Remarkable Decrease in Overpotential of Oxalate Formation in Electrochemical CO_2 Reduction by a Metal–Sulfide Cluster

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Triangular metal–sulfide clusters, $[\{Ir(C_5Me_5)\}_3(\mu_3\text{-}S)_2]^{2+}$ and $[\{Co(C_5H_4Me)\}_3(\mu_3\text{-}S)_2]^{2+}$, catalyse the electrochemical CO_2 reduction to selectively produce oxalate at −1.30 and −0.70 V (*vs.* Ag/AgCl), respectively, in MeCN.

Oxalate generation by uncatalysed electrochemical CO_2 reduction is a thermodynamically unfavourable process owing to the very negative redox potential of $E°(CO_2/CO_2^-)$ at −2.21 V (*vs.* SCE).[1] Electrochemical CO_2 reduction catalysed by metal complexes in anhydrous media, however, generally produces CO and CO_3^{2-} by the reductive disproportionation of CO_2 (eqn. 1)[2] rather than oxalate (eqn. 2). Palladium and

$$2CO_2 + 2e^- \rightarrow CO + CO_3^{2-} \qquad (1)$$

$$2CO_2 + 2e^- \rightarrow C_2O_4^{2-} \qquad (2)$$

silver octaethylporphinato complexes have been shown to be active for oxalate generation in electrochemical CO_2 reduction at −1.50 V (*vs.* Ag wire) in CH_2Cl_2 although the selectivity and yield were not elucidated.[3] Recently we reported oxalate formation in electrochemical CO_2 reduction catalysed by $[\{Rh(C_5Me_5)\}_3(\mu_3\text{-}S)_2]^{2+}$ in MeCN.[4] Similar M_3S_2 frameworks may provide suitable reaction sites for oxalate formation (eqn. 2) without the accompanying reductive disproportionation of CO_2 (eqn. 1). We report here selective oxalate generation in electrochemical CO_2 reduction by $[\{Ir(C_5Me_5)\}_3(\mu_3\text{-}S)_2]^{2+}$ ($[Ir^*]^{2+}$)[5] and $[\{Co(C_5H_4Me)\}_3(\mu_3\text{-}S)_2]^{2+}$ ($[Co']^{2+}$).[6]

The cyclic voltammogram of $[Ir^*]\{B(C_6H_5)_4\}_2$ in MeCN displayed two reversible $[Ir^*]^{2+/+}$, $[Ir^*]^{+/0}$ redox couples at $E_{1/2}$ = −0.83 (E_{cp} = −0.80, E_{ap} = −0.86 V) and −0.98 V (E_{cp} = −0.95, E_{ap} = −1.01 V) (*vs.* Ag/AgCl) under N_2, respectively.† A blue MeCN solution of $[Ir^*]^0$, prepared by the controlled potential electrolysis of $[Ir^*]\{B(C_6H_5)_4\}_2$ at −1.30 V in the presence of Me_4NBF_4, rapidly turned orange upon introduction of CO_2 into the solution by bubbling (dashed line in Fig. 1), and $(Me_4N)_2C_2O_4$ was obtained in a yield of 60% from the solution.‡ Furthermore, the controlled potential electrolysis of a CO_2-saturated MeCN solution (20 cm^3) containing $[Ir^*]\{B(C_6H_5)_4\}_2$ (0.5 mmol) and $LiBF_4$ (50 mmol) as supporting electrolyte at −1.30 V with a glassy carbon plate (4 cm^2) catalytically produced $Li_2(C_2O_4)$ (eqn. 2) as a white precipitate with a current efficiency of 60%,‡ and neither CO nor CO_3^{2-} was detected during the electrolysis. Discontinuation of the electrochemical CO_2 reduction in electrolysis also gave the electronic absorption spectrum of the dashed line in Fig. 1, and the subsequent electrolysis of the resulting orange solution under the same electrolysis produced oxalate with almost the same activity. Furthermore, addition of a dilute aq. HCl (0.1 mol dm^{-3}) solution to the electrolyte solution (after 40 s) in air regenerated the electronic absorption spectrum of $[Ir^*]^{2+}$ in MeCN.

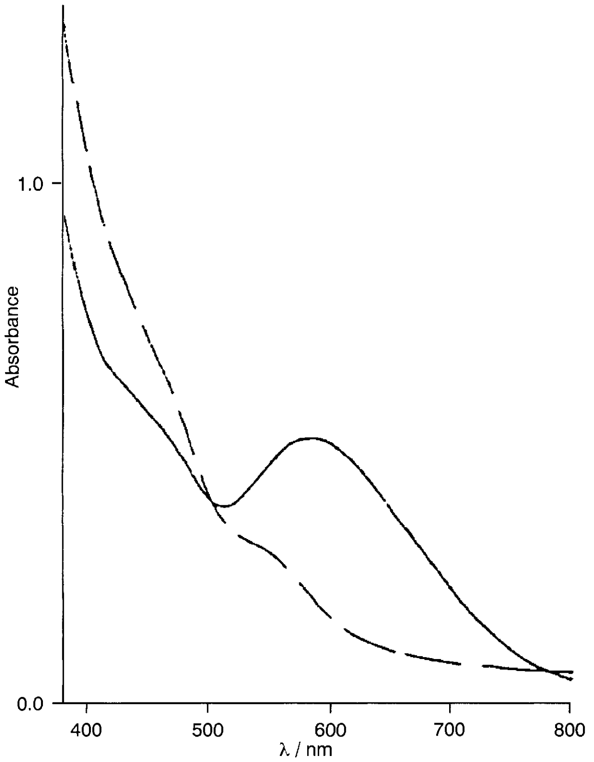

Fig. 1 The electronic absorption spectra of $[Ir^*]^0$ (1.5×10^{-4} mol dm^{-3}) in MeCN before (solid line) and after (dashed line) exposure to CO_2

The cyclic voltammogram of $[Co']BF_4$ showed three successive reversible $[Co']^{2+/+/0/-}$ redox waves at $E_{1/2}$ = +0.35, −0.37 and −1.36 V, respectively (*vs.* Ag/AgCl) in MeCN under N_2.§ Although a clear interaction between $[Co']BF_4$ and CO_2 was not observed in cyclic voltammograms in MeCN, the controlled potential electrolysis of the MeCN solution (20 cm^3) containing $[Co']BF_4$ (0.50 mmol) and $LiBF_4$ (50 mmol) as supporting electrolyte at −0.70 V under CO_2 also selectively produced $Li_2(C_2O_4)$ as a white precipitate with a current efficiency of 80%.‡ Reoxidation of the electrolyte solution (after 40 s) at 0 V brought about the regeneration of an absorption band of $[Co']^+$ at λ_{max} 432 nm in the electronic absorption spectrum. It is worth noting that the electrochemical CO_2 reduction by $[Co']^+$ at −1.50 V in the same solvent gave rise to a fragmentation reaction of the complex with the production of a trace amount of $C_2O_4^{2-}$ only in the initial stage of the electrolysis. Thus, only $[Co']^0$ and $[Ir^*]^0$ are active for $C_2O_4^{2-}$ formation. Similarly, the electrochemical CO_2 reduction by $[\{Co(C_5H_5)\}_3(\mu_3\text{-}S)_2]BF_4$[7] at −0.70 V in MeCN also selectively afforded oxalate with a current efficiency of 80%, although the reaction rate decreased to about 60% compared with that of $[Co']BF_4$.

The present study reveals that metal–sulfide clusters with the M_3S_2 (M = Ir and Co) framework selectively produce oxalate in the electrochemical Co_2 reduction (eqn. 2) without the accompanying reductive disproportionation of CO_2 (eqn. 1). The oxalate formation by the Co_3S_2 cluster at −0.70 V is particularly noteworthy in view of the standard redox potential of $H_2C_2O_4$ (−0.475 V *vs.* NHE) in H_2O (pH = 0) at 25 °C (eqn. 3).[8]

$$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4 \qquad (3)$$

Received, 13th March 1995; Com. 5/01583I

Footnotes

† The cyclic voltammogram of $[Ir^*](PF_6)_2$ in CH_2Cl_2 has been reported in ref. 5.

‡ Oxalate was identified as dimethyl oxalate by GC–MS after treatment of the reaction products with CH_2N_2 in diethyl ether, and the quantitative analysis was conducted by a use of isotachophoresis.

§ The cyclic voltammogram of $[Co']^0$ in CH_2Cl_2 has been reported in ref. 6.

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