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Mechanism of the solid state battery: magnesium/poly(thionaphtheneindole/gold)

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The mechanism of a battery, that was assembled by including poly(thionaphtheneindole) (pTNI) pressed pellets between a gold cathode and a magnesium or zinc anode, was investigated. The importance of the water content of the pTNI in assuring proton migration in the polymer was established. Electrochemical reactions for magnesium oxidation at the anode and H^+ reduction at the cathode are proposed.

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1. Introduction

One of the most promising applications of conducting polymers is in the battery field where such materials are used both as electrolyte (for example [1]) and as electrode [2–5]. Important problems met in the initial stage of these applications, such as cyclability, self discharge and capacity losses, were successfully solved using selected conducting polymers, mainly of the polyaniline, polypyrrole and polythiophene family [6].

In a previous paper [7] a new type of solid state battery was described based on poly(thionaphtheneindole), pTNI, conducting polymer. This battery offered some relevant characteristics, such as lack of self discharge and easy construction. However, its electrochemistry is not yet fully understood and the objective of this work was to further investigate the electrodic reactions of the pTNI battery, with the main objective of reaching a better understanding of its electrochemical mechanism and, thus, of providing the basis for improving its characteristics.

2. Experimental details

Poly(thionaphtheneindole), pTNI (Fig. 1(a)), was synthesized by anodic potentiostatic oxidation of TNI following the procedure described in previous papers [8]. The polymer was obtained in the form of a black powder having the overall formula: $\{[(C_{14}H_{6.6}NS)^+ClO_4^-].2H_2O\}_n$ [9]. PTNI contains approximately 10% water at room temperature.

The electrical properties of pTNI were obtained using pressed pellets of polymer powder (0.5 cm diameter and 0.8 mm thickness) maintained between two gold electrodes, in the configuration of Fig. 1(b). The current–time and current–voltage curves of these cells at different temperatures were obtained, in a home-made vacuum-tight housing, by an electrochemical multifunction AMEL Electrochemolab instrument connected to an AMEL Mod 863 x–y recorder. The batteries of the Mg/pTNI/Au type, were constructed by directly replacing one gold electrode with a magnesium electrode in the above (Fig. 1(b)) configuration. The constant current charge–discharge curves of these batteries were obtained by an AMEL Model 545 electrometer connected to an AMEL Mod. 863 x–y recorder.

Complex impedance spectroscopy was run using a Solartron, Mod. 1255 frequency response analyser coupled to a Solartron model 1286 electrochemical interface.

The mass spectra of pTNI were obtained with a VG ZAB 2F double focusing instrument in EI (electron ionization) conditions (70 eV) with a source temperature of 200 °C.

3. Results and discussion

3.1. *Transport mechanism in pTNI*

Figure 2 illustrates current–voltage and current–time responses to a square wave for the Au|pTNI|Au cell at two different temperatures, i.e. 26 °C and 106 °C. At low temperature the plots suggest the presence of capacitive elements in the cell, while at high temperature they reveal a purely ohmic resistance behaviour.

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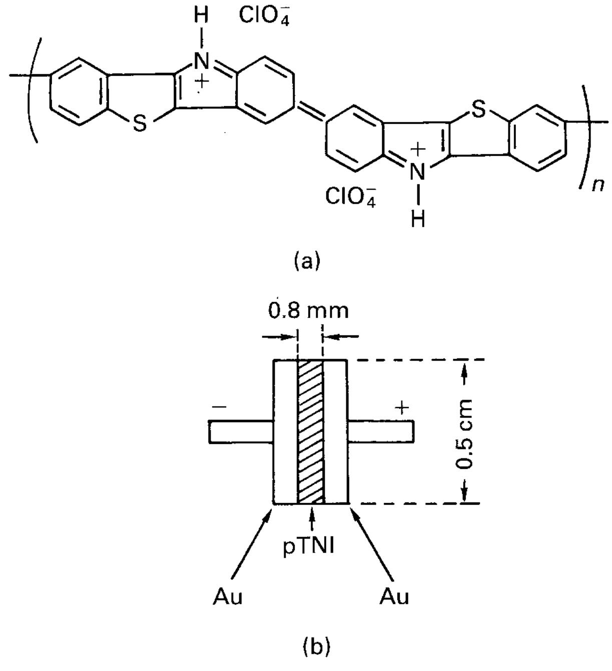

Fig. 1. (a) Poly(thionaphtheneindole), pTNI; (b) cell for the determination of the electrical characteristics of pTNI.

This behaviour is reversible with temperature and may be associated with the water content in the polymer, 10% at low temperatures and progressively smaller as the temperature increases. The presence of water enhances the overall conductivity of the pTNI samples as shown by the current–voltage curves; also the non-ohmic response to a square wave voltage at low temperature suggests a double layer capacitance at the interface Au|pTNI.

To explain the conduction mechanism in pTNI, an impedance analysis of Au|pTNI|Au cells was carried out and compared to the response obtained in the open atmosphere and in a humidity controlled (less than 10 ppm) dry box. Figure 3 illustrates the results. The experimental data are reported on the Z', $-Z''$ complex impedance plane. Figure 3(a) refers to the cell maintained at ambient conditions; in Fig. 3(b) the impedance spectrum of the same cell after storage for 2 h in a dry box is shown. Finally, the impedance response of the cell transported from the dry box back to the original environment is shown in Fig. 3(c); this matches well with the initial one in Fig. 3(a). This pattern suggests that, in the absence of water, the spectrum can be represented by the equivalent circuit of Fig. 3(b), where the capacitance is 1.6×10^{-9} F and the total value for the electronic (R_e) and ionic (R_i) resistances is 2350 Ω: it is not possible to separate the two components by this measurement. In the presence of water, the spectrum shows the impedance due to the interface processes and is in accord with the equivalent circuit of Fig. 3(c), where R_{ct} is the resistance inherent to the charge transfer at the electrodes and C_{dl} is the capacitance of the double layer: the values of the capacitances ($C_g = 1.6 \times 10^{-9}$ F, $C_{dl} = 1 \times 10^{-6}$ F) are reasonable if compared with those found in other similar systems [10, 11]. The value of a single resistance cannot be determined separately; however, a very good fit was obtained between the experimental result and the spectrum inherent to the model circuit of Fig. 3(c) for the following values of the components: $C_g = 1.63 \times 10^{-9}$ F, $C_{dl} = 1.12 \times 10^{-6}$ F, $R_e = 4500\,\Omega$, $R_i = 1490\,\Omega$, $R_{ct} = 2430\,\Omega$.

In a previous paper [12], acid-base equilibria, presumably localized on the heterocyclic nitrogen of pTNI, were demonstrated. Moreover, in the literature [13] papers are found dealing with acid–base equilibria in other conducting polymers containing heterocyclic nitrogen. On the basis of these results, it

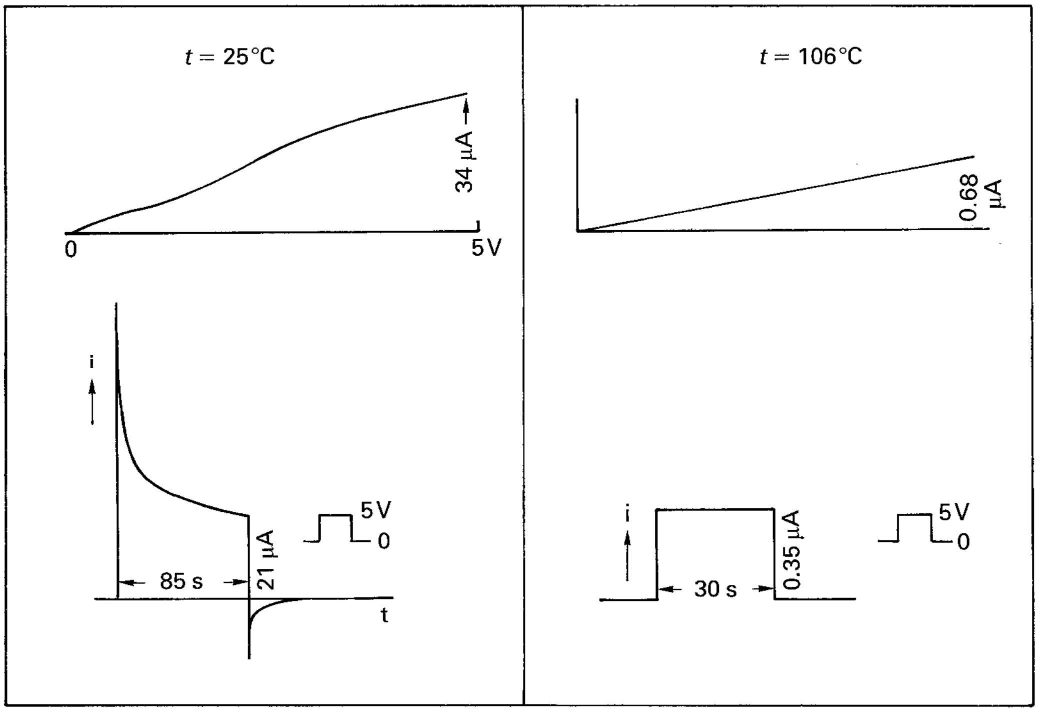

Fig. 2. Current–voltage (upper) and current–time (below) curves for a Au|pTNI|Au cell at 26 °C (left) and 106 °C (right).

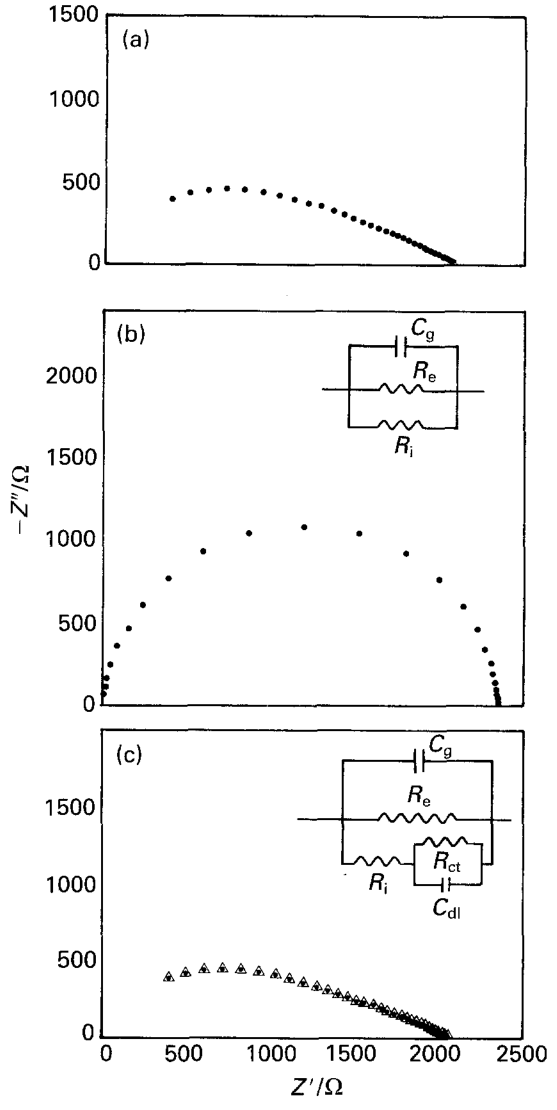

Fig. 3. (a) Impedance response of a Au|pTNI|Au cell maintained in ambient conditions. (b) Impedance response of the cell after storage for 2 h in a dry box; inset: equivalent circuit of the cell. (c) Impedance response after returning the cell from the dry box back to the original environmental conditions; triangles: experimental results, full points: values inherent to the equivalent circuit shown in the inset by setting $C_g = 1.63 \times 10^{-9}$ F, $C_{dl} = 1.12 \times 10^{-6}$ F, $R_e = 4500\,\Omega$, $R_i = 1490\,\Omega$, $R_{ct} = 2430\,\Omega$. Frequency range: 0.01 Hz–2 MHz.

may further be assumed that the ionic carriers in hydrated pTNI are protons, because the results of acid–base equilibria involving water and the polymer may be schematized as follows:

$$=N-\ldots H^+ + H_2O \leftrightarrow = N- + H^+ \ldots H_2O \qquad (1)$$

where $=N-\ldots H^+$ is the oxidized pTNI (Fig. 1(a)) and $=N-$ its deprotonated form (Fig. 4).

Accordingly, the ion transport in the polymer takes place by proton migration, aided by acid–base equilibria in which the heterocyclic nitrogen and the water are involved. The mechanism proposed also accounts for the recovery of the ionic behaviour when returning from dry to humid conditions and for the fact, as reported below, that the cell Mg|TNI|Au works only in the presence of H_2O. However, at this stage of the investigation, the exact values of the electronic and ionic components of the conductivity were not obtained by experimental methods. Consequently, the increase in the conductivity of pTNI, when the temperature is decreased from about 100–110 °C to ambient conditions, may be due to a higher electronic mobility when water is present in the polymer. In fact, the presence of water can decrease the interaction between the charges in the conducting polymer and/or increase the interchain hopping. This last possibility, which is not in contrast with an ionic component of the conductivity at ambient temperature, is in accord with results obtained in a study of the conductivity of polyanilines [14, 15].

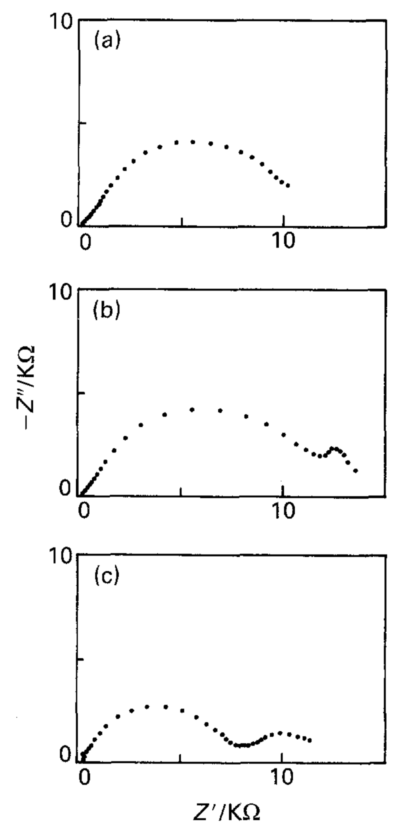

Fig. 5. Impedance response of a Mg|pTNI|Au battery taken at progressive storage times after assemblage. (a) 24 h; (b) 48 h; (c) 72 h. Frequency range: 0.01 Hz–100 kHz.

3.2. *Electrochemical mechanism of pTNI-based batteries*

The batteries considered in this work were formed by

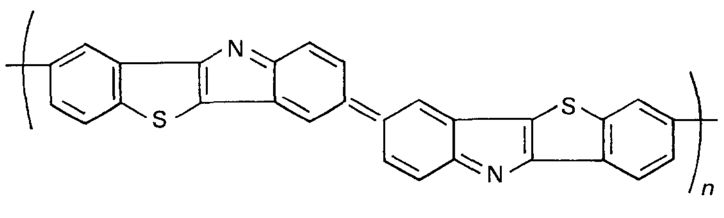

Fig. 4. Deprotonated form of pTNI.

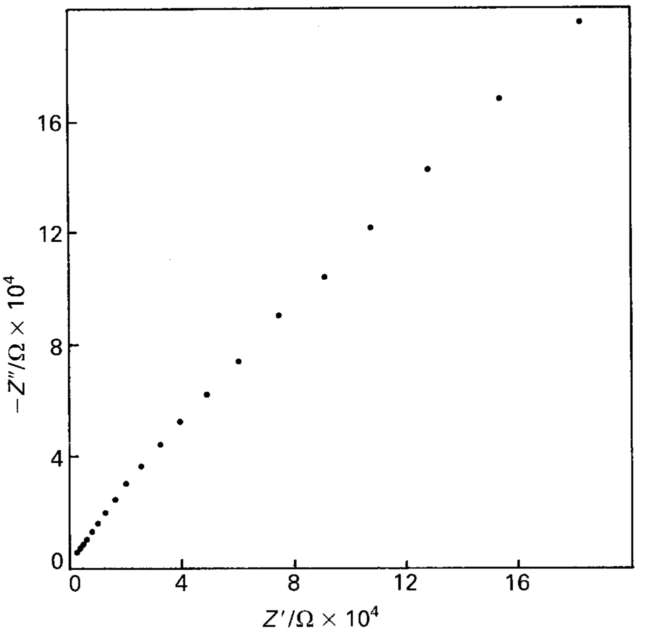

Fig. 6. Impedance response of a Mg|pTNI|Mg cell. Frequency range: 0.01 Hz–100 kHz.

placing in sequence a metal anode, a pellet of pTNI and a gold cathode. That is M|pTNI|Au where M = Mg or Zn.

A common characteristic is that the batteries do not show a stable open circuit voltage (o.c.v.) immediately after assembly: in the case of the magnesium battery, the o.c.v. reaches a stable value of 2.35 V only after 70 h.

Figure 5 shows a.c. impedance measurements of the battery, performed 24, 48 and 72 h after assembly. A second semicircle of increasing prominence can be observed in the impedance response which suggests that a passivation film is formed on the magnesium electrode upon storage of the battery.

To confirm this hypothesis, a.c. measurements were performed on a reciprocal Mg|pTNI|Mg cell. The response, illustrated in Fig. 6, is that typical of a high resistive system. This result can be explained by assuming the formation of a resistive film on both magnesium electrodes.

Based on impedance evidence, one can postulate the growth on the metal electrode of a film, possible of the $Mg(OH)_2$ or MgO type, which is a poor electronic conductor but which allows the migration of ions, possibly OH^- ions, through its matrix. Indeed, other oxides, such as Ta_2O_5 or SiO_2 are known to exhibit similar ionic transport [16, 17].

Therefore, the structure of the magnesium battery can be more precisely indicated as

$$^{(-)}\mathrm{Mg}|\mathrm{Mg(OH)_2}|\mathrm{pTNI}|\mathrm{Au}^{(+)} \quad (2)$$

and, accordingly, the electrode processes can be summarized as follows:

At the anode:

$$\mathrm{Mg} \text{ —} \mathrm{Mg}^{2+} + 2e^- \quad (3)$$

$$\mathrm{Mg}^{2+} + 2\mathrm{H_2O} \longrightarrow \mathrm{Mg(OH)_2} \quad (4)$$

At the cathode:

$$2\mathrm{H}^+ + 2e^- \longrightarrow \mathrm{H_2} \quad (5)$$

The overall battery electrochemical process is

$$\mathrm{Mg} + 2\mathrm{H_2O} \longrightarrow \mathrm{Mg(OH)_2} + \mathrm{H_2} \quad (6)$$

This mechanism confirms the crucial role of water and

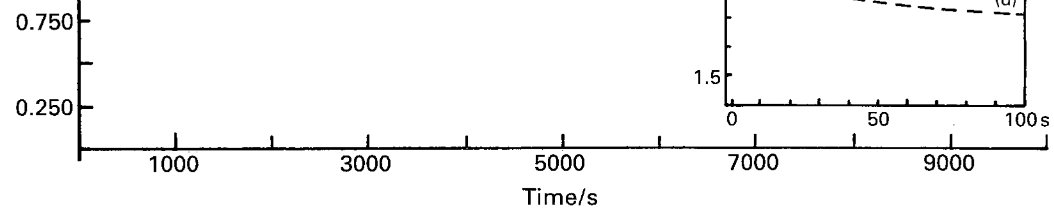

Fig. 7. Typical discharge curves of the Mg|pTNI|Au battery at 22 °C at various density currents: (a) 24, (b) 60, (c) 100 and (d) 150 $\mu A\,cm^{-2}$.

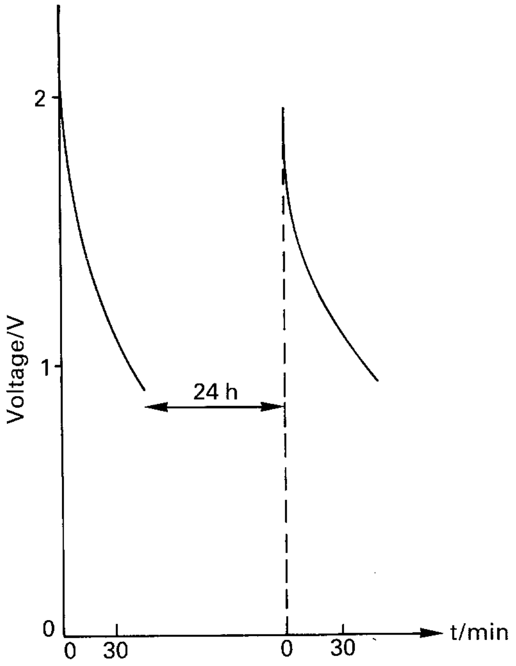

Fig. 8. Two subsequent discharge pulses ($I = 220\,\mu A\,cm^{-2}$) of the Mg|pTNI|Au battery at room temperature.

of the proton transport in the pTNI polymer in assuring the battery operation. Figure 7 shows typical discharge curves at various current density rates. Specific capacities of the order of 80 Ah kg^{-1} can be obtained at room temperature. Assuming an average voltage of 1.85 V for the low rate discharge, an energy density of 148 Wh kg^{-1} is obtained.

As can be seen from Fig. 7, at the beginning of cell discharge, the voltage decreases immediately by 350 to 400 mV and subsequently, upon high rate discharge ($i > 150\,\mu A\,cm^{-2}$), decays slowly with time. This is due to the overvoltage of the H^+ discharge reaction on gold and to ohmic polarization, as demonstrated by Fig. 8, which illustrates two subsequent discharge pulses of the battery. When the current is switched off at the end of the first pulse, the voltage recovers to the o.c.v. and the second discharge pulse matches the first.

The cell discharge does not modify the pTNI chain. In fact a sample of polymer (11 mg), included in a cell similar to the one shown in Fig. 1(b), showed the same mass spectra before and after five subsequent discharges with a consumption of 1.6 C. This mass spectra presents main peaks at $m/z = 222$, 411, 444 and 663.

The use of zinc as anode is also feasible. In this case the voltage of the battery decays to 0.8 V, as expected from the lower standard potential. Operation of a Li|pTNI|Au battery was unsuccessful since its assembly required the use of a water-free environment. No stable o.c.v. was attained in this case and no detectable current could be drawn from the battery.

4. Conclusions

The discharge mechanism of the M|pTNI|Au battery (where M = Zn or Mg) is explained on the basis of the function of an ionic conducting layer at the anode side and of proton transport in the bulk polymer. This mechanism requires the presence of water inside the pTNI. In fact, attempts to run the battery under dry conditions were not successful. Consequently, a lithium based battery was not successful. A magnesium anode may be used and the related battery gave an o.c.v. of 2.35 V and acceptable discharge capabilities as well as a promising energy density. A zinc anode can also be employed. In this case the voltage of the battery decayed to 0.8 V because of the lower standard potential of this metal with respect to magnesium.

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