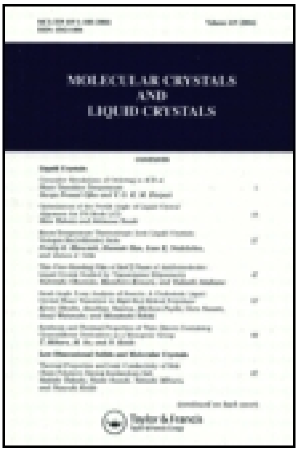

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Electronic and Ionic Conductivity of Poly(Thionaphthe-neindole)

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ELECTRONIC AND IONIC CONDUCTIVITY OF POLY(THIONAPHTHENEINDOLE)

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Abstract Current vs. time and current vs. voltage characteristics of poly(thionaphtheneindole) (pTNI) and discharge current of a solid-state battery: Mg/p(TNI)/Au were investigated in different conditions of temperature and humidity. The experimental conditions affect strongly the mechanism of charge transport, which depends on the presence in the polymer material of an amount of water, which can be reversibly extracted from or adsorbed by the sample.

INTRODUCTION

One of the main problems concerning the conducting polymers is the determination of the nature of the electrical conduction process.

In fact, these ionomers, besides showing high capacitive phenomena at the electrodes, are characterized by an electrical conductivity with charge transport occurring with an electronic or/and ionic mechanism, where the ratio between the electronic and ionic components can be put in evidence in some experimental conditions[1,2]. The trouble is to discriminate these components and to recognize the factors which determine the prevailing one.

Poly(thionaphtheneindole) (pTNI), synthesized in our Institute by electrochemical technique[3], was employed as a component of an all-solid-state battery[4]. Running this battery we found that pTNI behaves, in normal working conditions, as an ionic conductor. The ionic and electronic components of its conductivity and the conditions affecting their ratio were investigated and the results are reported in this paper.

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EXPERIMENTAL PART

PTNI was prepared by electrochemical oxidation of thionaphthene-indole (TNI) (Figure 1), as reported in a previous paper[3]. The formula of this product, $\{[(C_{14}H_{6.6}NS)^+(ClO_4)^-].2H_2O\}_n$, defined on the basis of analytical and mass-spectrometric measurements[5], denounces the presence of a 10% water content. For conductivity measurements, the pTNI powder, pressed, at 2 ton cm^{-2}, to 0.7-0.8 mm thick pellets with a diameter of 0.5 cm, was sandwiched between two golden disks (diameter 0.5 cm); for battery construction, polymer pellets of the same size were included between a Mg disk and a golden one (diameter: 0.5 cm). Conductivity measurements were performed at different temperatures, at atmospheric pressure and at low pressure (rotating pump vacuum), using a home-made vacuumtight cell. For investigation of the current vs. time (i-t) and current vs. voltage (i-V) characteristics a multifunction apparatus AMEL Electrochemolab was used.

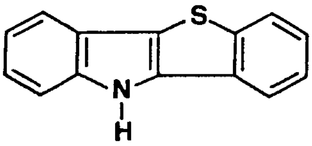

FIGURE 1. Thionaphtheneindole

RESULTS AND DISCUSSION

Figure 2 shows the i-t and i-V characteristics measured at room temperature and atmospheric pressure, for a polymer pellet between two golden electrodes, according to the conditions reported in the experimental part. An analysis of these curves shows that:

1. the current decreases with time, at constant voltage;
2. the specific conductivity, at t=0, is $5x10^{-4}+1x10^{-5}\Omega^{-1}cm^{-1}$;
3. during the i-t measurements at constant voltage, if the voltage is set to 0 V without disconnecting the electrodes, an inverse current can be observed;
4. the i-V characteristic does not show a linear trend, so meaning a non-strictly ohmic behaviour.

The same measurements described in Figure 2 were performed also at higher temperatures, till about 100 °C, and the corresponding plots are shown in Figure 3.

From these last measurements it turns out that at temperatures higher than 50-60 °C a clear change of the conductivity characteristics of pTNI occurs; in particular, as well as i-t curves at constant voltage are concerned, the current remains constant in the time and, if the voltage is set to 0 V without disconnecting the electrodes, no inverse current is observed. The conductivity in this "high" temperature range is lower than that measured at ambient temperature (from i-V measurements at 52 °C, $\sigma=1\times10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$). As the i-t plots show, also the ohmic i-V curves recorded in the "high" temperature range (see Figure. 3b) denounce an electronic mechanism of the charge transport. From the plot of Figure 4 an activation energy of 0.8 eV for the conduction process was calculated in the range 52-118 °C.

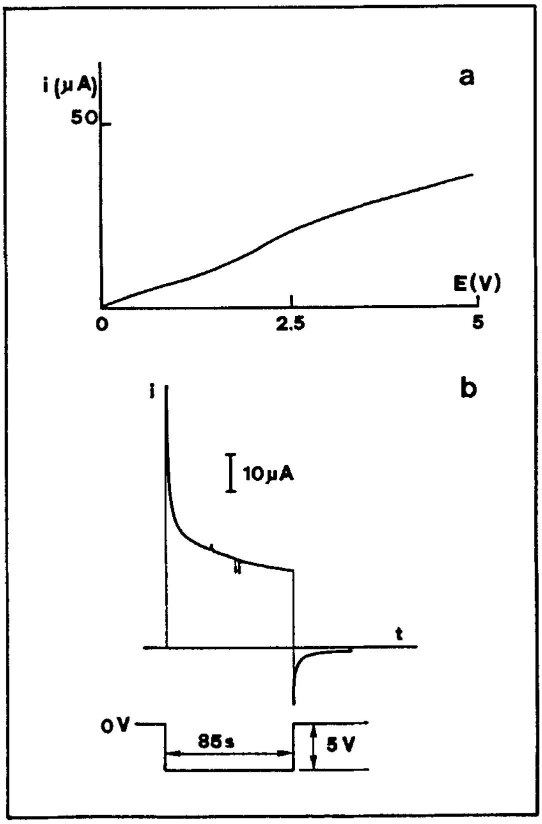

FIGURE 2. a: Current vs. voltage plot inherent to a pTNI pressed pellet (diameter 0.5 cm,thickness 0.08 cm) between two gold electrodes. b: Current vs. time inherent to the sample of fig 2a, subjected to a square wave voltage, as represented in the figure. The experiments were done in air at 22 °C.

The i-t and i-V characteristics show a reversible behaviour with changing temperature.

From all the measurements it can be concluded that the electric conductivity of pTNI presents two different characteristics at "higher" and "lower" temperatures respectively, being prevalently ionic in the latter case and electronic in the former. The reversibility of the phenomenon and the analytical results, from which a formula for pTNI was defined, lead us to put forward the hypothesis that the ionic character of the conductivity, as found at "lower" temperatures, could be due to the ascertained presence of water in the material, through an acid-base interaction between the heterocyclic nitrogen of pTNI and the water, involving the proton linked to the nitrogen atom of the polymer, as shown in the scheme below:

$\equiv N..H^+..H_2O..\equiv N..H^+..H_2O..$

where : $\equiv N..H^+$ represents the heterocyclic nitrogen in the oxidized polymer, as more clearly shown in Figure 5.

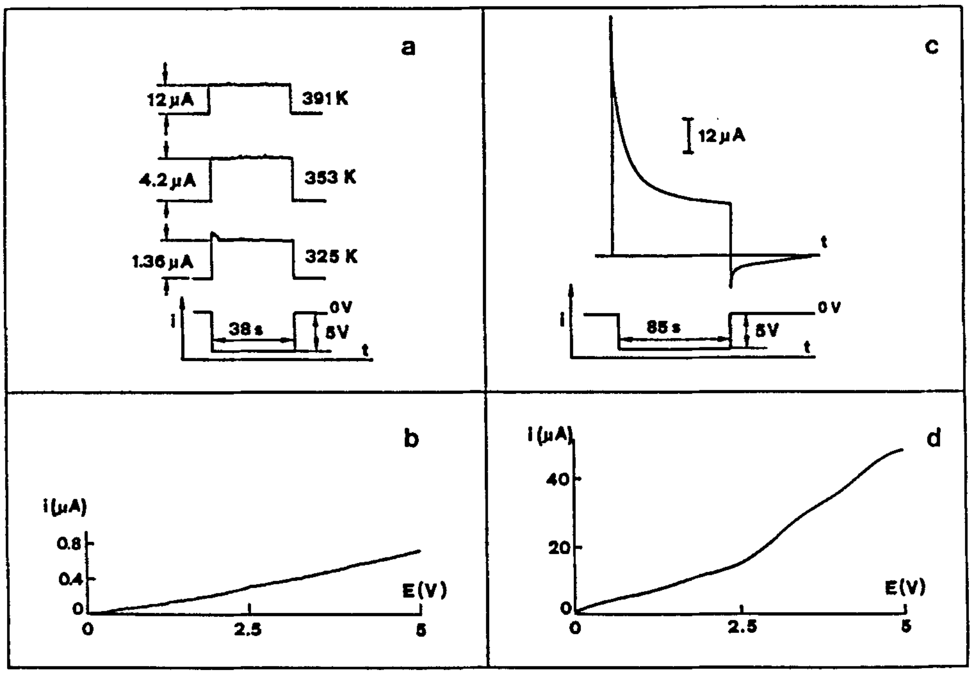

FIGURE 3. The experiments of fig.3 are inherent to the same sample of fig. 2. a: current vs. time at high temperatures (the square wave voltage is represented in the figure), and b: current vs. voltage at 106°C. c: current vs time and d: current vs voltage of the sample cooled at 22°C.

In a previous paper dealing with the preparation of pTNI[6], acid-base equilibria, presumably localized on the heterocyclic nitrogen, were put in evidence. These equilibria, utilizable for pH sensors, were found also in other conducting polymers which contain heterocyclic nitrogen atoms[7].

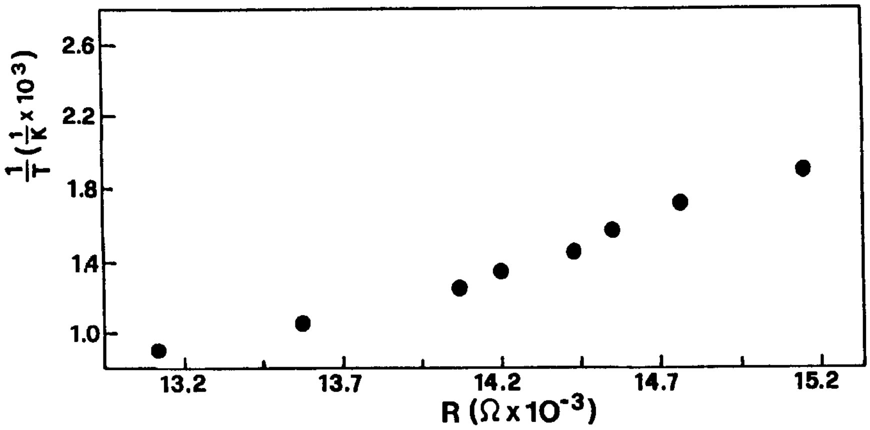

FIGURE 4. Temperature vs resistance plot for a pTNI pressed pellet (diameter=0.5 cm, thickness=0.08 cm) between two gold electrodes. The resistance was determined as Vi^{-1} (see fig. 3a).

The reversible change with temperature of the ionic-electronic charge transport in pTNI is attributed to the observed readsorption of the water content by the dehydrated polymer.

As said before, pTNI was employed as a component of an all-solid-state battery: Mg/pTNI/Au, where the electrode processes are schematically reported below :

at the anode: $Mg - 2e \rightarrow Mg^{++}$

$Mg^{++} + 2H_2O \leftrightarrow Mg(OH)_2 + 2H^+$

at the cathode: $\equiv N\text{-}H^+ \leftrightarrow \equiv N + H^+$

$H^+ + 2e \rightarrow 1/2H_2$

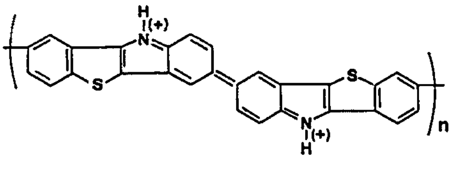

FIGURE 5. Oxidized pTNI.

In this connection, measurements of discharge current of the battery were carried out at increasing temperatures. It was found that at temperatures higher than 50-60 °C, the battery does not deliver current. If the room temperature is restored, the battery characteristics are reversibly re-established. This supports the fact that water promotes inside the polymer an ionic transfer of charges which, taking into account the structure of the material, can be identified as protons. At a certain temperature water tends to leave the polymer and does not contribute anymore to the conduction process with consequent stop of the battery.

This hypothesis was supported by the battery behaviour at low pressure (rotating pump vacuum). At 0.01 torr the cell stops delivering discharge current and its open circuit voltage decreases from 2.1V to 0.52 V; if the atmospheric pressure is restored in the cell, the voltage rises up again rapidly to 1.5-1.6 V (Figure 6), then more slowly reaches, after some days, the previous level of 2 V. At this point the battery can again deliver a discharge current.

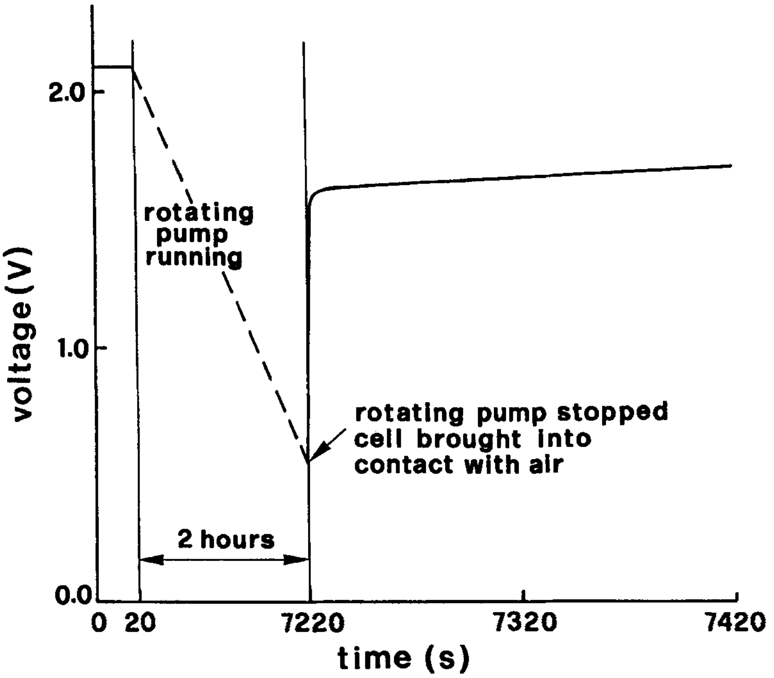

FIGURE 6. Open circuit voltage of a Mg/pTNI/Au cell at ambient and reduced pressure.

CONCLUSIONS

1. The conductivity characteristics of poly(TNI) depend on temperature and on ambient humidity.
2. The conductivity at "low" temperature and atmospheric pressure is characterized by an ionic charge transport mechanism.
3. At "high" temperature and reduced pressure (0.01 torr) the conductivity decreases and shows an electronic character.

This behaviour is connected with the hydrogen ion migration into the polymer backbone, which is made possible by the presence in pTNI of an amount of water which can be reversibly extracted from or adsorbed by the sample in relation with the experimental conditions.

The above mentioned characteristics look very promising for a possible use of the title material as sensitive element of humidity sensors; it can be also candidate for the construction of a solid state fuel cell.

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