Nickel(II)–Cyclam: an Extremely Selective Electrocatalyst for Reduction of CO_2 in Water

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CO_2 is electroreduced efficiently to CO on a mercury cathode, in the presence of $[Ni^{II}(cyclam)]^{2+}$; even in pure water, the selectivity for reduction of CO_2 *vs.* that of H_2O is huge.

The reduction of CO_2 is important in converting this abundant carbon source into organic products. On metal cathodes, the direct electrochemical reduction of CO_2 generally occurs at highly negative potentials.[1] Recently, several molecular electrocatalysts have been proposed that diminish the overvoltage; they are mainly based on nitrogen-containing macrocyclic complexes of cobalt or nickel.[2—5] A difficulty arises in the selectivity of reduction in that the presence of H_2O is necessary[4] and H_2 is generally one of the major products. Until now, one of the only selective electrocatalysts reported seems to be a rhenium(I) complex, operating in a mixed solvent.[6] We report here that (1,4,8,11-tetra-azacyclotetradecane)nickel(II) $\{[Ni^{II}(cyclam)]^{2+}\}$ is a selective electrocatalyst for the reduction of CO_2 to CO, even in pure water; in addition, the reaction is effective at potentials *ca.* 0.5 V below the thermodynamic value [$CO_2/CO : E^{\circ\prime} = -0.41$ V *vs.* normal hydrogen electrode (N.H.E.) at pH = 5]. Some results are listed in Table 1.

The experimental data clearly show that (i) without electrocatalyst or with $NiCl_2$, only H_2 can be detected (runs 1 and 2), (ii) in the presence of $[Ni^{II}(cyclam)]^{2+}$, the electroreductive process is effective at -0.9 V, the velocity of the reaction being remarkable (turnover frequency *ca.* 32 h^{-1}) at -1.05 V (run 6), (iii) $[Ni^{II}(cyclam)]^{2+}$ is quantitatively recycled (overall turnover numbers *ca.* 10^2 in runs 5 and 6), and (iv) the Faradaic yields are almost quantitative for runs 5 and 6, confirming the high selectivity of the process. Taking into account the respective concentrations of CO_2 (< 0.1 M) and H_2O (*ca.* 55 M) in the medium, the actual selectivity for reduction of CO_2 *vs.* that of H_2O is higher than 10^6.

The catalytic effect of $[Ni^{II}(cyclam)]^{2+}$ was demonstrated by cyclic voltammetry, as shown in Figure 1. Clearly, an

Table 1. Electrocatalytic reduction of CO_2 by $[Ni^{II}(cyclam)]^{2+}$ in water.[a]

Run	Electrocatalyst	*E* (V *vs.* N.H.E.)	Total volume[b] of CO produced (ml)	Turnover frequency (h^{-1});[c] overall turnover of Ni	Average current efficiency[d]/%	Volume of H_2 produced/ml; H_2 : CO in gas produced
1	—	−1.05	< 0.05	—	—	0.36 ; > 10
2	$NiCl_2 \cdot 6H_2O$	−1.05	< 0.05	—	—	1.6 ; > 30
3	$Ni(cyclam)Cl_2$	−0.90	0.4	0.3 ; 1.2	36	< 0.01 ; < 2×10^{-2}
4	$Ni(cyclam)Cl_2$	−0.95	3.6	2.9 ; 10.8	82	< 0.01 ; < 3×10^{-3}
5	$Ni(cyclam)Cl_2$	−1.00	23.7	18 ; 77.5	99	< 0.01 ; < 5×10^{-4}
6	$Ni(cyclam)Cl_2$	−1.05	35.6	32 ; 116	96	< 0.01 ; < 3×10^{-4}

[a] CO_2 (99.995% purity) saturated solutions (75 ml H_2O at 25 °C; pH *ca.* 4.1) containing the electrocatalyst (1.7×10^{-4} M) and KNO_3 (0.1 M) were placed in a gas-tight electrolysis cell; the working electrode (18 cm^2) was mercury (99.99999% purity). The total volume occupied by the gases in the electrolysis cell was 86 ml. The gases were analysed by g.c. [b] After 4 h of electrolysis. [c] Turnover numbers are calculated from mol of CO produced per mol of electrocatalyst. [d] Current efficiency ρ : ρ = $\frac{2n_{CO} \times 96\,500}{C}$, n_{CO}: mol CO produced, C = coulombs passed during the run.

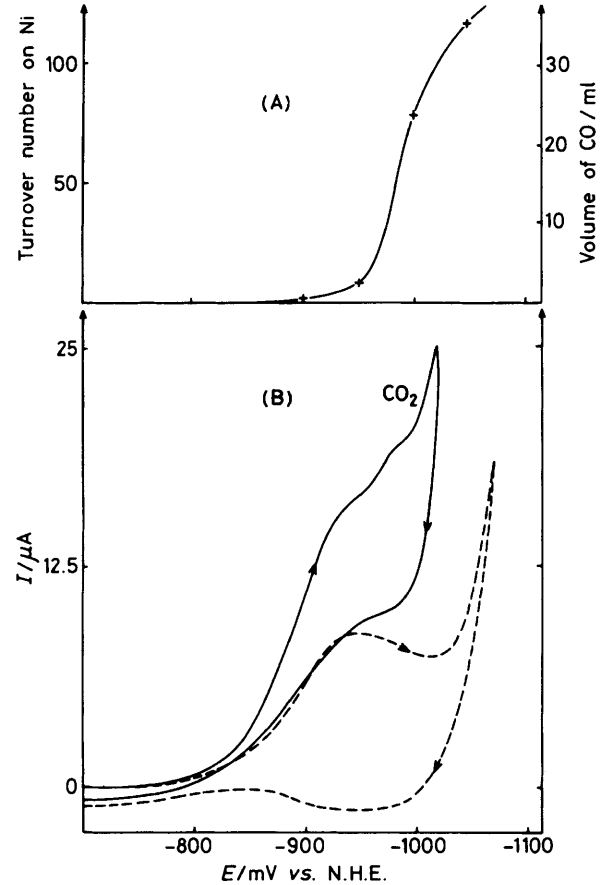

Figure 1. (A) Amount of CO produced in 4 h of electrolysis as a function of applied potential; experimental conditions: see footnote a, Table 1. (B) Cyclic voltammograms of $[Ni^{II}(cyclam)]^{2+}$ (2×10^{-3} M) in H_2O. Full line: CO_2 saturated solution (measured pH = 4.1); dashed line: argon degassed solution (pH = 4.1, adjusted with dilute HNO_3). Hanging mercury electrode; support electrolyte: KNO_3 (0.1 M); scan rate = 600 mV/s; room temperature.

important electrocatalytic current is observed when CO_2 is present; in MeCN, the reversibility of the $[Ni^{II}(cyclam)]^{2+}$/$[Ni^{I}(cyclam)]^{+}$ couple[7] was lost by addition of CO_2. Even at high scan rates (200 V/s), no reoxidation process could be observed after reduction of $[Ni^{II}(cyclam)]^{2+}$ in water under CO_2. Without CO_2, the $[Ni^{II}(cyclam)]^{2+}$/$[Ni^{I}(cyclam)]^{+}$ couple is reversible in aqueous $KClO_4$ ($E°$ = −1.33 V *vs.* N.H.E.), whereas reversibility is lost in dilute KNO_3; indeed $[Ni^{II}(cyclam)]^{2+}$ is an electrocatalyst for reduction of nitrate to NH_4^+.

Slight changes in the conditions used or in the nature of the catalyst have a significant influence on the course of the reaction: (1) the reaction becomes much less efficient when the pH is increased in a $KHCO_3/K_2CO_3$ buffer (pH = 10.6; 0.25 M), only trace amounts of CO and formate are formed after electrolysis at −1.05 V *vs.* N.H.E. CO_2 is thus the real substrate. (2) Surprisingly, among a large number of tetra-aza complexes of nickel investigated, only $[Ni^{II}(cyclam)]^{2+}$ displays exceptional electrocatalytic properties; unsaturated macrocyclic compounds or open chain complexes (containing 2,3,2-teten, 3,2,3-teten, or tren)† are very poor catalysts. Nickel complexes of saturated substituted tetra-aza 14 membered rings are acceptable electrocatalysts, but they are not selective for reduction of CO_2 *vs.* that of H_2O.[5] The particularity of $[Ni^{II}(cyclam)]^{2+}$ is due to its macrocyclic structure, making the reduced compound resistant to decomplexation;[8] in addition, steric factors are likely to be determinant: the highly accessible metal centre of $[Ni^{I}(cyclam)]^{+}$ reacts more readily with CO_2 than would that of, for instance, $[Ni^{I}(L)]^{+}$, L being 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane.[9] On the other hand, if the metal centre is hindered, it might react with a small substrate like a proton, making the process less specific with respect to reduction of CO_2.

In conclusion, these preliminary results indicate that the unencumbered complex, $[Ni^{II}(cyclam)]^{2+}$, is an active and selective electrocatalyst for reduction of CO_2 in aqueous medium, whereas acyclic or substituted compounds have drastically different properties as catalysts.

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† 2,3,2-teten = 1,3,7,9-tetra-azanonane; 3,2,3-teten = 1,4,7,10-tetra-azadecane; tren = 1,3,5-triaza-3-(2-aminoethyl)pentane.

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