## Remarkable Decrease in Overpotential of Oxalate Formation in Electrochemical CO<sub>2</sub> Reduction by a Metal–Sulfide Cluster

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

Oxalate generation by uncatalysed electrochemical CO<sub>2</sub> reduction is a thermodynamically unfavourable process owing to the very negative redox potential of  $E^{\circ}(CO_2/CO_2^{-})$  at -2.21 V (*vs.* SCE).<sup>1</sup> Electrochemical CO<sub>2</sub> reduction catalysed by metal complexes in anhydrous media, however, generally produces CO and CO<sub>3</sub><sup>2-</sup> by the reductive disproportionation of CO<sub>2</sub> (eqn. 1)<sup>2</sup> rather than oxalate (eqn. 2). Palladium and

$$2\mathrm{CO}_2 + 2\mathrm{e}^- \to \mathrm{CO} + \mathrm{CO}_3^{2-} \tag{1}$$

$$2\mathrm{CO}_2 + 2\mathrm{e}^- \to \mathrm{C}_2\mathrm{O}_4{}^{2-} \tag{2}$$

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

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<sub>2</sub>, respectively.† A blue MeCN solution of  $[Ir^*]^0$ , prepared by the controlled



**Fig. 1** The electronic absorption spectra of  $[Ir^*]^0$  (1.5 × 10<sup>-4</sup> mol dm<sup>-3</sup>) in MeCN before (solid line) and after (dashed line) exposure to CO<sub>2</sub>

potential electrolysis of  $[Ir^*]{B(C_6H_5)_4}_2$  at -1.30 V in the presence of Me<sub>4</sub>NBF<sub>4</sub>, rapidly turned orange upon introduction of  $CO_2$  into the solution by bubbling (dashed line in Fig. 1), and (Me<sub>4</sub>N)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was obtained in a yield of 60% from the solution. ‡ Furthermore, the controlled potential electrolysis of a CO<sub>2</sub>-saturated MeCN solution (20 cm<sup>3</sup>) containing  $[Ir^*]$ {B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>}<sub>2</sub> (0.5 mmol) and LiBF<sub>4</sub> (50 mmol) as supporting electrolyte at -1.30 V with a glassy carbon plate (4 cm<sup>2</sup>) catalytically produced Li<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>) (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<sub>2</sub> 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.

The cyclic voltammogram of [Co'] BF<sub>4</sub> showed three successive reversible [Co']<sup>2+/+/0/-</sup> redox waves at  $E_{1/2}$  = +0.35, -0.37 and -1.36 V, respectively (vs. Ag/AgCl) in MeCN under N<sub>2</sub>.§ Although a clear interaction between [Co']BF<sub>4</sub> and CO2 was not observed in cyclic voltammograms in MeCN, the controlled potential electrolysis of the MeCN solution (20 cm<sup>3</sup>) containing [Co']BF<sub>4</sub> (0.50 mmol) and LiBF<sub>4</sub> (50 mmol) as supporting electrolyte at -0.70 V under CO<sub>2</sub> also selectively produced Li<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>) 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  $\lambda_{max}$  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']<sup>0</sup> and [Ir\*]<sup>0</sup> are active for  $C_2O_4{}^{2-}$  formation. Similarly, the electrochemical  $CO_2$  reduction by  $[{Co(C_5H_5)}_3(\mu_3-S)_2]BF_4^7$  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<sub>4</sub>.

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<sub>2</sub> reduction (eqn. 2) without the accompanying reductive disproportionation of CO<sub>2</sub> (eqn. 1). The oxalate formation by the Co<sub>3</sub>S<sub>2</sub> 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).<sup>8</sup>

$$2\mathrm{CO}_2 + 2\mathrm{H}^+ + 2\mathrm{e}^- \to \mathrm{H}_2\mathrm{C}_2\mathrm{O}_4 \tag{3}$$

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## Footnotes

 $<sup>\</sup>dagger$  The cyclic voltammogram of  $[Ir^{\ast}](PF_{6})_{2}$  in  $CH_{2}Cl_{2}$  has been reported in ref. 5.

§ The cyclic voltammogram of [Co']<sup>0</sup> in CH<sub>2</sub>Cl<sub>2</sub> has been reported in ref. 6.

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