

Reduction of CO₂ by nickel (II) macrocycle catalyst at HMDE

M AULICE SCIBIOH¹, P V RAGINI², S RANI²,
V R VIJAYARAGHAVAN² and B VISWANATHAN^{1,*}

¹Kinetics and Catalysis Laboratory, Department of Chemistry, Indian
Institute of Technology, Chennai 600 036, India

²Department of Physical Chemistry, University of Madras,
Chennai 600 025, India

e-mail: bvnathan@iitm.ac.in

MS received 3 April 2001; revised 14 June 2001

Abstract. With the aim of finding a suitable electrocatalyst for the efficient reduction of carbon dioxide, the electrochemistry of nickel (II) complex of 1,3,6,9,11,14-hexaazatricyclo [12·2·1·1] octadecane was studied using cyclic voltammetry (CV) and controlled-potential electrolysis (CPE) techniques in the presence and absence of CO₂ in 100% H₂O, CH₃CN–H₂O mixtures (20–100%) and DMF–H₂O (70–100%) mixtures. The efficiency of this process is determined using the coulometry technique. CO is the major product in the gaseous phase and HCOOH the sole product formed in the solution phase.

Keywords. Nickel (II) azamacrocyclic; electrocatalytic reduction of CO₂; electrochemical reduction.

1. Introduction

Electrochemical processes for the conversion of carbon dioxide (CO₂) to organic substances have been proposed, but in general a large overpotential is required, making it an inefficient consumer of energy and restricting the possibility of practical application. To diminish the overpotential, considerable efforts have recently been devoted to developing various electrocatalysts involving homogeneous^{1–6} and heterogeneous (electrode mediator)^{7–12} systems. Metal complexes play a crucial role in the process and it is anticipated that the study of homogeneous solution chemistry of CO₂ and its metal complexes will offer valuable clues to the mechanistic steps involved in biogenic reduction.

Transition metal complexes used in conjunction with the metal cathodes lower the overpotential for this reaction and function as electrocatalysts for CO₂ reduction^{13–37}. These complexes can efficiently mediate the electron transfer from the cathode to the substrate, CO₂. In addition to lowering the overpotential, a good catalyst must increase the selectivity of the product being produced and yield high current efficiencies for a single product. When considering CO as the primary reduction product, macrocyclic complexes of nickel, particularly [Ni(cyclam)Cl₂]^{1,38–44} (where cyclam is 1,4,8,11-tetraazacyclotetradecane) and rhenium (I) polypyridyl complexes^{45,46} such as

*For correspondence

[Re(bpy)(CO)₃Cl] (where, bpy is 2,2'-bipyridine), have been found to catalyse the reduction of CO₂ to CO with high selectivity and current efficiency.

The choice of a suitable catalyst is based on its selectivity and efficiency towards the desired product formation and reduction in electricity consumption. The nickel (II) complex of 1,3,6,9,11,14-hexaazatricyclo [12.2.1.1]octadecane is a suitable choice due to its geometry, i.e. because square planar structure provides the axial site free for the approach and interaction of CO₂ with the metal centre and also due to its accessible reduction potential (-1.29 V/SCE) in the desirable range for the reduction of CO₂. In our earlier studies, the reduction of CO₂ in aqueous media at HMDE was performed and the results were presented elsewhere⁴⁷.

In the present study, CO₂ reduction in non-aqueous solvents has been carried out from electroanalytical⁴⁸⁻⁵⁰ and electrosynthetic⁵¹⁻⁵³ view points using the above complex. As the solubility of CO₂ is low in an aqueous medium, organic solvents are used in view of the much high solubility^{54,55} of CO₂ and also the suppression of hydrogen evolution which competes with CO₂ reduction especially in organic aprotic solvents.

2. Experimental

2.1 Materials

Aqueous solutions were prepared from analytical grade salts and double distilled water. Dimethylformamide (DMF) and acetonitrile (CH₃CN) were of spectroscopic grade. The complex [NiL] (ClO₄)₂ (where L = 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1]-octadecane) was prepared by a previously reported procedure^{56,57} and its IR, electronic spectra and conductivity measurements were consistent with those reported in the literature. The structure of the complex is shown in figure 1. Purified N₂ and CO₂ were used for deaeration.

2.2 Analytical methods

Gas samples (500 microlitres) were taken at various intervals with a gas-tight syringe through a septum and a valve, and analysed in a gas chromatograph (Hawlet-Packard 5890) provided with a thermal conductivity detector (TCD) and 20% carbowax on

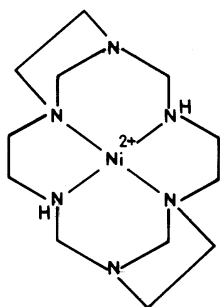


Figure 1. Structure of the Ni(II) complex of 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1]octadecane.

chromosorb column using nitrogen as carrier gas. The detecting limits for CO and H₂ are 0.25% and 0.012% respectively. Formic acid was determined by a colorimetric method⁵⁸.

2.3 Electrochemical measurements

Cyclic voltammetric experiments were performed with a Wenking ST 72 potentiostat and a voltage scan generator with a graphtec XY-recorder WX 2300, using a three-electrode system consisting of a locally fabricated hanging mercury drop working electrode, mercury pool auxiliary electrode and saturated calomel reference electrode (SCE), brought into the main compartment via., a luggin capillary. Solutions of 0.1 to 2.0 mM complex were used for the studies. 0.1 M aqueous LiClO₄ was used as a supporting electrolyte. All solutions were purged with N₂ (or CO₂) where required for 0.5 h, prior to each scan. In general cyclic voltammograms were recorded from -0.9 to -1.6 V at a scan rate of 50 to 400 mV s⁻¹. Experiments were run at 298 ± 2 K.

A two-compartment gas tight electrolysis cell was used for the controlled-potential electrolysis (CPE) experiments. The working electrode was a mercury pool and the reference electrode was a saturated calomel electrode. The counter electrode (Pt) was separated from the main compartment by a G0 sinter. The electrolytic solution was deaerated by bubbling CO₂ (or N₂) for 30 min and electrolysed at -1.6 V/SCE for 5 h.

3. Results and discussion

3.1 Electrochemistry of [Ni(L)²⁺] in 100% water

Cyclic voltammograms obtained for the complex [Ni(L)²⁺] in 100% water under N₂ and CO₂ atmosphere are shown in figure 2. The complex [Ni(L)²⁺] under N₂ atmosphere exhibits a redox potential at -1.29 V vs SCE with a Δ*E*_{*p*} of 60 mV indicating that the process is one-electron reduction. This reduction process is diffusion controlled and is confirmed by the plot of *I*_{*p,c*} vs [complex] and *I*_{*p,c*} vs *n*^{1/2} which is linear. In the CO₂ atmosphere, the cathodic current increases two-fold in height and the corresponding anodic peak diminishes and becomes a plateau at low scan rates (< 100 mV/s).

3.2 Electrochemistry of [Ni(L)²⁺] in CH₃CN-H₂O mixture

In 100% CH₃CN, the complex Ni(L)²⁺ showed a redox couple at -1.33 V vs SCE with a Δ*E*_{*p*} of 70 mV under N₂ atmosphere. The complex does not show any catalytic current under CO₂ atmosphere indicating that it does not catalyse the reduction of CO₂ under dry acetonitrile medium. Figure 3 shows the cyclic voltammograms of the complex [Ni(L)²⁺] in CH₃CN-H₂O mixture under N₂ and CO₂ atmosphere. In CH₃CN-H₂O mixtures, the complex under CO₂ atmosphere shows an increase in cathodic current and the corresponding anodic current diminishes in height. As the percentage of CH₃CN increases, the peak potential does not change. The ratio of *i*_{*k*}/*i*_{*d*} (where, *i*_{*k*} is the kinetic current measured under CO₂ atmosphere and *i*_{*d*} is the diffusion current measured under N₂ atmosphere) remains the same as that observed for 100% water (table 1).

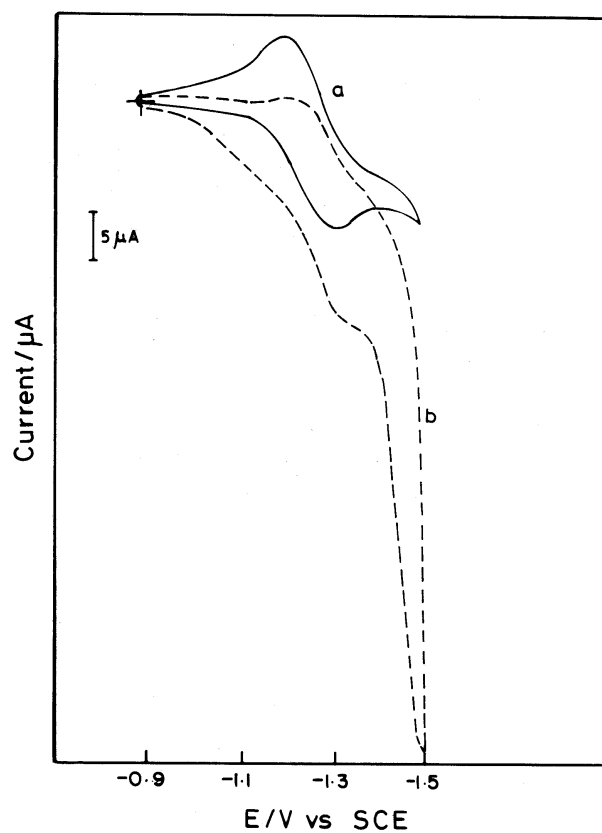


Figure 2. Cyclic voltammogram of $[\text{Ni}(\text{L})^{2+}]$ (1.0 mmol/dm^3) in 0.1 mol/dm^3 LiClO_4 in water at HMDE under N_2 (a) and CO_2 (b). Scan rate = 200 mV/s .

Table 1. Studies on scan rate variation in solvents of different composition.

$[\text{Ni}(\text{L})^{2+}] = 1.0 \text{ mmol/dm}^3$; solvent = $\text{CH}_3\text{CN-H}_2\text{O}$ mixtures;
 $[\text{LiClO}_4] = 0.1 \text{ mol/dm}^3$; temperature = $298 \pm 2 \text{ K}$

H_2O (%)	$I_{p,c}(\text{CO}_2)/I_{p,c}(\text{N}_2)$		
	Scan rate (mV s^{-1})		
	200	100	50
0	—	—	—
20	1.78	1.79	2.00
40	1.65	1.65	1.78
60	1.85	1.72	1.92
80	1.77	1.83	2.00
100	1.98	1.63	1.65

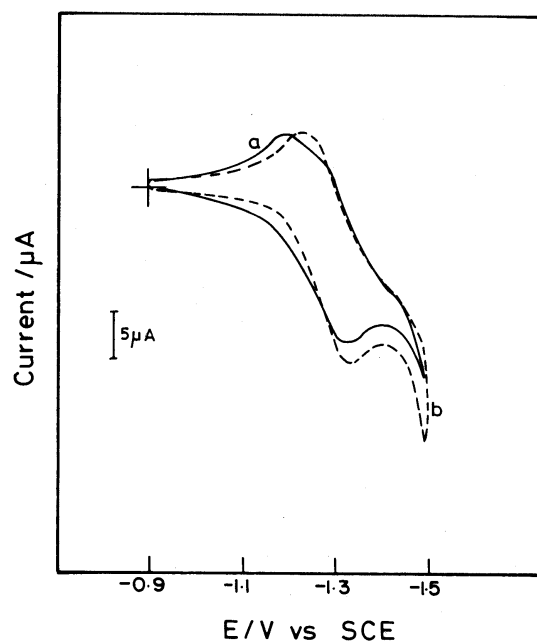


Figure 3. Cyclic voltammogram of [Ni(L)²⁺] (1.0 mmol/dm³) in 0.1 mol/dm³ LiClO₄ in 20%CH₃CN-H₂O at HMDE under N₂ (a) and CO₂ (b). Scan rate = 200 mV/s.

Table 2. Studies on scan rate variation in solvents of different composition.

[Ni(L)]²⁺ = 1.0 mmol/dm³; solvent = DMF-H₂O mixtures;
[LiClO₄] = 0.1 mol/dm³; temperature = 298 ± 2K

H ₂ O (%)	$I_{p,c}(\text{CO}_2)/I_{p,c}(\text{N}_2)$ Scan rate (mV s ⁻¹)		
	200	100	50
0	—	—	—
70	2.0	2.11	2.25
80	1.90	1.90	2.00
90	1.97	2.41	2.35
100	1.98	1.63	1.65

Table 3. Product analysis (controlled potential electrolysis, coulometry-gas chromatography).

[Complex] = 1.0 mmol/dm³; [LiClO₄] = 0.1 mol/dm³; temperature = 298 ± 2K;
current density = 0.7 mA/cm²; electrolysed at -1.6 V/SCE for 5 h

Solvent	Volume of CO produced (ml)	Volume of H ₂ produced (ml)	CO: H ₂ (vol/vol)	Current efficiency (%)
H ₂ O	20.0	10.0	1:2	72
20% CH ₃ CN-H ₂ O	22.0	10.5	1: 2.09	79
10% DMF-H ₂ O	25.0	12.0	1:2.08	75

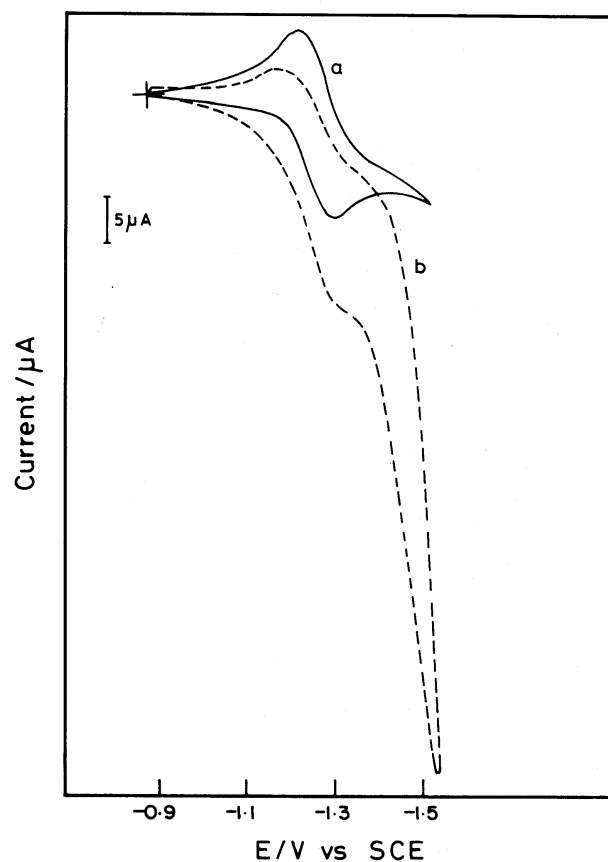
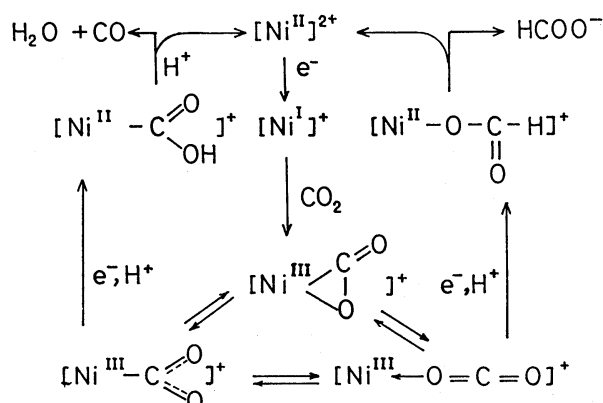


Figure 4. Cyclic voltammogram of $[\text{Ni}(\text{L})]^{2+}$ (1.0 mmol/dm^3) in 0.1 mol/dm^3 LiClO_4 in $10\% \text{ DMF-H}_2\text{O}$ at HMDE under N_2 (a) and CO_2 (b). Scan rate = 200 mV/s .

3.3 Electrochemistry of $[\text{Ni}(\text{L})^{2+}]$ in $\text{DMF-H}_2\text{O}$ mixture

Cyclic voltammograms of the complex $[\text{Ni}(\text{L})^{2+}]$ in $\text{DMF-H}_2\text{O}$ mixtures under N_2 and CO_2 atmospheres are shown in figure 4. The complex shows a redox couple with an $E_{1/2}$ value of -1.32 V vs SCE and ΔE_p of 70 mV . Under CO_2 atmosphere, the cathodic current increases in height two-fold and the corresponding anodic current diminishes and becomes a plateau at low scan rates ($< 100 \text{ mV/s}$). The ratio of i_k/i_d shows a maximum in $90\% \text{ DMF-H}_2\text{O}$ mixture as compared to that of $100\% \text{ H}_2\text{O}$ (table 2). This is attributed to the increased solubility of CO_2 in DMF than in water. When the percentage of water content was decreased, the catalytic current was not observed in the presence of CO_2 . The observations that the reduction of CO_2 was favored in the presence of $\text{DMF-H}_2\text{O}$ mixtures but no catalytic current was observed in dry DMF indicate the requirement of protons for the reduction of CO_2 .



Scheme 1. Carbon dioxide reduction mechanism.

3.4 Controlled-potential electrolysis (CPE) and coulometry studies

The electrochemical reduction of CO₂ in the presence of [Ni(L)²⁺] was further supported by controlled-potential electrolysis experiments followed by product analysis using gas chromatography for the gaseous phase and colorimetric analysis for solution phase. The gaseous products were found to be CO and H₂. Formic acid was the only reduction product found in the electrolysed solution phase as trace amounts in the range of 1.0 μM. Total volumes of CO and H₂ produced and the efficiency of this process are given in table 3. Based on the above observations, a tentative reaction mechanism is proposed in scheme 1.

References

1. Beley M, Collin J P, Ruppert R and Sauvage J P 1984 *J. Chem. Soc., Chem. Commun.* 1315
2. Balazs G B and Anson F C 1993 *J. Electroanal. Chem.* 149
3. Tezuka M and Iwashita 1993 *Chem. Lett.* 955
4. Bhugun I, Lexa D and Saveant J M 1994 *J. Am. Chem. Soc.* **116** 5015
5. Nagao H, Mizukawa and Tanaka K 1993 *Chem. Lett.* 955
6. Seshadri G, Lin C and Bocarsly A B 1994 *J. Electroanal. Chem.* **372** 145
7. Arana C, Keshavarz M, Potts K T and Abruna H D 1994 *Inorg. Chem. Acta* **225** 285
8. Yoshida T, Iida T, Shirasagi T, Lin R J and Kaneko M 1993 *J. Electroanal. Chem.* **344** 355
9. Ogura K, Mine K, Yano J and Sugihara M 1993 *J. Chem. Soc., Chem. Commun.* 20
10. Ogura K, Sugihara H, Yano J and Higasa M 1994 *J. Electrochem. Soc.* **141** 419
11. Ogura K, Higasa M, Yano J and Endo N 1994 *J. Electroanal. Chem.* **379** 373
12. Ogura K, Endo N, Nakayama M and Ootsuka H 1995 *J. Electrochem. Soc.* **142** 4026
13. Ikeda S, Tagaki T and Ito K 1987 *Bull. Chem. Soc. Jpn.* **60** 2517
14. Sullivan B P, Krist K and Guart H E (eds) 1993 *Electrochemical and electrocatalytic reactions of carbon dioxide* (Amsterdam: Elsevier)
15. Behr A 1988 *Carbon dioxide activation by metal complexes* (New York: VCH)
16. Hammouche M, Lexa D, Momenteau M and Saveant J M 1981 *J. Am. Chem. Soc.* **113** 8455
17. Amatore C and Saveant J M 1981 *J. Am. Chem. Soc.* **103** 5021
18. Kubiak C P and Ratliff K S 1991 *Israel J. Chem.* **31** 3
19. Ratliff K S, Lentz R E and Kubiak C P 1992 *Organometallics* **11** 1986
20. Tominaga K, Sasaki Y, Kawai M, Watanabe T and Saito M 1993 *J. Chem. Soc., Chem. Commun.* 629

21. Bolinger C M, Sullivan B P, Conrad D, Gilbert J A, Story N and Meyer T J 1985 *J. Chem. Soc., Chem. Commun.* 796
22. Bolinger C M, Story N, Sullivan B P and Meyer T J 1988 *Inorg. Chem.* **27** 4582
23. Bruce M R M, Megehee E, Sullivan B P, Thorp H, O'Toole T R, Downard A and Meyer T J 1988 *Organometallics* **7** 238
24. Bruce M R M, Megehee E, Sullivan B P, Thorp H H, O'Toole T R, Downard A, Pugh J R and Meyer T J 1992 *Inorg. Chem.* **31** 4864
25. Pugh J R, Bruce M R M, Sullivan B P and Meyer T J 1991 *Inorg. Chem.* **30** 86
26. Hori Y, Wakebe H, Tsukamoto T and Koga O 1994 *Electrochim. Acta* **39** 1833
27. Szymaszek A and Pruchnik F P 1989 *J. Organomet. Chem.* **376** 133
28. Ogura K, Migita C T and Nagaoka T 1989 *J. Mol. Catal.* **56** 276
29. Ogura K, Migita C T and Wadaka K 1991 *J. Mol. Catal.* **67** 161
30. Ogura K and Uchida H 1987 *J. Chem. Soc., Dalton. Trans.* 1377
31. Ogura K and Tagaki M 1986 *J. Electroanal. Chem.* **206** 209
32. Matsuoka S, Yamamoto K, Ogata T, Kusaba M, Nakashhima N, Fujita E and Yanagida S 1993 *J. Am. Chem. Soc.* **115** 601
33. Ishida H, Tanaka H, Tanaka K and Tanaka T 1987 *J. Chem. Soc., Chem. Commun.* 131
34. Ishida H, Fujiki K, Ohba T, Ohkubo K, Tanaka K, Terada T and Tanaka T 1990 *J. Chem. Soc., Dalton Trans.* 2155
35. Tomohiro T, Uoto K and Okuna H 1990 *J. Chem. Soc., Chem. Commun.* 194
36. Arana C, Yan S, Keshavarz M, Potts K T and Abruna H D 1992 *Inorg. Chem.* **31** 3681
37. Miedaner A, Curtis C J, Barkley R M and DuBois D L 1994 *Inorg. Chem.* **33** 5482
38. Beley M, Collin J P, Ruppert R and Sauvage J P 1986 *J. Am. Chem. Soc.* **108** 7461
39. Collin J P, Jouaiti A and Sauvage J P 1988 *Inorg. Chem.* **27** 1986
40. Petit J P, Chartier P, Beley M and Sauvage J P 1987 *New J. Chem.* 751
41. Pearce D J and Pletcher D 1986 *J. Electroanal. Chem.* **197** 317
42. Fisher B and Eisenberg R 1980 *J. Am. Chem. Soc.* **102** 7361
43. Lovecchio F V, Gore E S and Busch D H 1974 *J. Am. Chem. Soc.* **96** 3109
44. Petit J P, Chartier P, Beley M and Deville J P 1989 *J. Electroanal. Chem.* **269** 267
45. Breikss A and Abruna H D 1986 *J. Electroanal. Chem.* **201** 347
46. Hawecker J, Lehn J M and Ziessel R 1986 *Helv. Chim. Acta* **69** 1990
47. Ragini P V and Vijayaraghavan V R 1995 *Trans. Soc. Adv. Electrochem. Sci. Technol.* **30** 116
48. Haynes L V and Sawyer D T 1969 *Anal. Chem.* **39** 332
49. Lamy L, Nadjo L and Saveant J-M 1977 *J. Electroanal. Chem.* **78** 403
50. Eggin B R and McNeill J 1983 *J. Electroanal. Chem.* **148** 17
51. Tysee D A, Wagenknecht J H, Baiser M M and Chruma J L 1972 *Tetrahedron Lett.* 4809
52. Gambino S and Silvestri G 1973 *Tetrahedron Lett.* 3025
53. Gressin J C, Michelet D, Nadjo L and Saveant J-M 1979 *Nouv. J. Chim.* **3** 545
54. Stephen H and Stephen T (eds) 1963 In *Solubilities of inorganic and organic compounds* (New York: Macmillan) vol. 1, part 2, 1063
55. Clever H L and Battino R 1975 In *Solutions and solubilities* (ed.) M R J Cack (New York: Wiley) 386
56. Suh M P, Kang S-G, Goedken V L and Park S 1991 *Inorg. Chem.* **30** 365
57. Suh M P, Shin W, Kang S-G, Lah M S and Chung T-M 1989 *Inorg. Chem.* **28** 1602
58. Grant W M 1948 *Anal. Chem.* **20** 267