

Electrochemical Doping with *meso*-Tetrakis(4-sulphonatophenyl)-porphyrincobalt of a Polypyrrole Film Electrode

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A polypyrrole film electrode in which *meso*-tetrakis(4-sulphonatophenyl)porphyrincobalt is electrochemically doped as the counter anion shows excellent catalytic activity for the cathodic reduction of oxygen.

A polypyrrole film electrode prepared by the anodic deposition of pyrrole on a base electrode is of active interest because it has many applications in the field of electrochemistry owing to its good electroconductivity. This conductivity is based on charge-transfer complex formation between the cation radical of the polypyrrole and a counter anion such as ClO_4^- or BF_4^- .¹⁻³ These types of film, though, have no catalytic activity for any electrode reactions. Thus the preparation of a polypyrrole film electrode with catalytic activity was attempted using *meso*-tetrakis(4-sulphonatophenyl)porphyrincobalt (Co-TPPS₄) as the counter anion instead of ClO_4^- or BF_4^- . It was found that Co-TPPS₄ was electrochemically doped into the polypyrrole film and this film (a 'porphyrin-polypyrrole') showed excellent electrocatalytic activity in oxygen reduction.

Anodic deposition of the porphyrin-polypyrrole film onto an Au electrode was carried out in a methanolic deposition solution containing Co-TPPS₄ (1×10^{-3} M) and pyrrole (0.1 M) under a constant current of $400 \mu\text{A cm}^{-2}$ and usually for 60 s.

Figure 1 shows the variation of the concentration of Co-TPPS₄ in the deposition solution with the charge passed. The linear relationship means that 3.33×10^{-6} mol of Co-TPPS₄

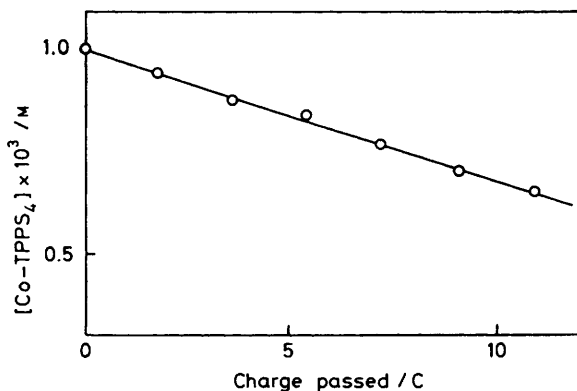


Figure 1. Variation of the concentration of Co-TPPS₄ in the deposition solution with the charge passed.

were consumed by passing a charge of 10.0 C (i.e., 1.04×10^{-5} F). If one assumes that two electrons per pyrrole monomer are consumed in its electrolytic polymerization,¹ the above

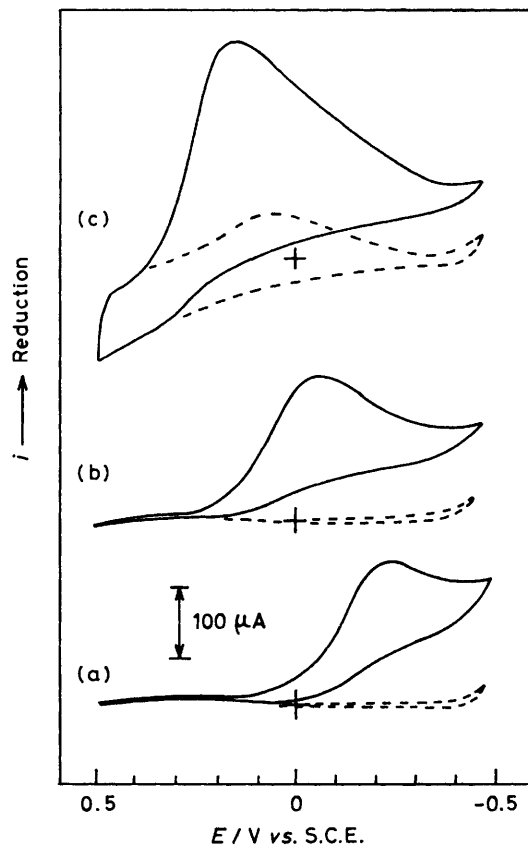


Figure 2. Cyclic voltammograms for O₂ reduction (--- N₂ sat.; — O₂ sat.) in 0.05 M H₂SO₄ for three types of electrode: (a) Au, (b) Au in 0.05 M H₂SO₄ containing 1×10^{-3} M Co-TPPS₄, and (c) porphyrin-polypyrrole-Au. S.C.E. = saturated calomel electrode, scan rate: 100 mV s^{-1} .

result makes it possible to calculate the number of pyrrole rings interacting with one sulphonate anion in Co-TPPS₄. This was evaluated to be 3—4 pyrrole rings constituting a cation radical and interacting with one sulphonate anion. This value was also confirmed by elemental analysis of the porphyrin-polypyrrole film, and was quite similar to that reported by Diaz and his co-workers for ClO₄⁻ and BF₄⁻ as counter anions.^{1,3,4}

Figure 2 shows the cyclic voltammograms for oxygen reduction on three types of electrode: (a) bare Au, (b) Au with adsorbed Co-TPPS₄, and (c) Au covered with the porphyrin-polypyrrole film. Figure 2 shows that the electrode in (c) has better electrocatalytic activity for oxygen reduction than those in (a) or (b). This suggests that the original catalytic activity of Co-TPPS₄ is enhanced by doping it in the polypyrrole matrix with high electroconductivity. In fact, the

reduction current of oxygen was higher than the reversible potential for O₂-H₂O₂, as confirmed by the rotating ring-disk technique.

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