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New Type of Secondary Fuel Cell using Cobalt(II)-2,9,16,23-tetracarboxyphthalocyanine Covalently Bound to Poly-(2-vinylpyridine-carbonyl-styrene) as a Cathodic Catalyst

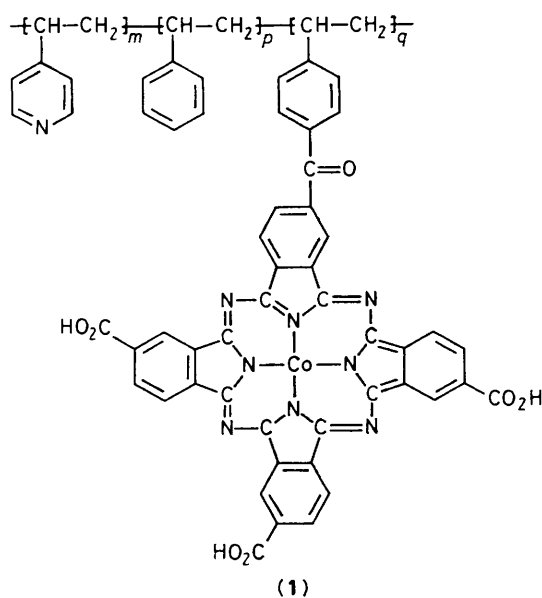
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Cobalt(II)-2,9,16,23-tetracarboxyphthalocyanine covalently bound to poly-(2-vinylpyridine-CO-styrene) was used as a cathodic catalyst for oxygen with hydrogen in a secondary fuel cell in which dioxygen produced by electrolysis of H₂O in the charging process is stored in the polymer matrix, and then electrochemically reduced in the discharging process.

There has been much recent interest in the electrocatalytic properties of phthalocyanine and porphyrin complexes which are used to activate the cathodic reduction of oxygen with hydrogen in fuel cells.^{1,2} We have reported the synthesis of metal-2,9,16,23-tetracarboxyphthalocyanine complexes covalently bound to poly-(2-vinylpyridine-CO-styrene) (M-tapc-P2VP-CO-St, M = Fe^{III}, Co^{II}, Ni^{II}, and Cu^{II}). The Fe^{III} and Co^{II} complexes were of the five co-ordinate high-spin type, with one axial co-ordination site occupied by an N atom of a pyridine group.^{3,4} This type of complex may be useful in many catalytic reactions, and Fe^{III}-tapc-P2VP-CO-St was, in fact, remarkably effective for the decomposition of hydrogen peroxide.⁴ We have used the Co^{II}-phthalocyanine polymer possessing this co-ordination structure as a cathodic catalyst for an oxygen-hydrogen fuel cell. It is well known that Co^{II}-phthalocyanine is useful as an oxygen carrier,⁵ and we have therefore examined its application to a new type of secondary fuel cell in which molecular oxygen evolved by the electrolysis of H₂O in the charging process is stored in the polymeric oxygen carrier on a platinum electrode, and then electrochemically reduced in the discharging process.

Co^{II}-tapc-P2VP-CO-St (content of Co-pc: 1.5 wt%) (1) was prepared and purified as described previously.⁴ Platinum sheets (surface area 1 cm²) were polished mechanically with emery paper (grade 1000), washed with distilled water using an ultrasonic cleaner, treated with alkaline detergent, and rinsed with 6 M HCl; they were then washed with distilled water using



an ultrasonic cleaner, and dried. The electrodes were dipped into methanol containing 5% of Co^{II}-tapc-CO-St (Co^{II} content: 1.5 wt%),⁴ and dried in air at about 50 °C. Constant current charge-discharge curves were measured potentiostatically with a potentiostat-galvanostat, with charging for 30 min at 500 μA, followed by discharging at 100 μA. The reference electrode was a saturated calomel electrode (S.C.E.)

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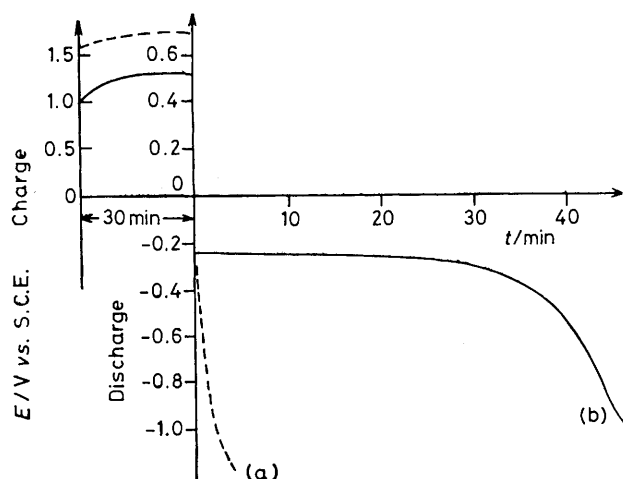


Figure 1. Constant current charge-discharge curves for a platinum electrode modified by (a) P2VP-CO-St and (b) Co^{II}-tapc-P2VP-CO-St in 30% KOH solution at 25 °C. The charging current is 500 μ A for 30 min and the discharging current is 100 μ A.

connected by a lugin capillary and the counter electrode was a platinum sheet. The agar salt bridge used contained 3.3 M KCl.

The results for the platinum electrode modified with Co^{II}-tapc-P2VP-CO-St or P2VP-CO-St in 30% aqueous KOH solution at 25 °C with argon bubbling are shown in Figure 1, for a 30 min charge at 500 μ A, followed by a 100 μ A discharge. These measurements were made after a number of initial charge-discharge cycles. The discharge curve for the electrode modified by Co^{II}-pc covalently bound to the copolymer showed a stable plateau at about -0.24 V vs. S.C.E. different from that for the electrode modified by P2VP-CO-St alone. The discharge capacity observed was 833 A h kg⁻¹ of Co-pc. This value is about 20 times greater than that for an electrode vacuum deposited with monomeric Co-pc, followed by coating with the copolymer P2VP-CO-St.⁶ The polymer attached Co^{II}-pc catalyst was found to be very effective for the operation of the cell. Its open circuit voltage, V_{oc} (vs. Zn), was 1.2 V, with an energy density (vs. Zn) of ca. 1000 W h kg⁻¹ Co-pc. There was no significant decay in its characteristics after more than 30 charge-discharge cycles. In the charging process, oxygen was evolved from the surface of the modified electrode, while hydrogen was evolved from the counter electrode. After the charging process, the Co-tapc-P2VP-CO-St film was cooled in liquid nitrogen, and peeled from the platinum sheet. The e.s.r. spectrum of the resulting Co-pc polymer at -140 °C is shown in Figure 2. A signal assigned to a Co^{III}-pc-O₂ radical was observed at g ca. 2.003,⁷ which was absent before the charge and after the discharge. This indicates that a Co^{III}-pc-O₂ complex is formed between the Co^{II}-pc in the polymer matrix and the dioxygen evolved from the electrolysis of H₂O in the charging process. As has previously been pointed out, the P2VP-CO-St supported Co^{II}-tapc complex is of the five co-ordinate high spin type,⁴ and this may favour the formation of a dioxygen complex.⁸ The cyclic voltammogram for the electrode modified by Co^{II}-tapc-P2VP-CO-St showed an anodic peak at -0.16 V vs. S.C.E. assigned to O₂ reduction which appears to be governed by the redox potential of Co-pc.² The Co-tapc-P2VP-CO-St coated electrode has a higher catalytic activity for O₂ anodic reduction. On the basis of these results and the mechanism proposed by Yeager *et al.*² the mechanism in equations (1)–(6) seems reasonable.

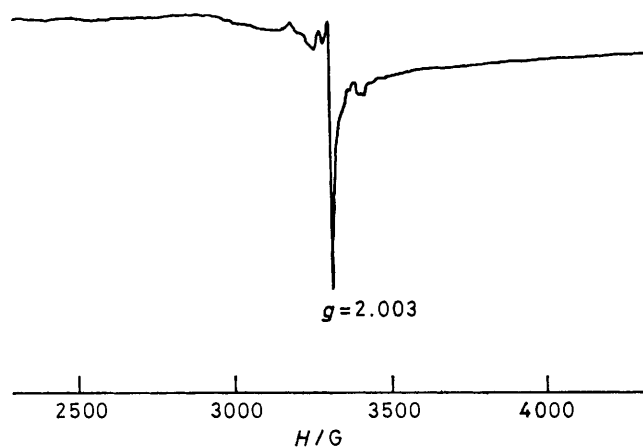
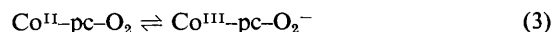
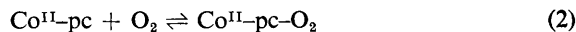
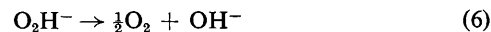
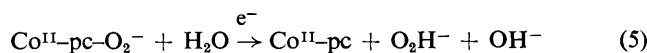
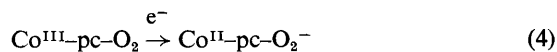


Figure 2. E.s.r. spectrum of a Co^{II}-tapc-P2VP-CO-St film cooled in a liquid nitrogen bath and peeled from the platinum electrode after the charge: -140 °C; 9.19 GHz; power 100 mW (1 G = 10⁻⁴ T).

(i) Charging process



(ii) Discharging process



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