Polypyrrole Complexed with Cobalt–Phthalocyanine. A Conducting Polymer which is Stable to Air and Moisture

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Polypyrrole–sulphonated cobalt-phthalocyanine films form electrodes which are stable on repeated recycling between −1.0 and 1.2 V in MeCN–Et_4NBF_4, and lose only 35% of the cobalt-phthalocyanine in aqueous electrolytes; the conductivity of the films increases on storing in air, in contrast to films containing BF_4^- counterions which show a decrease in conductivity.

Polypyrrole incorporating inorganic counterions (*e.g.* ClO_4^- or BF_4^-) is generally recognized as one of the more stable organic conducting polymers, with respect to its electronic conductivity upon exposure to the atmosphere. However, the conductivity still exhibits long term (weeks) irreversible decay. It is therefore important to determine whether other classes of conducting polymers can be synthesized, or the present materials modified, chemically or with complexes, to have the requisite environmental stability for practical use. In this context we have investigated polypyrrole films incorporating large organic macrocycles as counterions, specifically complexes formed between polypyrrole and various metal phthalocyanines.[1] We now discuss the complexes formed between polypyrrole (PP) and poly(*N*-methylpyrrole) (PMP) and the water-soluble sulphonated cobalt–phthalocyanine (CoPC). The PP–CoPC films exhibit unusual stability both as electrode and as electronic conductor.

PP–CoPC films were polymerized from aqueous solution containing 0.2 M pyrrole and 1mM of a sodium salt of tetra- or mono-sulphonated Co–phthalocyanine as the only anion present in the electrolyte, resulting in the incorporation of the CoPC anion into the PP matrix. The films were grown on indium–tin oxide (I.T.O.) substrates by electrochemical oxidation of pyrrole at a potential of 0.76 V *vs.* standard calomel electrode (s.c.e.), resulting in current densities of 200—300 μA cm^{-2}. The concentration of CoPC in the polypyrrole films corresponds to 3—6% by volume, irrespective of whether the CoPC is tetra- or mono-sulphonated. The electrochemical behaviour of the films was studied in both acetonitrile and aqueous electrolytes. We did not observe any difference in the behaviour between the tetra- and mono-sulphonated species either as electrodes or in the magnitude of the electronic conductivity. The catalytic properties of PP–CoPC films for oxygen reduction have already been investigated.[2—4]

The resulting films are strongly electrochromic, having four distinct colour stages in the voltage range 1.2 to −1.6 V (*vs.* s.c.e.) corresponding to the different states of oxidation of the Co–PC as well as that of the polypyrrole itself. The spectroelectrochemistry of the films will be published elsewhere.[1] The films could be cycled repeatedly without any significant decay between −1.0 and 1.2 V in acetonitrile electrolytes (MeCN–Et_4NBF_4) whereas the positive voltage limit of stability for PP incorporating inorganic anions is 0.6 V.

In contrast to BF_4 and ClO_4 anions, the CoPC does not leave the PP matrix when the film is reduced in MeCN–Et_4NClO_4 electrolyte. The CoPC is itself reduced and reoxidized upon cycling the film between the oxidized form of PP (0.65 V) and the reduced form (−1.0 V). After switching 10^5 times, 92% of the original CoPC remains in the film with all the loss taking place during the first five cycles. When the NH position of the pyrrole moiety is blocked by methyl groups as in poly(*N*-methylpyrrole) (PMP), grown under the same conditions and incorporating a similar quantity of CoPC, the loss of CoPC is continuous, and after 10^5 cycles only 36% remains. The slow loss is attributed to the lack of solubility of the CoPC in MeCN.

In aqueous electrolytes (0.1 M $NaClO_4$) complete loss of CoPC from PMP occurs after about 30 cycles whereas for PP the CoPC concentration stabilizes at 65% after about 100 cycles. The methyl substituted films also do not exhibit the range of colour changes associated with the CoPC in the PP–CoPC films, only switching between a dark (oxidized) and a somewhat lighter (reduced) blue colour, *i.e.* the CoPC does not undergo any colour changes, only the PP which is black when oxidized and semitransparent when reduced.[1] This suggests that the Co may be accepting the NH group of the pyrrole moiety as another ligand, or else some other form of complex formation may be occurring allowing electronic coupling between the CoPC and the PP.

Perhaps the most unusual property of PP–CoPC relates to its environmental stability as an electronic conductor. Figure 1 shows the typical room-temperature conductivity of PP–BF_4 and PP–CoPC (tetrasulphonated) plotted as a function of time. The conductivity was measured in air with a four-point

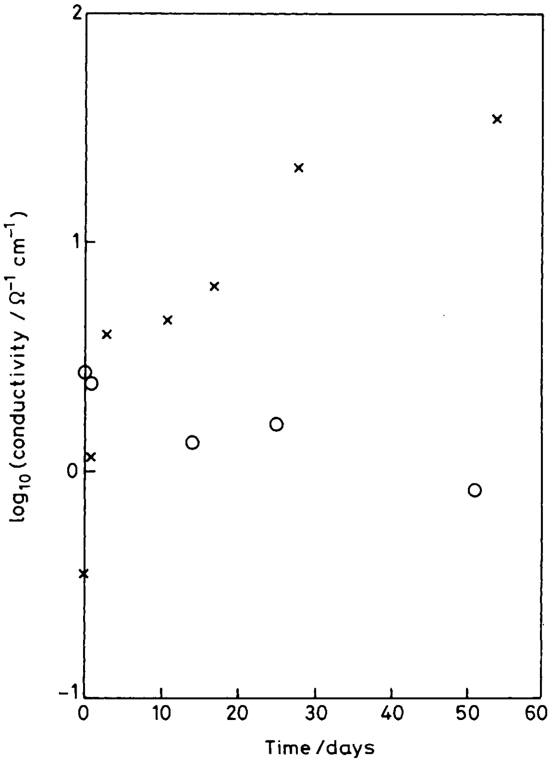

Figure 1. Room-temperature conductivity of a 0.65 μm thick film of PP–CoPC (tetrasulphonated) (×) and that of a 1.25 μm thick film of PP–BF_4 (○) as a function of time under ambient conditions. The films were made from aqueous solutions.

probe after the film had been removed from the electrode and placed on a glass slide. The films were stored under ambient conditions between measurements. The conductivity of PP–BF_4 declined continuously, reaching levels of 30—40% of the original conductivity after 2—3 months, depending on the sample thickness. In contrast, the conductivity of PP–CoPC increased with time and reached values about two orders of magnitude higher than the original conductivity after 2 months, when the conductivity was still increasing slowly. The conductivity of PP–CoPC reached values of 40—50 $\Omega^{-1}\,cm^{-1}$, which is more than an order of magnitude higher than the initial conductivity of PP–BF_4 grown on I.T.O. substrates from aqueous solution. As can be seen in Figure 1, the initial conductivity of PP–CoPC is lower than that of PP–BF_4. No long-term conductivity measurements on PP incorporating monosulphonated CoPC were done. The role of oxygen and moisture in increasing the conductivity will be discussed in the full paper.

This behaviour of the electronic conductivity is in sharp contrast to what has been previously observed with organic conducting polymers and may represent an important advance in the synthesis of practical materials.

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