

Electrical Conduction in Cellophane and Polypyrrole Composites and Its Use as an Electrode in Rechargeable Batteries

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SYNOPSIS

Electrical properties of cellophane and polypyrrole [cello + PPy] composite films were investigated by the two-probe method. The electrical conduction of composite films was studied as a function of voltage, temperature, and percentage content of PPy in the composite films. An attempt was made to use the [cello + PPy] composite films as electrodes in rechargeable batteries. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

One of the most valued properties of synthetic polymers is their ability to act as excellent electrical insulators. In spite of this, there has been interest for many years in the possibility of producing electrically conducting polymers.¹ Polymers with conjugated π electron backbones display unusual electronic properties,² such as low energy optical transitions, low ionization potential, and high electron affinities. The result is a class of polymers that can be oxidized or reduced more easily and more reversibly than conventional polymers. Charge transfer agents (dopants) effect this oxidation or reduction and in doing so convert an insulating polymer to a conducting polymer. The utilization of electrically conductive polymers in many technological applications is limited owing to the fact that they have poor atmospheric stability and processability. Hence, one of the methods to make such polymers into a tough, processable, stable form is to make composites with stable passive polymers. Composites have been prepared by mixing,³ vapor phase deposition,⁴ electrochemical deposition,⁵ plasma deposition,⁶ and interface techniques.⁷

In the present work, we have used the interface technique for the preparation of conducting poly-

meric composites from cellophane plus polypyrrole [cello + PPy]. Cello has good mechanical properties and imparts flexibility and strength to the composites; PPy is electrically conducting and stable and makes the composite highly conducting and stable to ambient conditions. The conductivity of the composite was studied as a function of percentage content of PPy in the temperature range of 30–90°C. Besides the conduction mechanism, mechanical properties like tensile strength and percentage elongation of these composites were tested and these conductive composites were used as electrodes in rechargeable batteries using aqueous electrolytes.

EXPERIMENTAL

[Cello + PPy] composite was prepared by the interface technique. Ferric chloride (FeCl_3) solution (10% w/v) was kept in a petri dish of 10-cm diameter. A cello sheet, 7 × 7 cm, was supported on a stand as shown in Figure 1 such that the lower surface of the film was in contact with the FeCl_3 solution. Diluted solution of Py in toluene (10% w/v) was spread uniformly on the top surface of the cellophane film. It was observed that the diffusion of Py across the film allows it to come in contact with the FeCl_3 , which acts as an oxidant for the polymerization of Py in the host film. It was observed that for the diffusion of Py and the polymerization to be complete, a time period of about 6 h was adequate. However, to ensure

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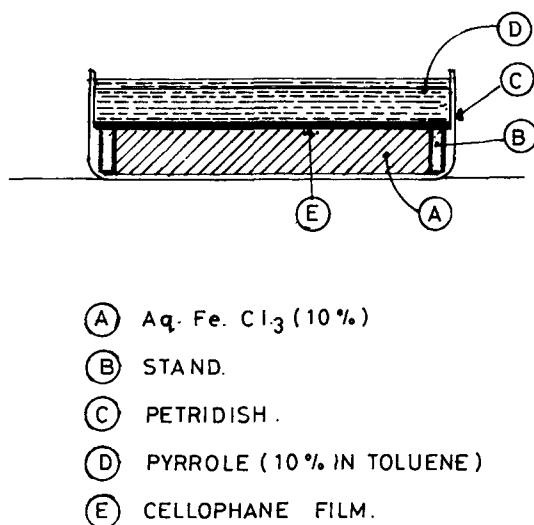


Figure 1 Experimental setup for the preparation of [cello + PPy] composite.

complete polymerization, the reaction was allowed to proceed up to 24 h. [Cello + PPy] composites having different PPy contents were synthesized so that a composite of [cello + PPy], having optimum contents of PPy with good mechanical and electrical properties, could be used for battery application. The electrical conduction was investigated by the two-probe method. The assembly mainly consists of a vacuum cryostat and electrical measuring accessories. The schematic diagram of the system is shown in Figure 2. The system consists of a low temperature cryostat, temperature control device, sample holder, and a rotary pump. The rotary pump yields a vacuum of 10^{-3} torr.

The sample holder is attached to the covering lid of the cryostat chamber such that during the experiment it remains in the central part of the chamber. It consists of six terminals, two for the heater, two for the thermocouple, and two for the measuring current in the specimen. The digital picoammeter (Scientific Equipment Co., Roorkee, Model DPA III) measures the current in the range of 10^{-3} – 10^{-11} A. Alternately, to measure higher values of current, a milliammeter or ammeter was used. The automatic temperature control device controls the necessary temperature within $\pm 1^\circ\text{C}$ and has a display for reading temperature. The regulated power supply gives a variable DC voltage up to 300 V. For low voltage, a voltage divider arrangement was used. In order to have good electrical contact, the control as well as other composite films were coated with a thin film of aluminum on both sides (area $1 \times 1 \text{ cm}^2$) using the vacuum evaporation technique. The spec-

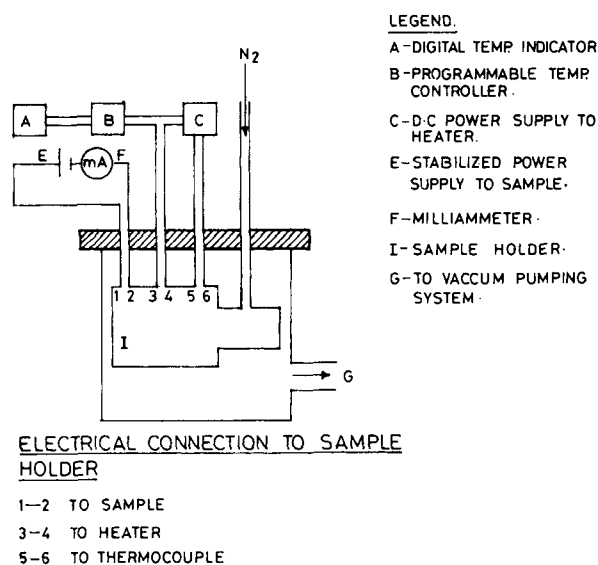


Figure 2 Block diagram for experimental set up of conductivity.

imen was then sandwiched between an aluminum coated glass plate and a small copper plate ($1 \times 1 \text{ cm}^2$) and was then mounted on the sample holder. After keeping the sample in the cryostat, the rotary pump was switched on and the measurements were carried out after it attained the vacuum of 10^{-3} torr.

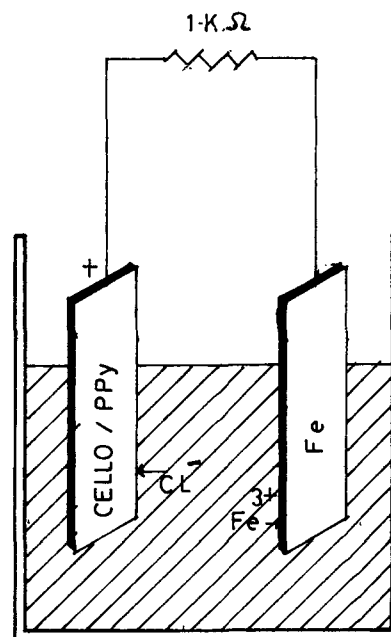


Figure 3 One compartment cell employing [cello/PPy] as one and metal as the other electrode dipped in aqueous electrolyte.

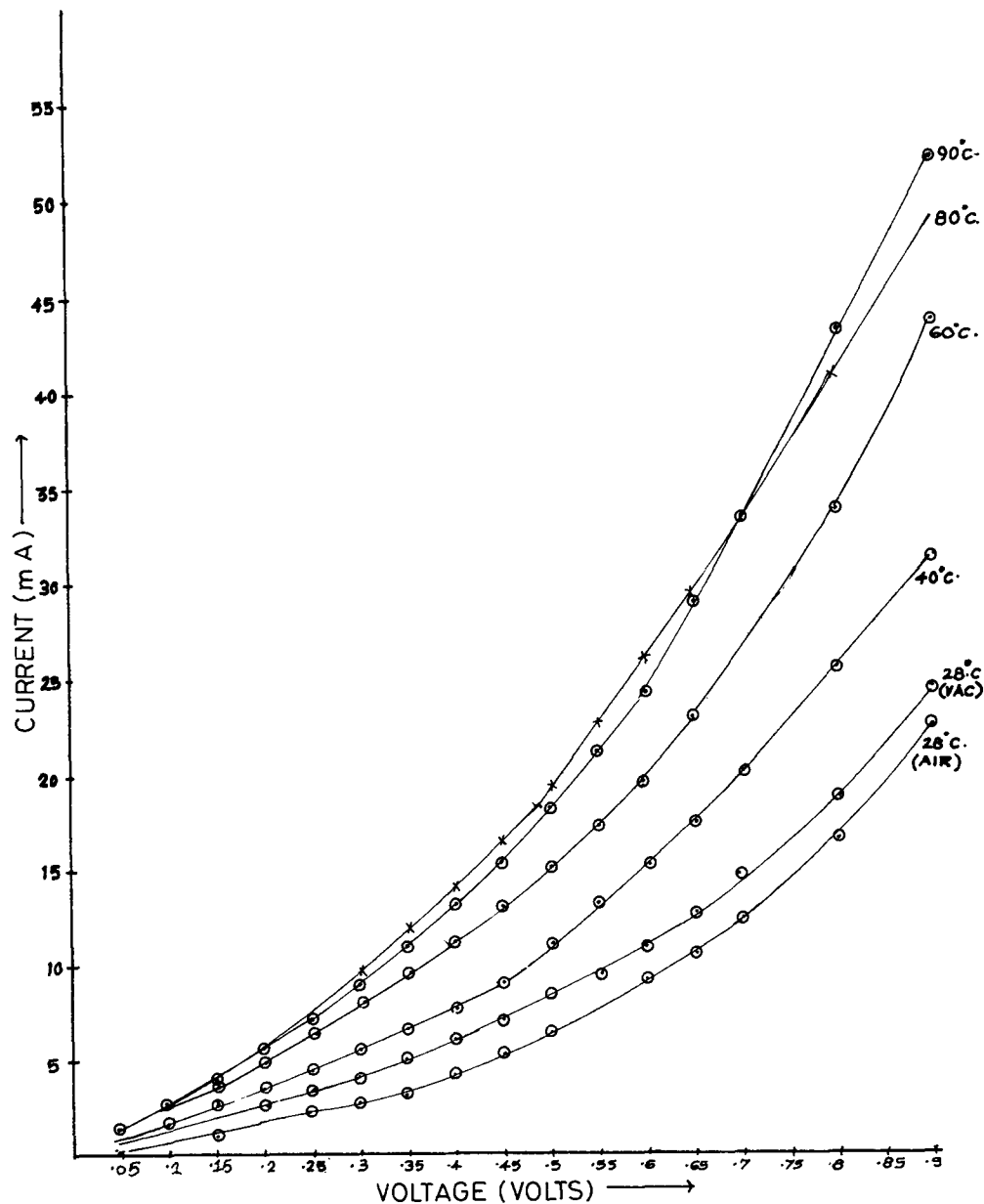


Figure 4 $I - V$ characteristics for [cello/PPy] composite film having 35.1% content of PPy.

The $I - V$ observations were carried out at room temperature as well as at higher temperatures. At least three sets of readings were taken for each sample.

The [cello + PPy] composite films obtained in the present investigation were free standing, tough, pliable, had high electrical conductivity, and were not easily attacked by water or weak acids. Hence, these composite films could be used as electrodes in batteries using aqueous electrolytes. A one compartment cell with [cello + PPy] film, 4×1 cm, was

used as one electrode and zinc/iron as the second electrode (Figure 3). Aqueous solutions of various salts such as LiCl and FeCl_3 were used.

RESULTS AND DISCUSSION

$I - V$ Characteristics

Electrical conductivity of composite films having different percentages of PPy were measured at el-

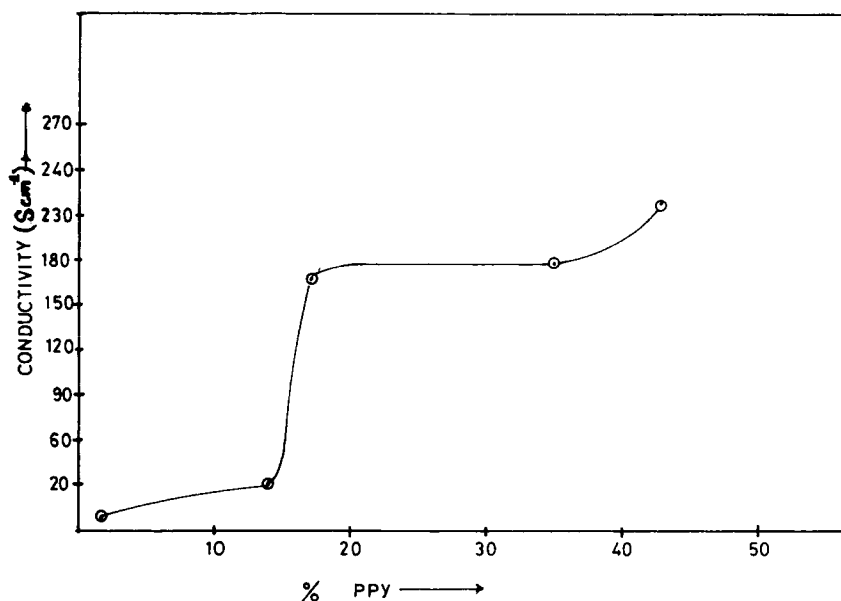


Figure 5 Plot of conductivity vs. % PPY for [cello/PPy] composites.

evated temperatures ranging from 25 to 90°C. The conductivity of the controlled cello film at the room temperature was on the order of 10^{-12} S cm^{-1} , whereas for the [cello + PPy] samples conductivity was on the order of 10^{-4} S cm^{-1} , which shows an increase in conductivity by an order of eight. Figure 4 shows I - V characteristics for the composite film having a PPy content of 35.1% at various temperatures. The behavior is linear up to 0.4 V. However, above 0.4 V, the characteristic is nonlinear indicat-

ing nonohmic behavior. It may be observed that the actual current values at 80 and 90°C for all the composite films are almost the same irrespective of the PPy content. It is seen that current increases with voltage as well as temperature, but at higher temperatures and higher voltages, the rate of increase is much higher.

The conductivity for the composites, having different percentages of PPy were calculated using the relation,

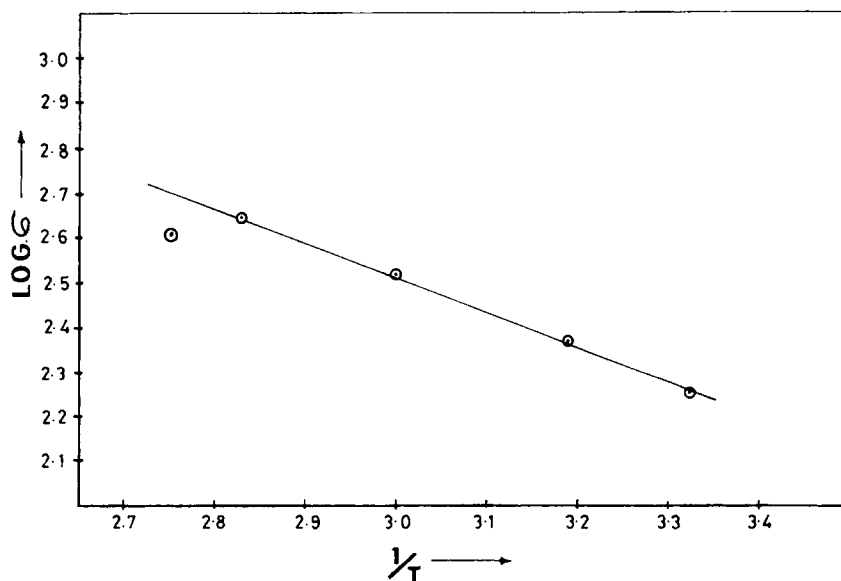


Figure 6 Plot of $\log \sigma$ vs. $1/T$ at 0.4 V for [cello + PPy] composite, 35.1% PPy content.

Table I Values of Activation Energy for [Cello/PPy]

Sample (mL)	% PPy	Activation Energy (eV)
Cello/PPy (0.5)	13.9	0.211
Cello/PPy (1)	17.4	0.220
Cello/PPy (1.5)	35.1	0.165
Cello/PPy (2)	42.8	0.158

$$\sigma = \frac{I}{V} \times \frac{l}{a} \text{ S cm}^{-1}$$

where I/V is the slope of the I/V plot, l is the thickness of the sample, and a is the area of cross section. It was observed that as the percentage of PPy content increased, conductivity of the composites increased. This behavior is depicted graphically in Figure 5.

ACTIVATION ENERGY

The activation energies for the composites having different percentage content of PPy were calculated from an Arrhenius plot. A plot of $\log \sigma$ vs. $1/T$ for

a 35.1% PPy doped sample at a voltage of 0.4 V is shown in Figure 6 just for illustration. Similar plots were also made for other compositions. The activation energies of all [cello + PPy] composite films were calculated from the slopes of the graphs and are given in Table I. It may be seen that the activation energy decreases with increasing PPy content. The activation energies for pure PPy, doped PPy, and pure cello were found to be 2.5, 0.2, and 0.54 eV, respectively, which compares well with the reported values.^{8,9} Thus the formation of composite with cello does not significantly increase the energy band gap found in the present studies (0.15–0.21 eV) and therefore the composites having improved mechanical properties in no way suffer adversely in their electrical properties.

CONDUCTION MECHANISM

Figure 7 shows a typical plot of $\log I$ vs. $\log V$ for 35.1% [cello + PPy] composite at two different temperatures (in air and vacuum). Similar plots of $\log I$ vs. $\log V$ were made for other composites. Each plot consists of two straight lines having different slopes. In the low field region, the slope is nearing 1 showing ohmic behavior, whereas in the high field region, the behavior is nonohmic having slope 2.

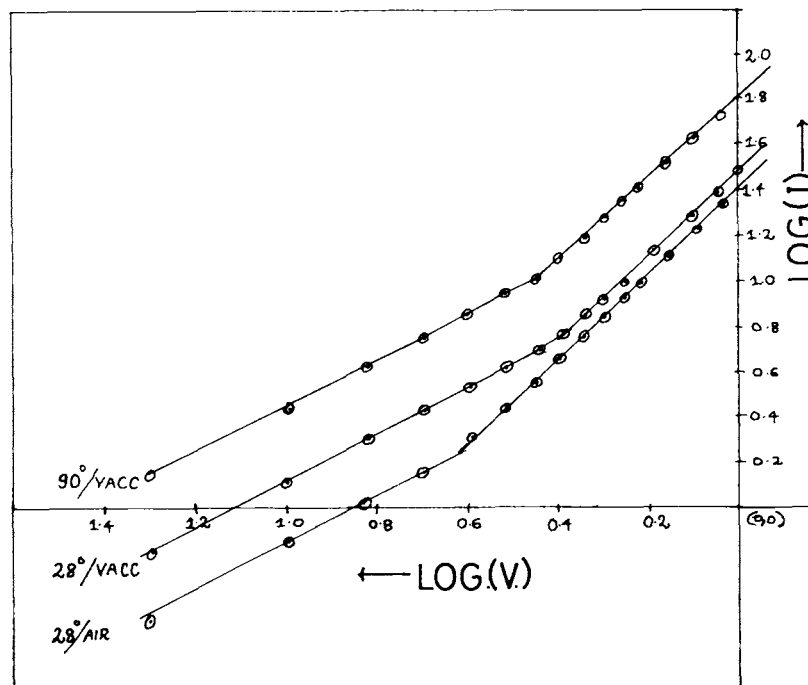


Figure 7 Plot of $\log I$ vs. $\log V$ for [cello/PPy] composite at 25 and 90°C, 35.1% PPy content.

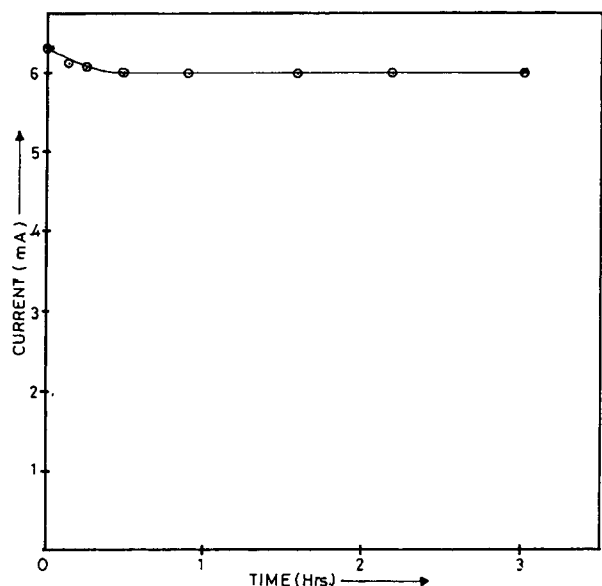


Figure 8 Plot of current vs. time at 0.4 V for [cello/PPy] composite (35.1% PPy).

This shows that the current in the high field region is space charge limited. It was of interest to further investigate whether the conduction is due to ions or electrons. If the conduction is ionic, then there is always the polarization effect in the DC field that results in a decrease in the conductivity of the film at a constant applied voltage with time. In the present studies, the variation of current with respect to time, at a particular voltage, was studied for all samples over a period of 3 h. A typical plot of current vs. time for a sample having 35.1% PPy content is shown in Figure 8. It was found that the variation was very small, the current reaching almost steady value after about 30 min after the application of voltage. This indicates that the main mode of current is electronic in nature. It was also observed that for the controlled cello as well as composites having a low percentage of PPy, up to 13% PPy, the current decayed rapidly with time at a given voltage. This indicated that for such a sample, the predominant mode of conduction is ionic. This observation is in conformity with an earlier studies on cello film

(electrical conduction of cello).⁹ The moisture content of cello is 8%; under the application of thermal excitation or electrical potential, protonation takes place and the ions play a dominant role in the conduction process. It can be seen from Figure 5 that there is a sudden increase in conductivity when the percent PPy is about 10–12%. In a separate set of experiments, we verified that there is a sudden increase in tensile strength when the percentage of PPy is about 10–12%. Similarly, a drastic decrease in percentage crystallinity was noted when the PPy content was about 10–12% (results not reproduced here). These observations indicate that the percolation threshold exists at about 10–12% PPy content. The behavior is similar to the one reported for + PPy] composite film can be prepared having good mechanical properties and high electrical conductivity.

It was of interest to study the performance of [cello + PPy] composite in battery applications. Recently^{12,13} the use of polymers in rechargeable batteries is being investigated vigorously because of various advantages over conventional batteries. The performance of the [cello + PPy] composite as electrode material was studied. For various combinations of electrodes, electrolytes, and doped cello, the voltages were developed in the range of 0.9–1.46 V. The polymer film was always found to be positively charged, thus acting as an anode. The details of these results are shown in Table II. It may be seen that when the percentage content of PPy was increased from 13.4 to 42%, the voltage increased from 1.15 to 1.46 V for the LiCl/Zn combination (Table III). It was also noted that the initial current is high when the level of doping is high. The discharge of current was allowed to take place through 1 K Ohm resistance and its variation with time was noted. A typical discharge curve is shown in Figure 9. It was found that for most of the films the current becomes steady and attains a low value after about 1 h.

The following symbols are used to denote charge, discharge cycles, and voltages of battery:

1. V_{oci} = initial open circuit voltage of battery when freshly formed;

Table II Value of V_{oci} , I_{sc} , and Capacity for Different Combinations of Electrodes and Electrolytes

Electrolyte	Anode	Cathode	V_{oci} (V)	I_{sc} (μ A)	Capacity (Ah/kg)	Recyclability
LiCl–water	Cello/PPy	Zn	1.15	100	47.02	10
FeCl ₃ –water	Cello/PPy	Fe	0.978	260	30	25

Table III Values of V_{oc} , I_{sc} , and Capacity of Various [Cello + PPy] Composites as Anode in Battery

Electrolyte	Anode	Cathode	V_{oc} (V)	Initial I_{sc} (mA)	Capacity (Ah/kg)
LiCl water (40%)	Cello/PPy (13.9%)	Zn	1.15	0.155	12
LiCl water (40%)	Cello/PPy (17.4%)	Zn	1.40	1.0	18
LiCl water (40%)	Cello/PPy (35.1%)	Zn	1.42	1.8	31.6
LiCl water (40%)	Cello/PPy (42.8%)	Zn	1.46	2.7	47.02

- V_{ocf} = final open circuit voltage of battery after discharging;
- V_{ocs} = voltage of battery due to self-charging;
- V_{occ} = voltage of battery after external charging;
- I_{sc} = short circuit current when battery terminals are shorted through 1 K Ohm resistance.

The cell was then recharged by applying an external voltage of 2.5 V for about 12 hrs. The Voltage and current in proportion noted after full charging

was found to be higher than the initial voltage values. A typical charging curve is shown in Figure 10.

It was of interest to observe the type of reactions when battery is allowed to idle. It was noted that the voltage (V_{ocf}) rises on allowing the battery to stand for sometime. This may be termed as self-charging effect. Self-charging is the process in which the battery is allowed to stand and no current is drawn or supplied externally. During this period the migration/diffusion of ions takes place and PPy⁺ goes back to the neutral state. However, this reaction is slow. The voltage observed after self-charging is

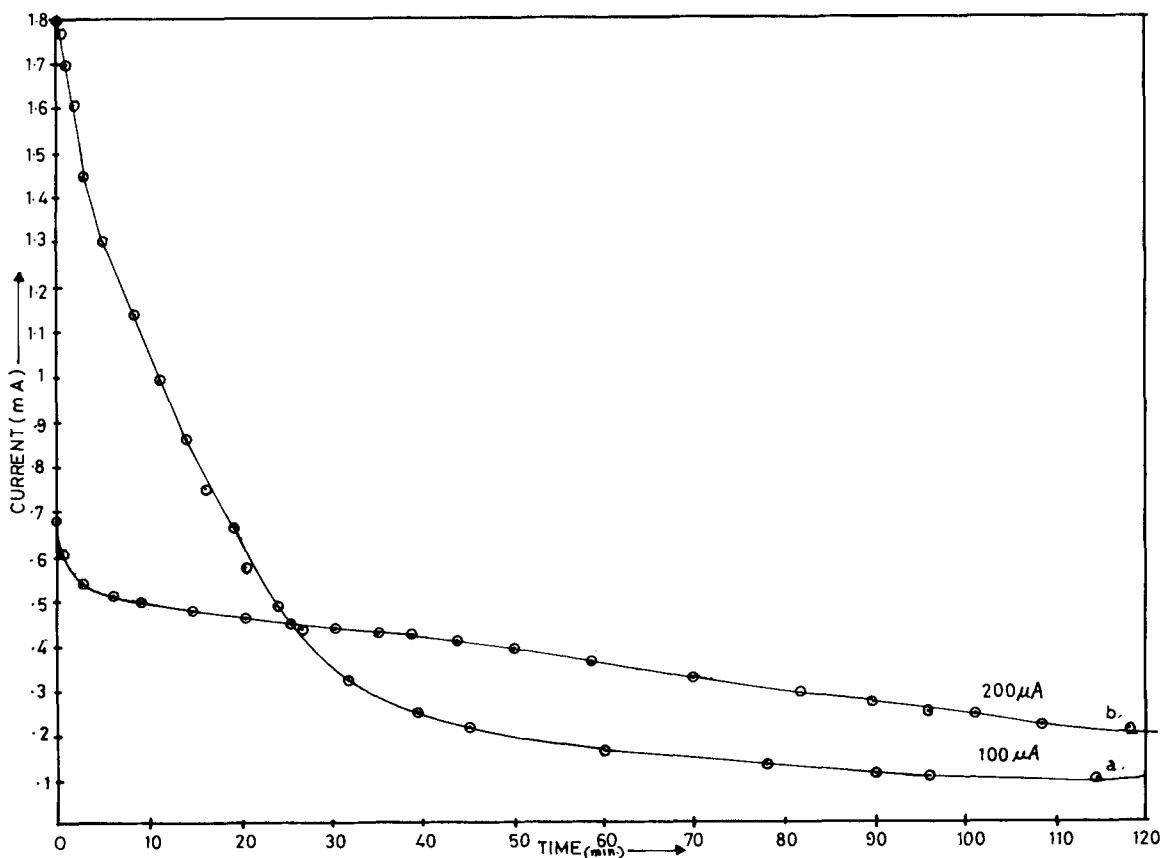


Figure 9 Plot of current vs. time for [cello/PPy]/LiCl/Zn system, composite 35.1% PPy content: (a) initial discharge and (b) after external charging.

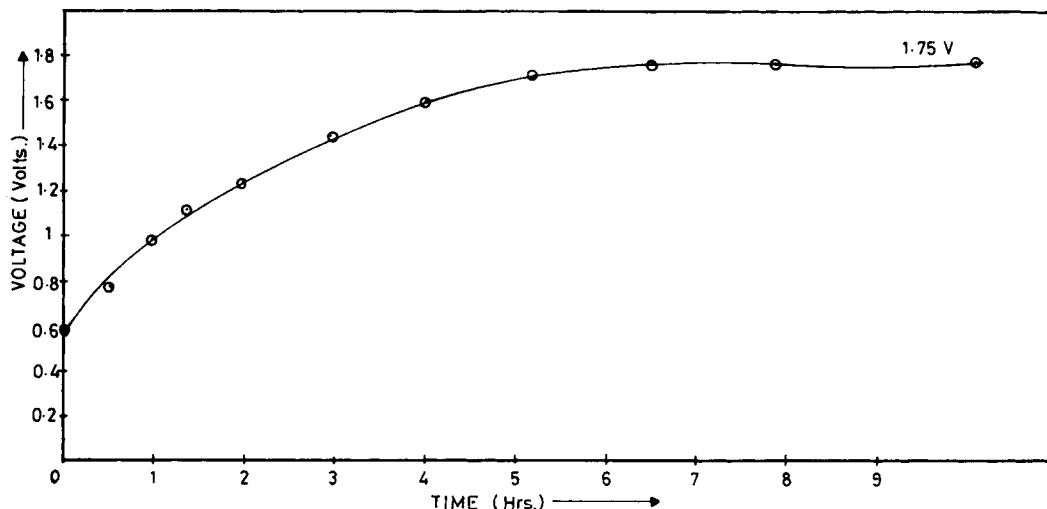


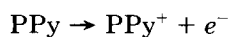
Figure 10 Plot of voltage vs. time for cello/PPy/LiCl/Zn system during external charging, composite 35.1% PPy content.

much higher than V_{ocf} but slightly lower than the initial voltage (V_{oci}).

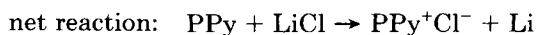
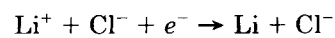
On the basis of the present investigation, the reactions occurring during the process of discharging and charging are, respectively:

discharge process:

at positive terminal: oxidation



at negative terminal: reduction



charging process:

at positive terminal: reduction

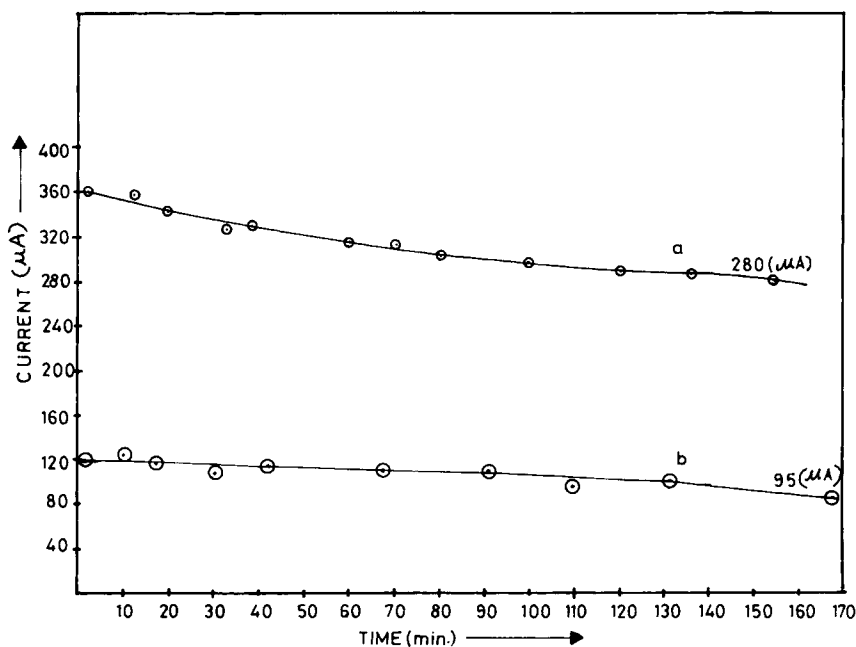
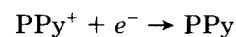
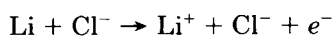


Figure 11 Plot of current vs. time for [cello/PPy]/FeCl₃/Fe system, composite 35.1% PPy content: (a) initial discharge and (b) after external charging.

at negative terminal: oxidation



net reaction: $\text{PPy}^+\text{Cl}^- + \text{Li} \rightarrow \text{PPy} + \text{LiCl}$

On the basis of discharge current, the capacity of the battery was calculated and the values are shown in Table II.

It was of further interest to find out whether other combinations of metals and their salts could be used for the development of the battery. Aqueous FeCl_3 (0.5M) solution was used as an electrolyte and a strip of iron as another electrode. It was found that a voltage of 0.98 V was developed and the short circuit current (I_{sc}) was about 360 mA. A typical charge-discharge cycle for this combination is shown in Figures 11 and 12. In this system also the battery could be extremely charged to a value higher than initial V_{oci} . Besides, self-charging was also observed and on self-charging the maximum voltage reached was lower than the initial V_{oci} .

The lower values of the initial currents observed in the discharge characteristics executed after external charging are due to the following reasons. When the battery is constructed from the fresh electrolyte, the PPy molecules in the composite are in the neutral state. All these neutral PPy molecules will contribute to the discharge current, hence it will

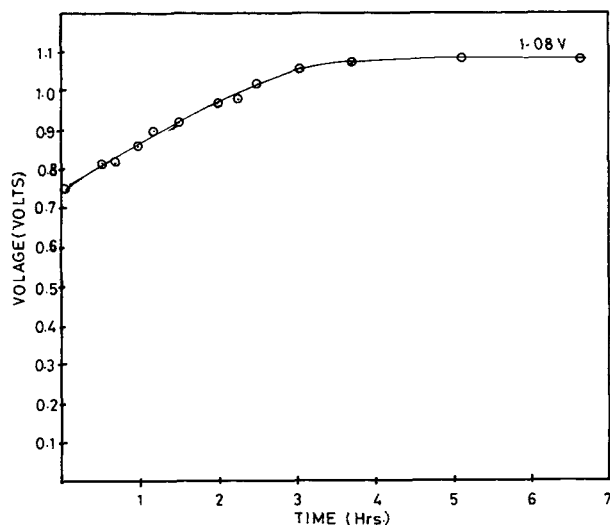


Figure 12 Plot of voltage vs. time for [cello/PPy]/ FeCl_3/Fe system during external charging, composite 35.1% PPy content.

be high. The discharge current falls rapidly with time as the rate of diffusion of Cl^- ions reaches a limiting value. In this process neutral PPy goes to the PPy state, with Cl^- acting as the dopant counterion. When the battery is charged by applying an external voltage, PPy reverts to the neutral state. However all the diffused Cl^- ions acting as dopant counterions (PPy^+Cl^-) cannot be removed fully from the interior of the polymer film. As a result the initial current during the next cycle of discharge is lower.

In the commercial application of such batteries, it is necessary that the battery has a long lifetime. The batteries developed in the present investigation were subjected to a large number of charge-discharge cycles. It was found that for the LiCl/Zn combination V_{oc} drops appreciably after 10 cycles. However, in the case of the FeCl_3/Fe combination, the V_{oc} retained its original voltage even after 25 cycles.

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