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Carbon Dioxide Reduction Mediated by Electropolymerized Electrodes of a Nickel Tetraazaannulene Complex, Ni[Me_4Bzo_2[14]tetraeneN_4]

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Currently there is considerable interest in catalyzing the reduction of CO_2 into reusable energy forms. The thermodynamic potentials at pH 7 for reduction of CO_2 to CO or HCO_2H, as given in eqns. (1) and (2), would be readily assessable, were it not

$$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O \quad E° = -0.52 \text{ V} \quad (1)$$

$$CO_2 + 2H^+ + 2e^- \rightleftharpoons HCO_2H \quad E° = -0.61 \text{ V} \quad (2)$$

for the large overvoltage required to drive the reaction electrochemically. In practice the electrode potentials necessary for reducing CO_2 directly are more negative than −2.0 V *versus* SCE. The goal researchers in the area would like to achieve, then, is to lower this large energy requirement either by homogeneous [1–5] or heterogeneous [6, 7] electrocatalysis [1–7].

Metallotetraazaannulenes would appear to be likely candidates for CO_2 reduction catalysts, yet their usage remains unreported. In particular, cobalt tetraazaannulene has been exploited as a dioxygen reduction catalyst at cathodes in fuel cells [8] and a nickel tetraazaannulene surface modified electrode was used to catalyze the oxidation of water [9].

We have previously reported the redox properties in solution [10] and characterization of surface modified electrodes [11] of nickel(II) tetraazaannulenes based on the ligand depicted in Fig. 1. Subsequent studies have now shown that CO_2 can be reduced electrochemically at −1.85 V *versus* SSCE at an electrode containing a thin polymeric film of $\{Ni[Me_4Bzo_2[14]tetraeneN_4]\}_n$. The only observed product upon reduction is formate ion, whereas CO was the predominant product of electroreduction at electrodes modified with $Re(vbpy)(CO)_3Cl$, (vbpy) is 4-vinyl-4′-methyl-2,2′-bipyridine) [7], and metallophthalocyanines [6].

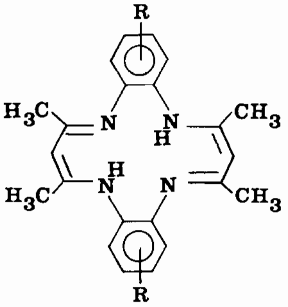

Fig. 1. Structure of $[H_2(Me_4(RBzo)_2[14]tetraeneN_4)]$.

Our experiments consisted of cyclic voltammetric measurements and controlled potential electrolysis. The working electrode for cyclic voltammetric measurements was a glassy carbon disk electrode and for controlled potential electrolysis was a surface modified Pt flag electrode. Controlled potential electrolysis was carried out in a gas-tight electrolysis cell under a $^{13}CO_2$ saturated atmosphere. The cell had a volume of *ca.* 50 ml, of which 35 ml was occupied by $^{13}CO_2(g)$. In a typical experiment, $^{13}CO_2(g)$ was added to a solution of *ca.* 15 ml of CD_3CN:CH_3CN (1:4) containing 0.10 M TEAP and 2% *v*/*v* of methanol. The electrolysis cell was an 'H' cell equipped with ground glass joints for the electrode connections, a vacuum stopcock to evacuate the system prior to the addition of $^{13}CO_2(g)$, and a side arm through which aliquots of the reaction solution could be withdrawn for analysis using ^{13}C FT-NMR spectroscopy.

The experimental results are illustrated in Figs. 2 and 3. Figure 2 consists of a series of cyclic voltammograms used to define the system. As shown in Fig. 2a and 2b, CO_2 is not reduced using a bare GC (glassy carbon) electrode, either in the presence or absence of a proton source. In the absence of CO_2, $\{Ni[Me_4Bzo_2[14]tetraeneN_4]\}_n$ films exhibit surface waves (Fig. 2c), in wich the Ni(II/I) redox couple occurs at *ca.* −1.82 V. Fig. 2d represents the response of a modified GC electrode in a CO_2-saturated solution, in which the increase in current indicates the film is functioning as an electron mediator and probably reducing CO_2. Additional evidence for CO_2 reduction includes the increase in current that is observed following the addition of a proton source (Fig. 2e). This indicates the presence of a proton source promotes electron transfer to CO_2, which results in an increase in CO_2 reduction mediated by the Ni(II) film.

The same reaction was carried out in CO_2-saturated acetonitrile 0.10 M TEAP solutions containing

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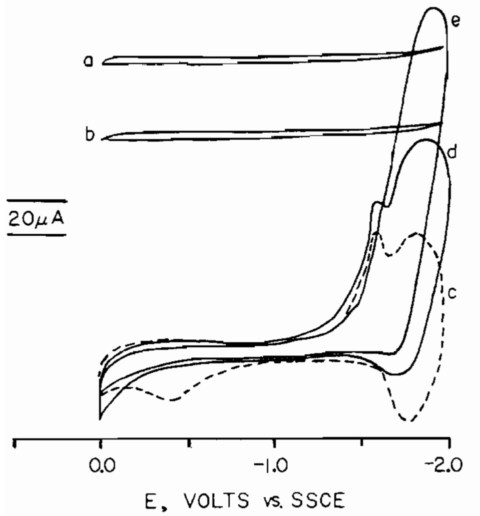

Fig. 2. Cyclic voltammograms of acetonitrile –0.1 M TEAP solutions: (a) using a bare GC electrode in a CO_2-saturated solution; (b) using a bare GC electrode in a CO_2-saturated solution containing 2 vol.% methanol; (c) using a GC electrode modified with a $\{Ni[Me_4Bzo_2[14]tetraeneN_4]\}_n$ film in an N_2-saturated solution; (d) using a GC electrode modified with a $\{Ni[Me_4Bzo_2[14]tetraeneN_4]\}_n$ film in a CO_2-saturated solution; (e) using a GC electrode modified with a $\{Ni[Me_4Bzo_2[14]tetraeneN_4]\}_n$ film in a CO_2-saturated solution containing 2 vol.% methanol.

1×10^{-3} M $Ni[Me_4Bzo_2[14]tetraeneN_4]$. There was no evidence for CO_2 reduction in the same scan range used for Ni(II) films, either in the presence or absence of a proton source. That is, the Ni(II/I) reduction potential did not shift and there was no observable increase in the current associated with the Ni(II/I) wave following the addition of CO_2. This indicates the $\{Ni[Me_4Bzo_2[14]tetraeneN_4]\}_n$ film serves as an electron mediator in the reduction of CO_2.

In order to determine the products formed upon the electrocatalytic reduction of CO_2, ^{13}C enriched CO_2 was used for controlled potential electrolysis experiments, followed by ^{13}C FT-NMR spectroscopic determination of the reaction products. A series of control experiments were run in order to determine under what conditions catalysis would be observed. Figure 3a represents the NMR spectrum of the electrolytic solution prior to addition of $^{13}CO_2$; all peaks correspond to solvent (1.31 and 117.90 ppm), electrolyte (7.33 and 52.95 ppm), or methanol (49.56 ppm). Addition of *ca.* 1 mmol of $^{13}CO_2(g)$ results in an additional peak at 125.46 ppm, attributed to $^{13}CO_2$ (Fig. 3b). Controlled potential electrolysis at –1.85 V *versus* SSCE of the solution using a bare Pt flag electrode results in no change in the ^{13}C NMR spectrum (Fig. 3c), indicating the

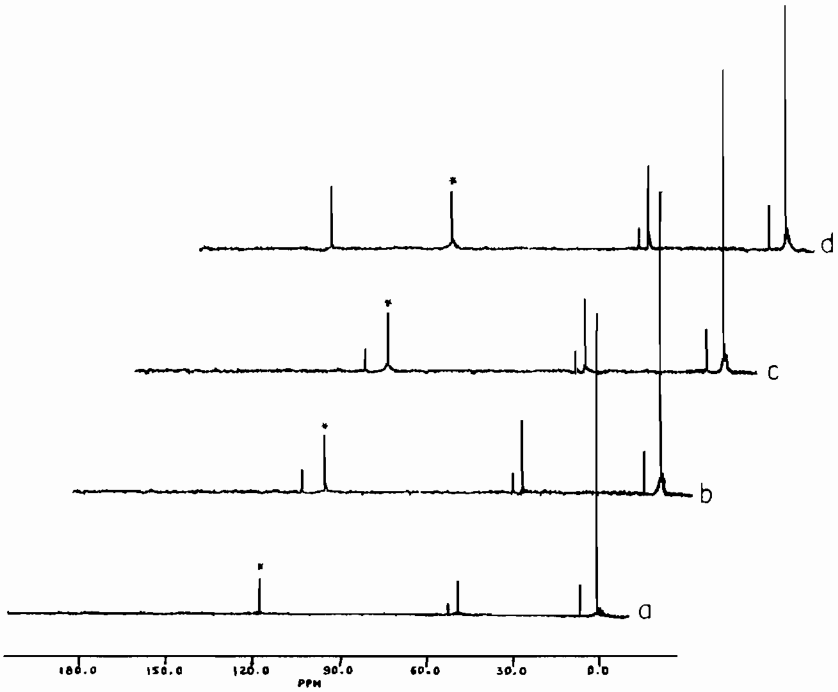

Fig. 3. ^{13}C NMR spectra of $^{13}CO_2$ solutions prior and subsequent to controlled potential electrolysis experiments. (a) ^{13}C NMR spectrum of a $CD_3CN:CH_3CN$ (1:4) solution containing 0.10 M TEAP and 2% *v/v* of methanol; (b) ^{13}C NMR spectrum of a $CD_3CN:CH_3CN$ (1:4) solution containing *ca.* 2 mmol $^{13}CO_2$, 0.10 M TEAP and 2% *v/v* of methanol; (c) ^{13}C NMR spectrum following controlled potential electrolysis at –1.85 V using a bare Pt flag electrode; (d) ^{13}C NMR spectrum following controlled potential electrolysis at –1.85 V using a Pt electrode modified with a $\{Ni[Me_4Bzo_2[14]tetraeneN_4]\}_n$ film.

bare electrode was not electrocatalytically active towards the reduction of CO_2. However, when the Pt electrode was modified with $\{Ni[Me_4Bzo_2[14]\text{-}tetraeneN_4]\}_n$, the ^{13}C NMR spectrum of the solution following controlled potential electrolysis experiments clearly indicates that reduction of $^{13}CO_2$ has occurred. Figure 3d represents the ^{13}C NMR spectrum, in which the peak attributed to $^{13}CO_2$ has disappeared, while a new peak at 158.42 ppm, attributed to $H^{13}CO_2^-$, has appeared. There is no evidence to indicate the presence of any additional products.

The fact that introduction of $CO_2(g)$ results in a 30 mV shift of the Ni(II/I) wave compared to the same wave under Ar and a large increase in the current (*ca.* 90%) was observed when the Ni(II/I) wave was scanned in the presence of $CO_2(g)$ at the surface modified disk electrode seem to indicate that, initially, CO_2 coordinates to Ni(II) sites within the film. Transfer of an electron from reduced Ni(II) sites within the film results in the formation of bound CO_2^-. Subsequent protonation, followed by a second reduction, accounts for the observance of a $H^{13}CO_2^-$ signal in the ^{13}C NMR spectrum. A similar mechanism has been proposed for the reduction of CO_2 in protic solvents, in which Ni(II) and Co(II) tetraaza macrocyclic complexes catalyzed the electrochemical reduction [5].

In conclusion, it has been demonstrated that electropolymerized films of $\{Ni[Me_4Bzo_2[14]tetraeneN_4]\}_n$ catalyze the reduction of CO_2 to HCO_2^- and serve as electron mediators between the electrode surface and coordinated CO_2 to Ni(II) sites within the film. While the potential was lowered compared to the bare electrode, the potential still is too negative to be commercially viable. To this end, we are examining the properties of other metallotetraazaannulene derivative such as Co(II) and Cu(II) and have found that these also undergo oxidative electropolymerization. We are now exploring their usage for catalytic CO_2 reduction.

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