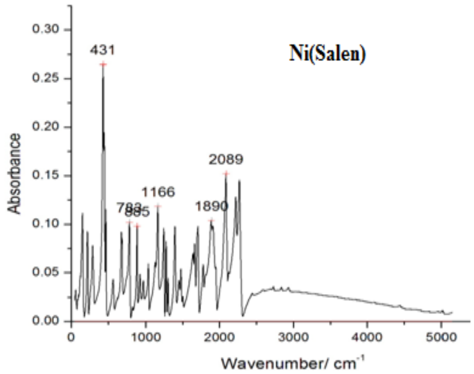

Fig. 2. FTIR spectrum for the synthesised [Ni(Salen)] complex.

TABLE I: REPORTED AND OBSERVED FTIR DATA FOR THE [NI(SALEN)] COMPLEX

Observed band / cm^{-1}	Reported band [1] / cm^{-1}	Functional group present
1704	1617.7	$\mathrm{C{=}N}_{\text{Stretch}}$
1658	1580.7	$\mathrm{C{=}C}_{\text{Stretch}}$
680	400–700	$\mathrm{Ni\text{-}O}_{\text{Stretch}}$
1166	1000-1320	$\mathrm{C\text{-}O}_{\text{Stretch}}$
1454	1400-1500	$\mathrm{C\text{-}C}_{\text{Stretch}}$
782	675-900	$\mathrm{C\text{-}H}_{\text{“oop”}}$
2089	2850-3000	$\mathrm{C\text{-}H}_{\text{Stretch}}$

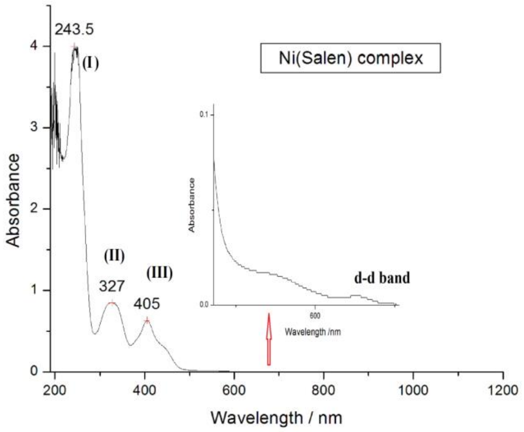

Fig. 3. UV-visible spectra for the synthesised [Ni(Salen)] complex.

TABLE II: THE UV–VISIBLE BANDS OBSERVED FOR THE REPORTED [CO(SALEN)] AND SYNTHESIZED [NI(SALEN)] COMPLEXES

Compound	Absorbance($\lambda_{\max}$: nm)			
	λ_1 / (nm)	λ_2 / (nm)	λ_3 / (nm)	λ_4 / (nm)
[Ni(Salen)]	243.5	327	405	651
[Co(Salen)]	243	354	412	557

UV-Visible spectra recorded for the complex in acetonitrile (1×10^{-4} mol dm^{-3}, 10 mL) between 190-1100 nm are shown in Fig. 3. In the UV-Visible spectrum, four bands appeared at 243, 327,405 and 651 nm. Comparison between reported [Co(Salen)] and synthesized complexes is presented in Table II. The absorption bands in the 600–700 nm range indicate an octahedral structure for this complex in solution, as reported elsewhere [1]. The IR data of the [Ni(Salen)] complex are identical with those of [Co(Salen)] reported [1].

A. *Electrocatalytic Activity of the [Ni(Salen)] Complex*

The [Co(Salen)] complex has shown electrocatalytic activity towards molecular O_2 reduction [1]. In our research the target was to use [Ni(Salen)] complex to study the electrocatalytic activity in DMF. In DMF medium, redox couple appeared at -1.82 V as shown in Fig. 4. Catalytic activity of the complex was studied in DMF medium at two potential ranges; from 0 to -2 V and from 2 to -2.0 V. In this potential window, the band at -1.82 V is due to Ni(II) / Ni(I) reduction. The pseudo reversible band at +0.84 V and the oxidation peak at + 1.5 V may be due to Ni (II) / Ni(III) oxidation and ligand oxidation, respectively.

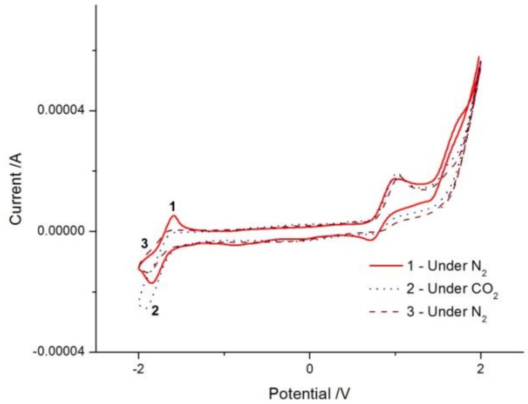

Fig. 4. Cyclic voltamogrames for the [Ni(Salen)] in N_2 and CO_2 atmospheres 2 V - (-2) V.

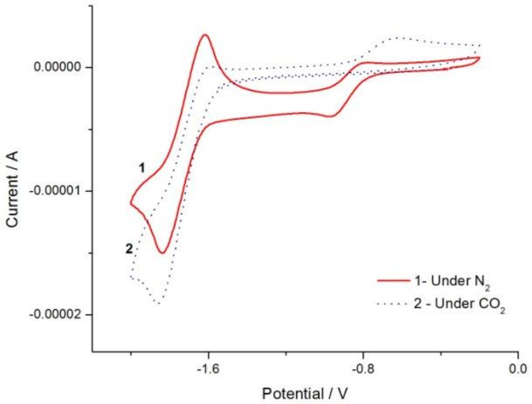

Fig. 5. Cyclic voltammogrames for the [Ni(Salen)] in N_2 (1) and CO_2 (2) atmospheres on the Potential range 0 - (-2) V.

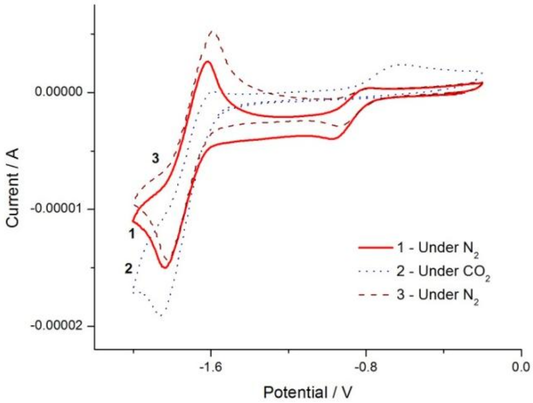

Fig. 6. Reversibility of the electrocatalyst under N_2 (1, 3) and CO_2 (2) when scanned from 0- (-2) V.

Cyclic Voltammogram provided evidence for the electrocatalytic reduction of CO_2. The reversible reduction couple (Ni(II) / Ni(I)) became irreversible with the disappearance of the oxidation peak and an intensity gain was observed at the reduction peak upon passing CO_2 (Fig. 4 - Fig. 6). The efficiency in terms of i (CO_2) / i (N_2) ratio was 1.10 (Table III). Upon passing N_2 back to the same solution, the original CV reappeared, implying the catalytic activity of [Ni(Salen)] [1]-[12].

Even though, it shows the electrocatalytic activity, efficiency of the catalyst is lower than 2. Catalytic activity calculated by using the following equation (Eq. 1).

$$Efficiency = \frac{Cathodic\ peak\ current\ after\ passing\ CO_2}{Cathodic\ peak\ current\ after\ passing\ N_2} \qquad (1)$$

Upon passing CO_2, a new oxidation band appeared at – 0.65 V. This band may be due to the reduction product as reported elsewhere [2]-[5]. The FT-IR data taken, after electrolysis show new bands at 941, 1782 and 1380 cm^{-1}. The new bands appeared in the FT-IR are consistent with the reported data [2]-[5], [13] for the oxalate so that the product obtained due to the CO_2 reduction may be oxalate (Fig. 7). Further studies for identifying the products formed and the effect of accelerators to enhance the efficiency of the process are underway.

TABLE III: SUMMARIZING ELECTROCHEMICAL DATA

Reduction Peak Changes	Peak potential (V)	Peak current (A)
Under N_2	-1.8263	-6.65E-06
Under CO_2	-1.8364	-7.31E-06
Oxidation peak changes	**Peak potential (V)**	**Peak current (A)**
Under N_2	-1.6199	9.20E-06
Under CO_2	-1.6249	5.42E-06

The changes of the UV-Visible spectra before and after running the CV under CO_2 are shown in the Fig. 8. The UV-Visible spectra, taken after running the CV under CO_2 also show evidence for the formation of new product [2]-[5]. Supporting to this argument, the difference spectrum also shows new bands at 245, 290, 370, 650 nm (Fig. 9).

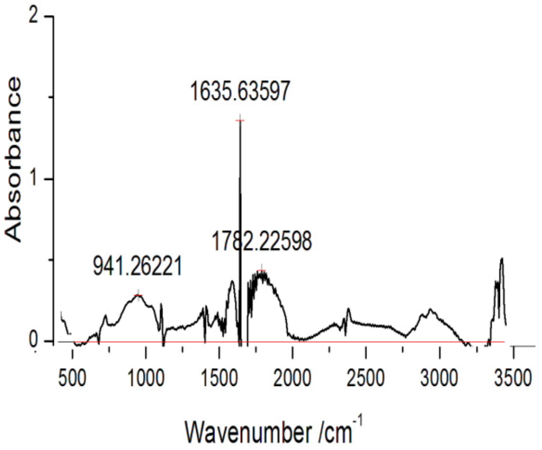

Fig. 7. The difference FT-IR spectrum for the product formed.

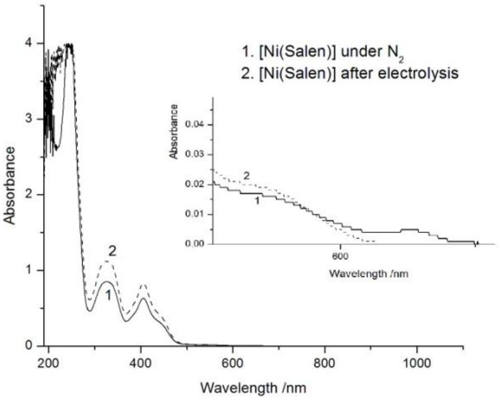

Fig. 8. UV-Visible changes before and after electrolysis.

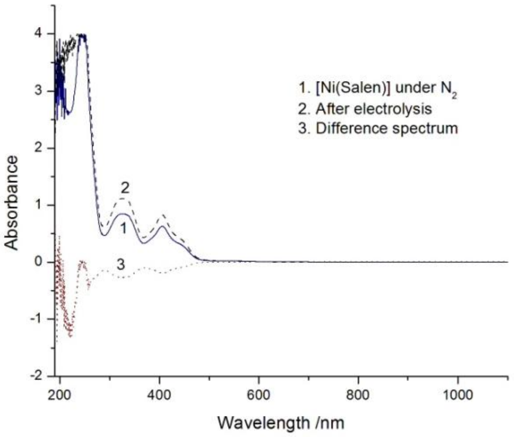

Fig. 9. UV-Visible spectra 1. Before; 2. After the electrolysis and 3. Difference spectrum.

IV. CONCLUSIONS

[Ni(Salen)] was synthesized using a modified procedure and the FT-IR, UV-Visible and XRF data of the synthesized complex were consistent with the reported data. [Ni(Salen)] complex electrocatalytically reduces CO_2. The catalytic efficiency in terms of $i(CO_2)/i(N_2)$ is 1.10. The difference FT-IR spectrum of the complex before and after carrying out the electrolysis provided clues for the formation of oxalate as the CO_2 reduction product. Further identification, isolation of the CO_2 reduction products and possible ways of enhancing CO_2 reduction efficiency are underway.

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