

Doping-enhanced electrical conductivity and electrocatalytic activity in cobalt phthalocyanine

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Metal phthalocyanines have attracted wide attention as the material of choice in chemical, thermal and electro-optical devices [1, 2]. This is mainly due to their environmental and thermal stability and favourable optoelectronic properties. The electrical properties of semiconducting metal phthalocyanines have been investigated by various workers [3, 4]. Metal phthalocyanines undergo an α to β transition on heating and this transformation is accompanied by a change in the electrical conductivity. We have already reported [5] that the electrocatalytic activity of cobalt phthalocyanine (CoPc) is enhanced by random cross-linking by plasma treatment in air, which also results in the incorporation of a partial oxidation state in the phthalocyanine ring. The phthalocyanines are transformed to a highly conductive state by iodine doping [6]. The high electrical conductivity of iodine-doped material is believed to be due to the induction of a partial oxidation state in the phthalocyanine moiety. Here we report the results of our studies on the temperature-dependence of electrical conductivity in iodine-doped CoPc and its cyclic voltammetric characteristics.

CoPc was prepared and purified by the procedure already reported in the literature [7]. The samples were

further purified by Soxhlet extraction using benzene. The electrical conductivity from ambient to 300°C was measured in a high-temperature cell. Pellets of 10 mm diameter and 0.5 to 2 mm thickness were prepared at 600 kg cm⁻². A two-electrode configuration was used for measuring conductivity. The applied voltage was obtained from a potentiostat. Electrical contacts were provided with solid silver discs and measurements were done in a dynamic air atmosphere. The temperature of the cell was measured using a chromel-alumel thermocouple positioned very close to the sample. Cyclic voltammograms were recorded by coating CoPc on graphite electrodes by evaporation from solution, or using solutions of the sample. Doping was done by exposing CoPc-coated electrodes to iodine vapour and also from carbon tetrachloride (CCl₄) solution. The excess of iodine was washed out with CCl₄. Sodium perchlorate was used as the supporting electrolyte in cyclic voltammetric studies.

The log σ against 1/T plot for CoPc in air shows a knee around 170°C (Fig. 1). This plot is not retraced by temperature cycling, indicating that the α to β transformation is irreversible. The electrical conductivity is considerably enhanced by iodine doping. The dopant iodine does not undergo thermal desorption.

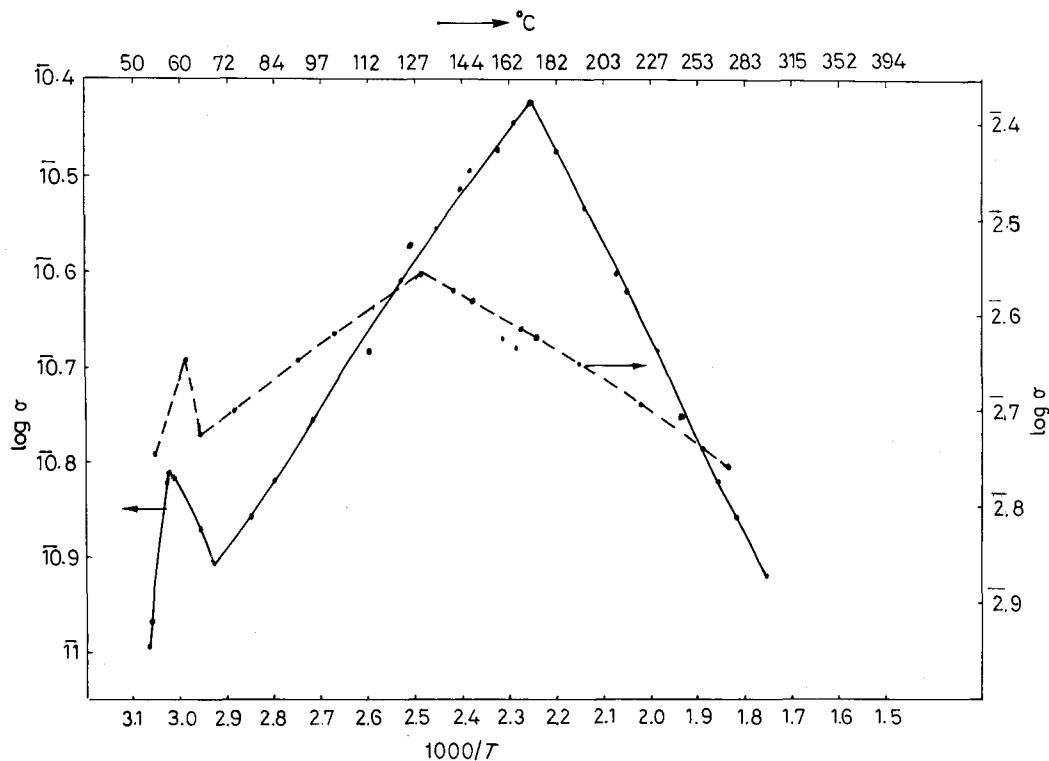


Figure 1 Log σ against 1/T plots: (—) CoPc, (---) CoPcI.

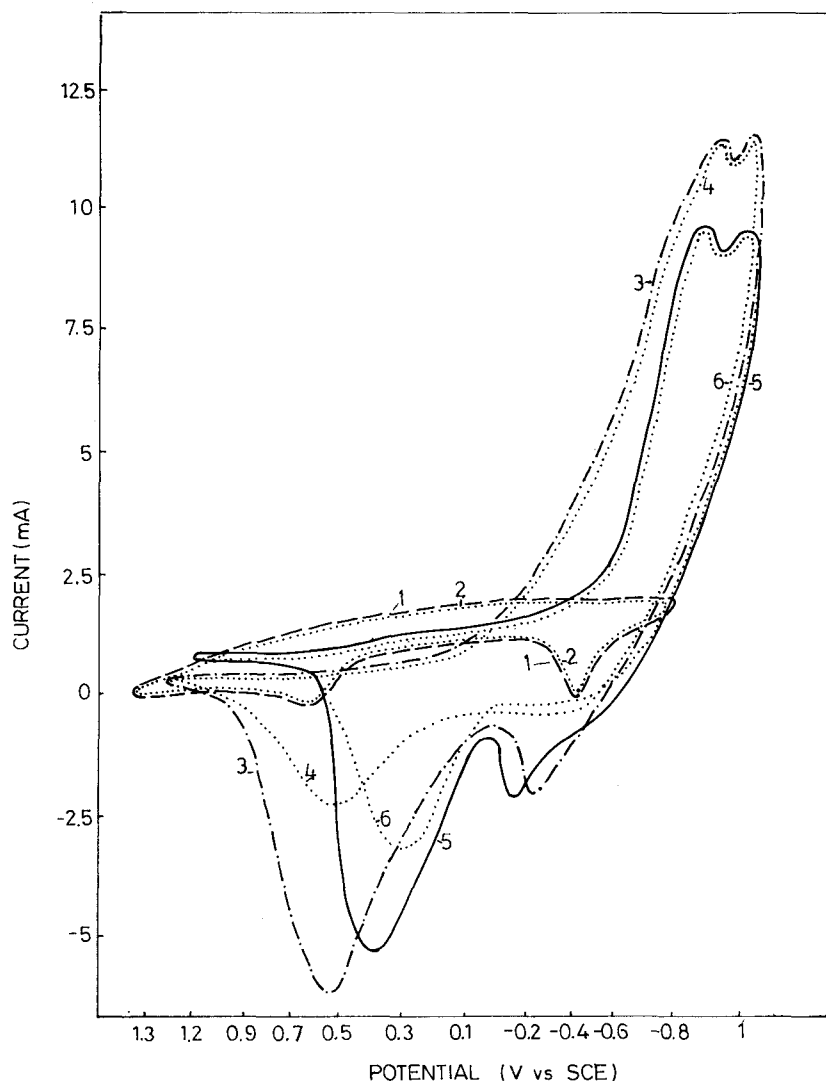


Figure 2 Cyclic voltammograms of doped and undoped CoPc in the presence and absence of dissolved O_2 ; supporting electrolyte 0.1 M $NaClO_4$; scan rate 100 mV sec^{-1} . (1) CoPc (O_2 saturated), (2) CoPc (N_2 sparged), (3) CoPcI (O_2 saturated), (4) CoPcI (N_2 sparged), (5) annealed CoPcI (O_2 saturated), (6) annealed CoPcI (N_2 sparged).

In addition to the enhanced electrical conductivity, the α to β transition temperature is lowered by doping, but the shape of the $\log \sigma$ against $1/T$ plot remains the same.

An interesting observation is that CoPc as such is insoluble in acetone, but the iodine-doped CoPc is partially soluble in acetone. The acetone-soluble portion has a visible spectrum which matches with that of undoped CoPc. This behaviour is similar to the doping and concurrent dissolution of polymeric semiconductors described by Frammer [8]. CoPc deposited on graphite gives a characteristic cathodic peak at 0.57 V, and the catalytic O_2 reduction peak appears at -0.59 V (Fig. 2). The peak at -0.59 V disappears when sparged with nitrogen. Iodine-doped CoPc (CoPcI) gives a cathodic peak at 0.57 V and two overlapping anodic peaks at -0.87 and -0.61 V .

The cathodic peak due to I_2 is absent, indicating that I^0 does not exist. I^0 has undergone reduction by accepting electrons from the phthalocyanine. The conductivity of CoPcI increases after heating. Simultaneously the cathodic peak which appears at 0.57 V shifts to 0.37 V. This shows that the phthalocyanine part has undergone partial oxidation with an increase in its catalytic activity. The anodic peaks appear at -0.9 and -0.61 V , which are close to the peaks appearing in unheated samples. The O_2 reduction peak is shifted to -0.21 V , showing that the catalytic

reduction of O_2 is further enhanced. In general, it may be concluded that I_2 doping of phthalocyanine increases the electrical conductivity and catalytic activity for O_2 reduction. This can be further enhanced by thermal annealing of the doped samples. The behaviour of thermally annealed iodine-doped electrodes derived from other phthalocyanines is under investigation.

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