NEW GENERATION OF CONDUCTING POLYMER BATTERIES

DINESH CHANDRA TRIVEDI
Central Electrochemical Research Institute, Karaikudi-623 006, INDIA

[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 ClPyCo (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 $10^{-14}$ 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 $110^\circ$ for the sulphur bond with phenyl ring [1]. PPS can be made conducting by doping with strong oxidising agents like AsF₅ and SbF₅ [2-4].

It is reported that sulphur trioxide which is slightly less strong electron acceptor than AsF₅ or SbF₅ can dope PPS to produce conducting polymer with a conductivity of order $10^{-3}$ 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 Cu²⁺, Fe²⁺, Co²⁺ and Ni²⁺. 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 insitu doping of PPS by ClO₄⁻ was carried out electrochemically to avoid interference from atmospheric oxygen and moisture.

The cathode material was chloro (pyridine) bis alkyl glyoximato cobalt (III) (ClPyCo(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 ClPyCo(DH)₂, was synthesised by the following method. To a hot solution (0.021 mol) of CoCl₂ 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 $9 \times 10^{-4}$ 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.
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 ClO₄⁻ 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:

\[
\text{Cl Py Co (DH)₂} \xrightarrow{t.e} \text{Py Co (DH)₂ + Cl⁻}
\]

The structure of Cl Py Co (DH)₂ can be written as:

\[
\begin{align*}
R & = \text{Alkyl group} \\
X & = \text{Cl} \\
Y & = \text{Pyridine}
\end{align*}
\]

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.

REFERENCES


**BULLETIN OF ELECTROCHEMISTRY**

**ADVERTISING RATES**

<table>
<thead>
<tr>
<th>POSITION</th>
<th>Approximate print area cm x cm</th>
<th>Single insertion at Rs.</th>
<th>Six insertions at contract rate Rs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4th cover</td>
<td>22 x 18</td>
<td>1000</td>
<td>5000</td>
</tr>
<tr>
<td>3rd cover</td>
<td>22 x 18</td>
<td>750</td>
<td>3750</td>
</tr>
<tr>
<td>Inner full page</td>
<td>22 x 18</td>
<td>600</td>
<td>3000</td>
</tr>
<tr>
<td>Inner half page</td>
<td>11 x 18</td>
<td>400</td>
<td>2000</td>
</tr>
<tr>
<td>Inner quarter page</td>
<td>11 x 9</td>
<td>300</td>
<td>1500</td>
</tr>
</tbody>
</table>

Please write for other terms to:

Publication Manager
Bulletin of Electrochemistry
CECRI Unit, CSIR Complex
Madras 600 113 INDIA