Electrocatalysis by Metal Phthalocyanines in the Reduction of Carbon Dioxide

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Summary It is shown that cobalt and nickel phthalocyanines are active catalysts for the electrode reduction of carbon dioxide.

ELECTROCHEMICAL reduction of carbon dioxide has been studied by several groups of workers[1] using lead or mercury electrodes which have high hydrogen overvoltages. We have investigated the reduction of carbon dioxide, using metal complexes as electrocatalysts. The use of metal complexes in fuel cell cathodes has been studied.[2] We have synthesised metal phthalocyanines (M–Pc) from phthalonitrile and metal chloride in quinoline; they were purified by sublimation. Graphite electrodes were immersed in a suspension of a metal phthalocyanine in benzene and then dried in air. Fixing the metal complex to the graphite by means of polystyrene bonding produced an electrode of similar behaviour but, owing to the increased resistance, only one tenth of the current could be passed. The surface areas of the graphite rods were about 1·0 cm^2. NEt_4ClO_4, NEt_4Cl, and NBu_4ClO_4 (0·05—0·1M) were used as supporting electrolytes. An *H* type cell was employed and anolyte and catholyte were separated by a glass filter. The counter electrode was a Pt plate of surface area 2·0 cm^2. The potential of the cathode was applied with reference to a saturated calomel electrode.

The current potential curves of Co–Pc electrode for the passage of CO_2 and N_2 through aqueous NEt_4ClO_4 are shown in the Figure. The position of the peak when CO_2 was passed was dependent upon the potential sweep rate in the range 0·2—0·008 Vs^{-1}. The height of this peak had a linear relation to the square root of the sweep rate suggesting that the diffusion of CO_2 is the rate-determining step. The peak height was also proportional to [CO_2]. In NEt_4Cl, NBu_4ClO_4, and KCl solutions CO_2 reduction peaks were also observed. In Na_2CO_3 or $NaHCO_3$ solutions (0·1M) no waves were observed in the absence of CO_2. Therefore, CO_2 dissolved in water is reduced at the electrode, no carbonate or bicarbonate ion taking part in the electrocatalysis. Co–Pc and Ni–Pc were very active. When quaternary ammonium salts were used for the supporting electrolyte, oxalic acid and glycolic acid were detected in the catholyte by the colour reactions of thiobarbituric acid and 2,7-dihydronaphthalene respectively. Formic acid was not detected by the chromotropic acid test. Reduction products were not detected in reactions involving metal salts indicating that the products were decomposed successively on the electrode. The hydrophobic nature of the quaternary ions might produce a more suitable environment for CO_2 reduction on the electrode. Mn–Pc, Pd–Pc, and graphite alone were inactive while Cu–Pc and Fe–Pc were slightly active, estimated by the height of the CO_2 peak (Figure) and by the colour reactions.

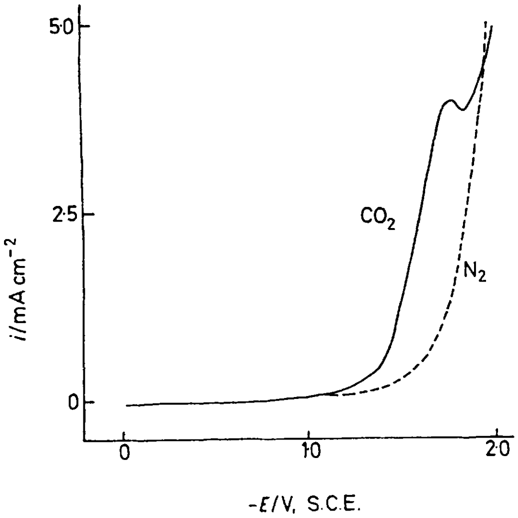

FIGURE. Current-potential curves of a Co–Pc (graphite) electrode, potential sweep rate 0·016 Vs^{-1}, surface area 0·96 cm^2, NEt_4ClO_4 (0·05M), room temperature.

At the potentials required for reduction of CO_2 it has been shown that metal phthalocyanines are reduced to their dinegative states.[3] Taube's studies[4] suggest that active Co–Pc and Ni–Pc in their dinegative states have the d_{z^2} orbital occupied and have an excess of ligand π-electrons, whereas Mn–Pc and Fe–Pc which show poor activity do not have an occupied d_{z^2} orbital or an excess of π-electrons. Consequently the occupied d_{z^2} orbital of the metal atom of the phthalocyanine complex plays an important role in electrocatalysis of CO_2 reduction, while the ligand π-electrons might enhance the activity of the axial d_{z^2} orbital.

(*Received*, 29*th August* 1973; *Com.* 1223.)

[1] J. Jordan and P. Smith, *Proc. Chem. Soc.*, 1960, 246; A. Bewick and G. P. Greener, *Tetrahedron Letters*, 1969, 4623; A. Bewick and G. P. Greener, *ibid.*, 1970, 391; W. Paik, T. N. Andersen, and H. Eyring, *Electrochim. Acta*, 1969, **14**, 1217; J. Ryn, J. N. Andersen, and H. Eyring, *J. Phys. Chem.*, 1972, **76**, 3278.

[2] R. Jasinski, *J. Electrochem. Soc.*, 1965, **5**, 526.

[3] L. D. Rollmann and R. T. Iwamoto, *J. Amer. Chem. Soc.*, 1968, **90**, 1455.

[4] R. Taube, *Z. Chem.*, 1966, **6**, 8.