Cobalt(II)–Tetraphenylporphyrin–Pyridine Complex fixed on a Glassy Carbon Electrode and its Prominent Catalytic Activity for Reduction of Carbon Dioxide

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Cobalt(II)–tetraphenylporphyrin (Co^{II}tpp)-fixed glassy carbon (GC) electrodes were prepared using 4-aminopyridine (pyNH$_2$) in the form of Co^{II}tpp–pyNH–CO/GC, which were active for electroreduction of CO$_2$ to CO at potentials 100 mV more positive than water-soluble Co^{II} porphyrins, and the overall turnover number of Co^{II}tpp for CO production exceeded 10^5.

Metalloporphyrins have been reported to be active as catalysts in the electroreduction of CO$_2$ in aqueous[1] and nonaqueous[2] media. In aqueous media, water-soluble Co^{II}tetraphenylporphyrin sulphonate and Co^{II}*meso*-tetracarboxyphenylporphyrin have been reported to be catalytically active for the electroreduction of CO$_2$. Pyridine (py) is reported to coordinate at the axial position of planar Co^{II}(salen) (H$_2$salen = bissalicylideneethylenediamine) and stabilizes CO$_2$ in the opposite coordination site.[3] In the present work, we attempted to obtain a Co^{II}tpp–py (tpp = tetraphenylporphyrin) complex-fixed electrode by applying the water-insoluble Co^{II}tpp on glassy carbon (GC) substrate plates modified initially with 4-aminopyridine (pyNH$_2$). 4-Aminopyridine is expected not only to immobilize Co^{II}tpp on the GC electrode, but also to provide the Co^{II}tpp-fixed GC electrode with new properties.

Co^{II}tpp–pyNH–CO/GC (**I**) was prepared as follows.[4] Glassy carbon (GC) plates (Tokai GC-30, 27 mm × 5 mm, 1 mm thick) were subjected to anodic oxidation in 0.5 mol dm^{-3} H$_2$SO$_4$, and refluxed in SOCl$_2$ for 24 h, for chlorination as COCl/GC. The electrodes were then immersed in 4-aminopyridine-saturated benzene solution for 24 h at room temperature to produce pyNH–CO/GC (**II**). Finally, the electrodes were refluxed in a 0.6 mmol dm^{-3} Co^{II}tpp solution in benzene for 24 h to produce **I**.

The fixation of 4-aminopyridine was confirmed by the diffuse reflectance FT IR spectrum of **II**, which showed a peak at 1665 cm^{-1} due to C=O stretching of the -CO–NH- amide group together with pyridine ring C=C and C=N stretching peaks at 1610 and 1537 cm^{-1}, respectively. These results showed that 4-aminopyridine was fixed in the form of pyNH–CO/GC. Fig. 1(*a*) shows the diffuse reflectance UV–VIS spectrum of **I**, together with spectra of (*b*) Co^{II}tpp and (*c*) Co^{II}tpp–py in CH$_2$Cl$_2$ for comparison. Spectra (*a*) and (*c*) show the Soret band at 440 nm, whereas that of (*b*) is at 420 nm. These spectra indicated that Co^{II}tpp was fixed as the pyridine complex, Co^{II}tpp–py, and the electron density of the central Co^{II} ions of **I** was increased by the pyridine ligand.[5]

Fig. 2 shows cyclic voltammograms (CV) of **I** in standard phosphate buffer solution at pH 6.86 saturated with He or CO$_2$. No Co^{II}tpp/Co^{I}tpp redox peak was observed, but this is probably due to the small amount of Co^{II}tpp distributed on the electrode which has a high roughness factor (3 × 10^3). The surface concentration of Co^{II}tpp of (10^{-12} mol cm^{-2}; apparent surface area) was evaluated by ESCA. A pronounced increase of the cathodic current was observed at potentials more negative than −0.95 V [*vs.* saturated calomel electrode (SCE)] in CO$_2$-saturated solution, this increase starting at potentials 100 mV more positive than when water-soluble Co^{II} porphyrins are employed.[1] This result demonstrates that the Co^{II}tpp–py complex fixed on glassy carbon is catalytically

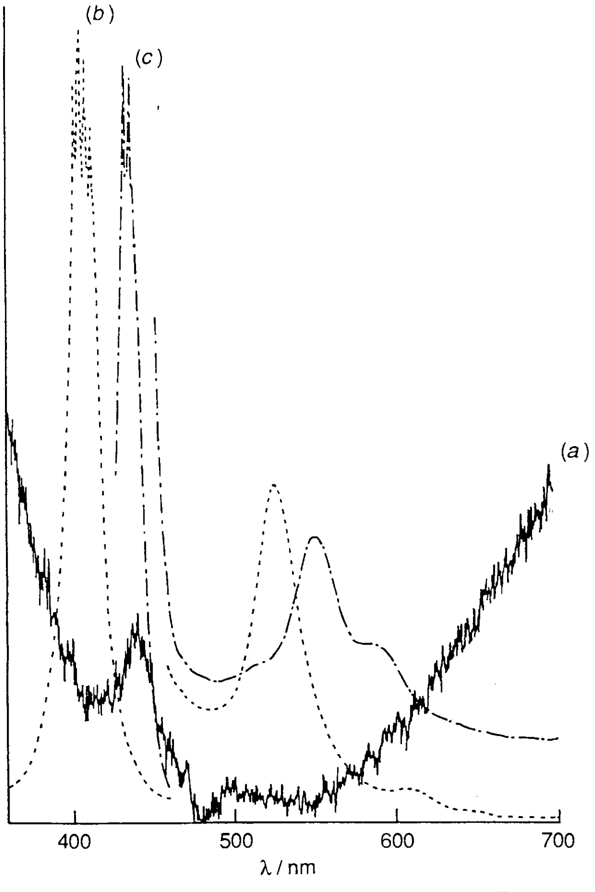

Fig. 1 (*a*) Diffuse reflectance UV–VIS spectrum of Co^{II}tpp–pyNH–CO/GC (electrode **I**) and UV–VIS spectra of (*b*) Co^{II}tpp and (*c*) Co^{II}tpp–py in CH$_2$Cl$_2$

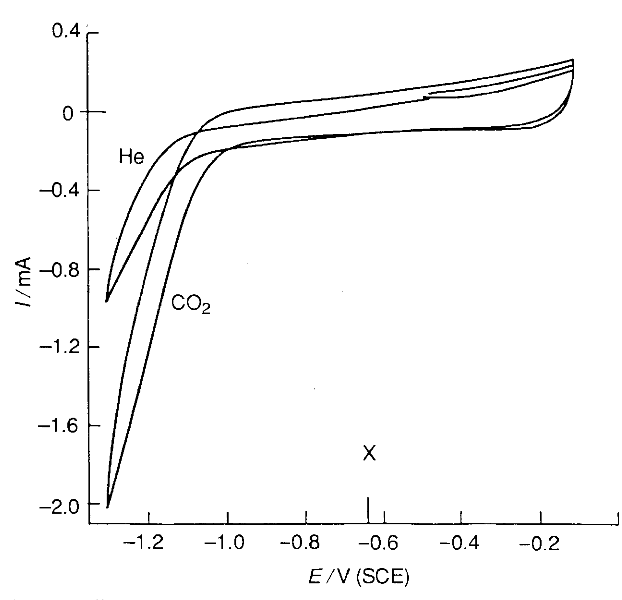

Fig. 2 Cyclic voltammograms of electrode **I** in phosphate buffer (pH 6.86) in the presence of (*a*) CO$_2$ and (*b*) He at room temperature; scan rate 1 mV s^{-1}. X = 0 V *vs.* reversible hydrogen electrode

active for CO_2 electroreduction in aqueous medium, even though Co^{II}tpp is insoluble in water. Such an increase in the CO_2 reduction current was not observed on a plain GC electrode and electrode **II**, having no Co^{II}tpp–py complex. The potential at which CO_2 reduction starts is close to the half-wave potential of Co^{II}tpp/Co^{I}tpp of -1.03 V (SCE) in pyridine.[6] These facts imply that the Co^{I}tpp, which was generated by the Co^{II}/Co^{I} redox reaction, catalysed the reduction of CO_2.

Prolonged potentiostatic electrolysis was carried out at -1.2 V (SCE) in CO_2-saturated solution. Gaseous products of the electrolysis were found to be CO and H_2 by gas chromatography. Neither formate ions nor other possible species produced in the catholyte were observed by FT IR ATR (attenuated total reflection) spectrometry. The current efficiency for CO was higher than 50%, with the balance H_2. No significant decrease of the reduction current was observed for more than 4 h. The overall turnover number of the fixed complex, Co^{II}tpp–py, for CO_2 reduction exceeded 10^5, contrasting with earlier data which showed that in most cases the overall turnover number of such metal complex catalysts is limited to 10^2;[7–9] the electrode **I** is thus very stable for the electroreduction of CO_2.

To sum up, significantly high electrocatalytic activity and stability of **I** for CO_2 reduction to CO was observed in aqueous solution. This was probably caused by the increased electron density of the central Co^{II} ions by coordination of pyridine. Indeed, in the case of Co(salen),[3] pyridine is known to stabilize Co(salen)-coordinated CO_2 by the increased electron density of the central Co^{II} ions. A similar role of pyridine may be expected for the Co^{II}tpp–pyNH–CO/GC, which accommodates CO_2 in the partially charged form $CO_2^{\delta-}$ and so easily reduces it to CO in aqueous medium.

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