

NEW GENERATION OF CONDUCTING POLYMER BATTERIES

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[Received: 1988 January; Accepted: 1988 June]

In this communication it has been shown that a successful polymer battery can be devised by the use of in situ doped poly-paraphenylene sulphide as an anode material and $\text{ClPyCo}(\text{DH})_2$ as a cathode material

Key words: Conducting polymer battery, poly para phenylene sulphide

INTRODUCTION

Conducting polymers are candidates for rechargeable battery electrodes. Therefore, the reversibility of charging discharging process is an important criterion of the quality of such materials.

The conduction in these polymers is associated with partially filled valence band, making available large number of electrons for conduction, and the scattering of these electrons by lattice vibrations with increase of temperature brings down the electrical conductivity. The majority of conducting polymers suffer instability in presence of moisture and atmospheric oxygen, because they get stabilized as cationic polymer on anode. Therefore a complete organic battery has two problems associated with electrode materials: (i) suitable cathode material (ii) stability of polymer in presence of moisture and oxygen.

In the present work, an attempt has been made to solve the aforementioned two problems using polyparaphenylene sulphide as an anode material and trivalent cobalt complex as a cathode material. The polyparaphenylene sulphide (PPS) is a good insulating material with a conductivity of less than $10^{-16} \text{ S cm}^{-1}$ and has a wide industrial application due to its processibility. The structural study indicates that in the PPS chain, there is an angle of 110° for the sulphur bond with phenyl ring [1]. PPS can be made conducting by doping with strong oxidising agents like AsF_5 and SbF_5 [2-4].

It is reported that sulphur trioxide which is slightly less strong electron acceptor than AsF_5 or SbF_5 can dope PPS to produce conducting polymer with a conductivity of order $10^{-3} \text{ S cm}^{-1}$ [5]. It has been suggested that on doping, irreversible structural changes are also possible [6]. Metallomacrocycles like phthalocyanine have gained importance [7], mostly due to their stack type of arrangement. The common metal ions used for polyphthalocyaninato (Pc) metal are Cu^{2+} , Fe^{2+} , Co^{2+} and Ni^{2+} . It is reported that polymeric Pc Cu has a conductivity 10^{10} times higher than the monomeric Pc Cu [8]. The reason for high conductivities of these compounds is still not fully understood. It appears that one of the essential prerequisites for a facile charge mobility is indeed a molecular stacking with a planar ring containing π electrons and with distances allowing the intermolecular interactions necessary for establishing a conduction pathway. In the present work the in situ doping of PPS by ClO_4^- was carried out electrochemically to avoid interference from atmospheric oxygen and moisture

The cathode material was chloro (pyridine) bis alkyl glyoximate cobalt (III) ($\text{ClPyCo}(\text{DH})_2$) complex mixed with acetylene black.

EXPERIMENTAL

The PPS was synthesised in the laboratory by taking 1:4 dichlorobenzene and sodium sulphide in a stoichiometric ratio in a polar organic solvent in presence of phase transfer agent under solid-liquid phase transfer conditions at 320K. On completion of reaction in two hours, the PPS was filtered, washed thoroughly with distilled water and benzene and dried at 333K in vacuum. This PPS sample gave glass transition temperature of 365K.

The other cathode material, namely $\text{Cl Py Co}(\text{DH})_2$, was synthesised by the following method. To a hot solution (0.021 mol) of CoCl_2 and 0.047 mol of alkyl glyoxime in 200 ml of 95% ethanol, 0.043 mol of pyridine was added. After cooling to 300K, cobaltous was oxidised to cobaltic by aerial oxidation. The brown crystals thus obtained were washed with water, ethanol and diethyl ether and dried at 320K, and the yield was 75%. The conductivity of loosely packed pellet of this compound was found to be $9 \times 10^{-6} \text{ S cm}^{-1}$. This compound showed highly reversible oxidation characteristic in propylene carbonate containing lithium perchlorate at around 0.8V vs SCE.

During the preparation of battery, cobaltic compound was made as a cathode and PPS mixed with acetylene black as anode material. The propylene carbonate containing one mol of anhydrous sodium perchlorate was used as an electrolyte. The charging was carried out by keeping constant voltage of 3V. The initial current on charging was 400 mA which fell to 10 mA at complete charging. The self discharge of battery, open circuit voltage vs time has been plotted in Fig. 1.

RESULTS AND DISCUSSION

Initial observation of anode and cathode reveals that no macroscopic damage such as pitting or cracking occurred during charging or discharging experiments. Upon charging, both the electrodes undergo a colour change, the PPS anode assumes yellow colour, and the co-complex cathode turns to shining green from yellow brown colour. This colour change is analogous to that observed on oxidation and reduction in a separate experiment.

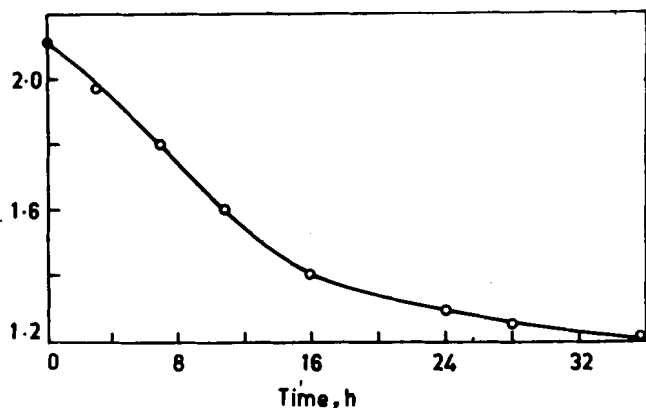
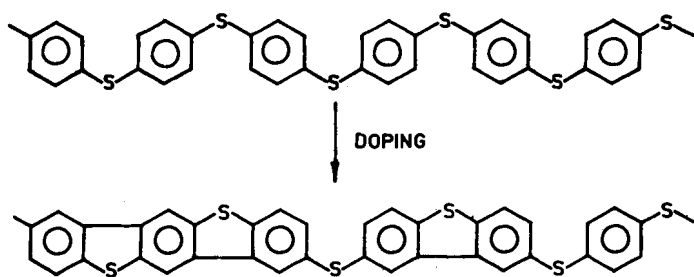


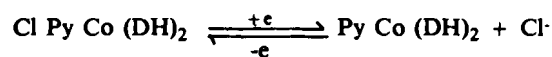
Fig. 1: Self discharge of battery

The I.R. spectra of oxidised and reduced cobalt complex were found to be essentially identical, which indicates that the ligand attached to the central metal ion does not get affected during the oxidation or reduction process. The bands at 1230 cm^{-1} and 1550 cm^{-1} are assigned (by comparison with the spectra of corresponding d5-pyridine complexes to the C-H— bending vibration and ring vibration). The sulphur link in PPS plays a unique role. It provides both the flexible link between the aromatic rings necessary for processibility and the p- orbitals on sulphur atom for continuous orbital overlap along the polymer. The interesting feature of PPS was on doping with ClO_4^- ion. Some irreversible change occurs. The careful I.R. analysis suggests that the intramolecular crosslinking (cyclization) occurs whereby phenyl ring coupling forms dibenzothiophene units along the polymer chain and this fused polymer derives its high conductivity due to the new back bone structure which is more compact. The reaction can be represented as:



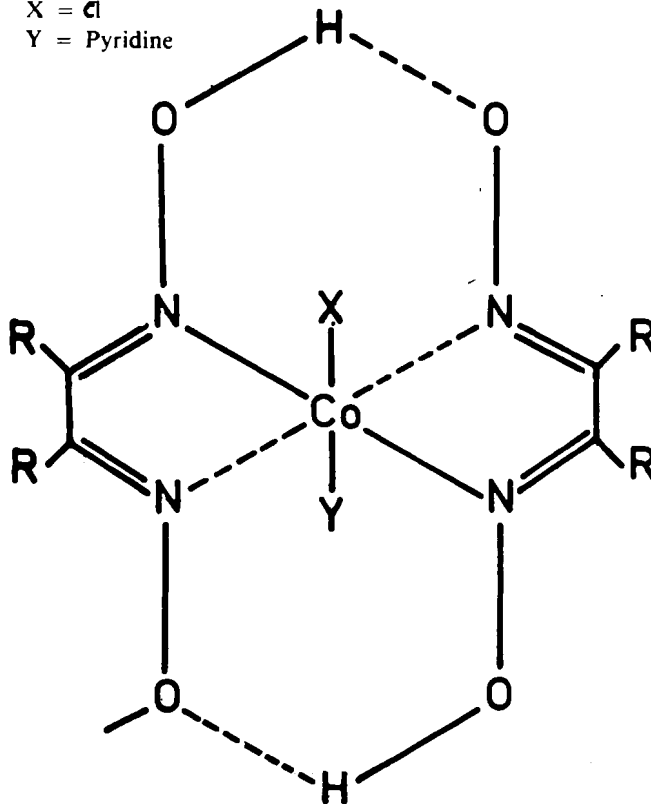
Unlike organic polymer, these inorganic stacked type macro-cycles get stabilized by incomplete charge transfer, mixed valence, and/or non- integral oxidation state by dopant. Generally in macrocycles central metal atom plays inferior role, as for example, in Pc Ni I , where the central Ni^{2+} does not change in formal oxidation state; however, in the present case, the redox

process affects ClPyCo(DH)_2 , which oscillates between Co^{3+} and Co^{2+} , without disturbing ligand environment, as indicated by IR studies where major bands remain unaltered, thereby establishing a conduction pathway associated with the central metal atom in addition to the macrocyclic path way. The redox reaction can be represented as



The structure of Cl Py Co (DH)_2 can be written as:

R = Alkyl group
X = Cl
Y = Pyridine



CONCLUSION

This battery is particularly suitable for high discharge i.e. power density is quite high and even on complete discharge, it is possible to recharge it any number of times (100 cycles have been studied) without affecting the stability of the component.

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Dinesh Chandra Trivedi — New generation of conducting polymer batteries

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