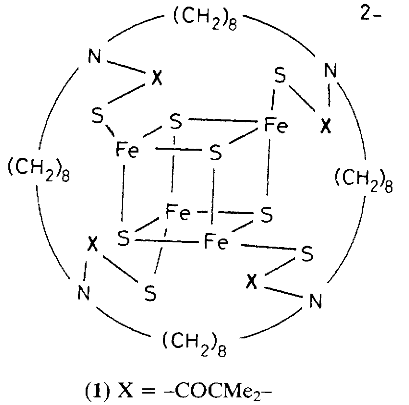
Electrochemical Reduction of Carbon Dioxide catalysed by Macrocyclic Fe_4S_4 Iron–Sulphur Clusters

Takenori Tomohiro, Kouichi Uoto, and Hiroaki (Yohmei) Okuno*

National Chemical Laboratory for Industry (NCLI), Tsukuba, Ibaraki 305, Japan

Electrochemical fixation of CO_2 into formate was efficiently carried out by using Fe_4S_4 cubane clusters bearing a 36-membered methylene backbone in dimethylformamide with initial current efficiencies of 40 and 23%, respectively, for t-butyl and benzyl type macrocyclic Fe–S derivatives; these derivatives are several times more efficient than conventional clusters bearing small thiolate ligands.

The reduction of CO_2 to give useful materials is a fundamental challenge in chemistry. We have recently reported that CO_2 can be fixed chemically[1] and photochemically[2] to give biologically active compounds (*e.g.*, oxazolidone derivatives) coupled with a redox reaction of thiols, Fe_4S_4 clusters being active catalysts in chemical CO_2 fixation. As part of our studies on Fe–S chemistry, we now report results for CO_2 reduction catalysed by the macrocyclic Fe_4S_4 clusters (**1**) and (**2**)[3] to give formate under controlled-potential electrolysis. A mercury pool (8.0 g) and Pt plate (12.6 cm^2) were used as working and auxiliary electrodes, respectively. The reduction product, HCO_2^-, was determined by three different methods: isotachophoresis,† HPLC,‡ and enzymatic reaction with formic acid dehydrogenase.[4] The direct electroreduction of CO_2 proceeded at an extremely negative potential in non-aqueous media.[5] In CO_2-saturated dimethylformamide (DMF) solution, −2.4 V (*vs.* Ag/AgCl) was required to reduce CO_2. However, in a solution containing the Fe_4S_4 cluster (**2**) (1 mM), the reduction current observed under N_2 at potentials more negative than −1.7 V [Figure 1(c)] was markedly increased after bubbling CO_2 for 30 min [Figure (1d)]. This indicated that CO_2 interacted with the cluster. By using the Fe_4S_4 clusters (**1**) and (**2**) (1 mM) as catalysts, the electrolysis was then performed in DMF solution (8 ml) containing 0.1 M $[Bu^n{}_4N][BF_4]$ as an electrolyte throughout this work at −2.0 V *vs.* Ag/AgCl, with a continuous supply of CO_2. In the cluster-free system the formation rate of HCO_2^- was very slow (not detectable by isotachophoresis). While it was reported that a trace amount of CO was produced with 1—2% current efficiency from systems using conventional Fe_4S_4 clusters with small thiolate ligands,[6] the gaseous phase was not analysed in the present work. CO_2 was bubbled through the solutions during the electrolyses, resulting in enhanced reaction rates. The relation between yield of formate and electricity applied is shown in Figure 2.



(**1**) X = $-COCMe_2-$
(**2**) X = $-COC_6H_4CH_2-$ (*p*)
(**3**) X = $-COC_6H_4-$ (*p*)

(The CO part of X is bonded to N)

The current efficiencies for the production of formate were 40 and 23% for (**1**) and (**2**), respectively, during the initial period of the reactions. This implies that our Fe_4S_4 clusters contained within a macrocycle are more efficient catalysts for the electrochemical reduction of CO_2 than the corresponding Fe_4S_4 clusters with a small thiolate ligand.[6] These differences may be attributable to the stability of the clusters.[3] The current efficiency gradually decreased with time or the current applied, however, probably owing to the decomposition of the clusters (*cf.* ref. 6). When water (14.5 µl, 100 molar excess with respect to the cluster) as a proton source was added to the solution, the current efficiency improved significantly (Figure 2). It has been reported, however, that in the absence of added water the protons, at least in part, seemed to be derived from the tetra-alkylammonium ion of the electrolyte in a less efficient process.[7] By using the cluster (**3**), a phenyl thiolate type with a 36-membered ring, the electrolysis gave no formate even though a marked increase in reduction current resulting from the interaction of the cluster (**3**) and CO_2 was

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† Shimadzu IP-2A; leading: L360, terminal: T348, 1st stage: 200 µA, 2nd stage: 100 µA, at 25 °C.

‡ Shimadzu LC-6A; column: Shimadzu SCR-101H, eluant: aq. $HClO_4$ (pH 2.1), 1.2 ml min^{-1}, at 20 °C.

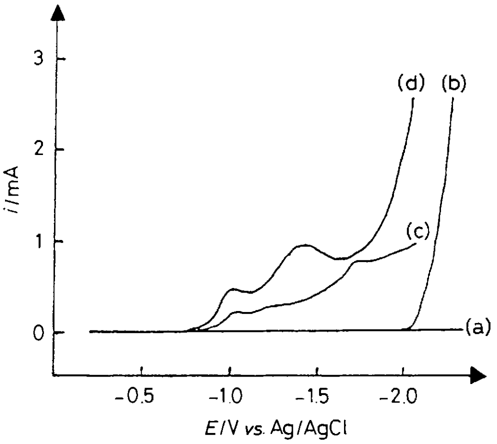

Figure 1. Current–potential curves: DMF solution containing 0.1 M $[Bu^n{}_4N][BF_4]$ as electrolyte: (a), cluster-free under N_2; (b), cluster-free under CO_2; (c), in the presence of 1 mM cluster (**2**) under N_2; (d), in the presence of 1 mM cluster (**2**) under CO_2.

observed around −1.4 V under CO_2-saturated conditions. A similar result was obtained with the unclad Fe_4S_4 cluster,[7] but the explanation for these results is not yet clear. A detailed study will be presented elsewhere.

Consequently, electrochemical reduction of CO_2 leading to formate proceeded more efficiently when catalysed by the Fe_4S_4 clusters (**1**) and (**2**) with a macrocyclic ring than with the corresponding clusters containing small thiolates.

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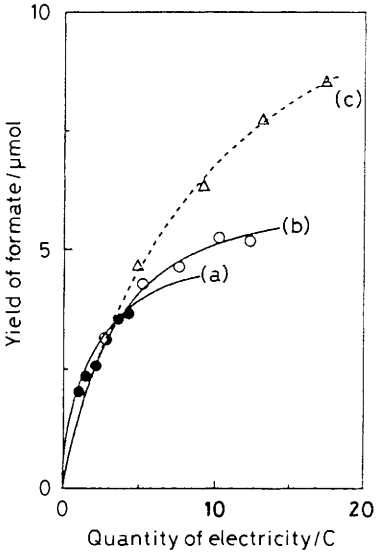

Figure 2. Yields of formate formed by electrolysis: DMF solution at −2.0 V *vs.* Ag/AgCl containing 1 mM cluster: (a), cluster (**1**); (b), cluster (**2**); (c) cluster (**2**) in the presence of water.

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