

L. Micaroni · F.C. Nart · I.A. Hümmelgen

## Considerations about the electrochemical estimation of the ionization potential of conducting polymers

Received: 18 January 2002 / Accepted: 23 April 2002 / Published online: 4 July 2002  
© Springer-Verlag 2002

**Abstract** The energy gap and ionization potential of some conducting polymers such as polypyrrole and the polythiophene derivatives, poly(3-methylthiophene) and poly(3-hexylthiophene), are estimated using optical and electrochemical techniques. With these parameters we have constructed the energy level diagrams of the polymers.

**Keywords** Conducting polymers · Ionization potential · Energy diagram

### Introduction

Conducting polymers are constituted by a system of conjugated double bonds. To make these polymers electrically conductive it is necessary to introduce mobile charge carriers. This is typically done by oxidation or reduction reactions, commonly called “doping”, that can be made by chemical or electrochemical processes. Chemical doping occurs when the polymer is exposed to an oxidizing or to a reducing agent, whereas its electrochemical counterpart can be driven either by cathodic or anodic polarization of the polymer in a suitable electrochemical cell [1].

The process can be denoted p-type doping or n-type doping, corresponding to a positive or negative sign, respectively, of the generated charge available for transport in the polymer chain, a terminology analogous

to doping in inorganic semiconductors. These charges remain delocalized as they are neutralized by the incorporation of counter-anions (or cations, depending on the case), called dopants, from the electrolyte solution [2].

The redox reactions in the conducting polymers are responsible for the electrical conductivity as well as for the electrochemical and electrochromic properties of these materials. These, in a wide range of modifiable and controllable properties, are the driving power for the strong activity on the research and development of devices with great potential in energetics and optoelectronics. For example, it is possible to use these p-type or n-type doped conducting polymers as electrode materials in storage batteries [3], as a p-n heterojunction in light-emitting electrochemical cells [4] and in photovoltaic devices [5]. In the latter case, the n-type conjugated polymer can act as electron acceptor, with high electroaffinity, and the p-type polymer can act as a hole conductor, with low ionization potential. The term hole will, in this article, for simplicity denote a polaronic-like quasi-particle responsible for positive charge carrier transport. Similarly, the term electron will be used to denote a polaronic-like quasi-particle responsible for negative charge carrier transport.

Parameters such as ionization potential (IP), electroaffinity (EA) and energy gap ( $E_g$ ) are important to understand and control the electrical and optical properties as well as the doping process of conducting polymers. In particular, the IP gives a good indication of whether a given p-type dopant is capable of ionizing the polymer chain, while  $E_g$  can be associated with the observed optical transitions and intrinsic electrical properties. The difference between  $E_g$  and IP provides an estimate of EA, which is important for understanding the n-type doping process [6].

These parameters are useful to construct the energy level diagrams of conducting polymers [7]. Methods to determine the energy diagram are important in order to develop a further understanding of, and to optimize, device performance. Both IP and EA are of crucial importance when device applications are considered

I.A. Hümmelgen (✉)  
Departamento de Física, Universidade Federal do Paraná,  
Caixa Postal 19044, 81531-990 Curitiba PR, Brazil  
E-mail: iah@fisica.ufpr.br  
Fax: +55-41-3613645

L. Micaroni  
Departamento de Química, Universidade Federal do Paraná,  
Caixa Postal 19081, 81531-990 Curitiba PR, Brazil

F.C. Nart  
Instituto de Química de São Carlos, Universidade de São Paulo,  
Caixa Postal 369, 13560-970 São Carlos SP, Brazil

because IP and EA are the polymer-related major factors determining electrode/polymer interfacial energy barriers [8], despite the fact that the contribution of other factors cannot be neglected [9].

In this letter, employing optical and electrochemical techniques we obtain  $E_g$  and IP of some conducting polymers, such as polypyrrole (PPy) and two polythiophene derivatives, poly(3-methylthiophene) (PMeT) and poly(3-hexylthiophene) (PHT). With these parameters we have constructed their energy level diagrams. Additionally, it is important to stress that, compared to other available techniques, the methodology used is simple, non-expensive and easy to run, so that it may be used in routine work, e.g. to control different polymer batches used in device applications.

## Experimental

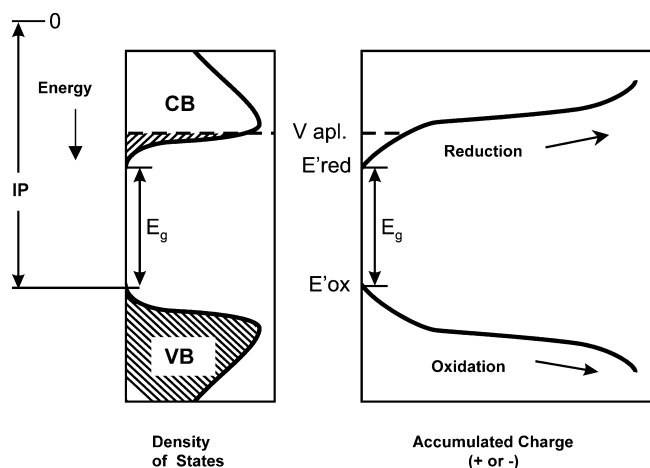
PPy, PMeT and PHT films were galvanostatically deposited onto ITO (indium-tin-oxide) by applying current densities of 1.00, 3.75 and 3.50 mA cm<sup>-2</sup>, respectively. For all the syntheses, the electrolyte was a 0.1 mol L<sup>-1</sup> solution of Me<sub>4</sub>NBF<sub>4</sub> in acetonitrile containing the respective monomer in 0.1 mol L<sup>-1</sup> concentration. PPy and PMeT films were deposited with charge densities of 50 mC cm<sup>-2</sup> and the PHT film with 75 mC cm<sup>-2</sup>.

The cyclic voltammograms of the polymers were performed in a single cell with three electrodes at a sweep rate of 30 mV s<sup>-1</sup>. The counter electrode was a Pt wire and the reference electrode was Ag/AgCl. The electrolyte was a 0.1 mol L<sup>-1</sup> solution of Me<sub>4</sub>NBF<sub>4</sub> in acetonitrile. The measurements were accomplished with a Microquímica model MQPG-01 potentiostat. The absorption spectra were obtained by in situ spectroelectrochemical measurements in a 8452-A HP diode UV-visible spectrophotometer, at room temperature, with the same cell and electrolyte described above and the polymers PPy, PMeT and PHT polarized at, respectively, -1.2, -0.2 and 0.2 V vs. Ag/AgCl.

## Results and discussion

The relationship between electrochemical parameters considering a simplified energy level structure for the polymers is shown schematically in Fig. 1. On the left-hand side, the density of states is drawn for two relevant bands, the valence band (VB) and the conduction band (CB). The energy gap ( $E_g$ ) is then the energy difference between the top of valence band and the bottom of the conduction band, and the ionization potential (IP) is the energy from the valence band edge to the vacuum level. On the right-hand side of Fig. 1, the potentials for a reduction or oxidation cycle as a function of accumulated charge are schematically shown [6].

Rigorously, the existence of conduction and valence bands would require the charge carriers to be described by Bloch wave functions, which presuppose at least one-dimensional periodicity. Real polymer chains are far from this perfect condition, actually presenting several conformational defects that break conjugation and produce disorder in the spatial arrangement and energy levels. Apart from isolated molecules, local IP and EA values are still influenced by polarization effects and



**Fig. 1.** Relationship between the electrochemically measured onset potentials,  $E'_{ox}$  and  $E'_{red}$ , and the ionization potential, IP, and the energy gap,  $E_g$ , derived from a simplified polymer band structure [6]

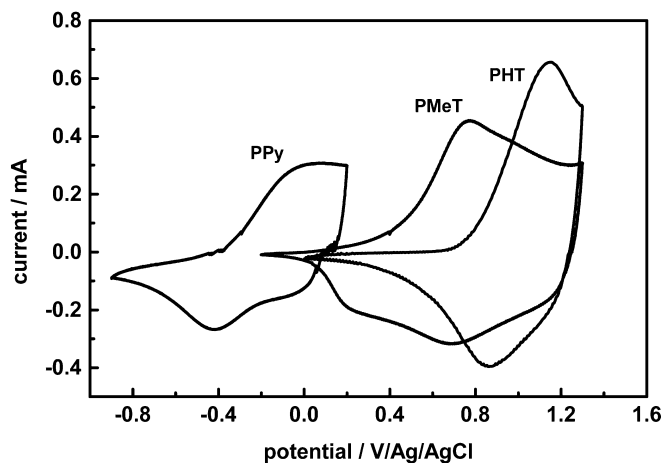
structural relaxation. Under these conditions, conjugated polymers do not present a band as in inorganic crystalline semiconductors; there are only energy intervals with a high density of states that correspond to the HOMO (highest occupied molecular orbital) or LUMO (lowest unoccupied molecular orbital) of polymer molecules or chain segments (local quantities) that are energetically distributed (larger disorder implies a broader distribution). In spite of evident differences, in order to simplify and permit an analogy with well-established inorganic semiconductor concepts, the limits of high density of the HOMO and LUMO levels are commonly denoted polymer valence and conduction band edges, respectively. The charge transport in these non-ideal conjugated polymers then occurs via a hopping (phonon-assisted quantum mechanical tunneling) mechanism.

In the case of the oxidation process, no charges will be removed from the polymer electrode until the applied voltage reaches an onset value, which corresponds to the highest occupied states in the valence band (Fig. 1). As the voltage is further increased, more and more states are emptied. The opposite is true for the reduction cycle. If one is able to do both oxidation and reduction in the same electrolyte system, the difference between the two onset potentials should closely correspond to the energy gap and can be directly compared to the optical band gap [6]. This has not generally been the case for conjugated polymers, where often only reduction or oxidation is observed, or where only one process is found to be reversible. Moreover, in order to correlate the oxidation and reduction potentials to IP and EA values, respectively, the electrochemical processes must keep the molecular structure of the polymer, i.e. no degradation of the polymer chain can occur. In this case, the oxidation or reduction potential will be related not only to the loss or capture of an electron, but to the overall chemical processes like bond dissociation. The injection of charge must only convert the polymer chain into an ion.

Unfortunately, only the oxidation process is easily achieved for the polymers used in this work. Figure 2 shows typical voltammograms for PPy, PMeT and PHT, which correspond to the oxidation process of the polymer, with anion insertion of the electrolyte (p-type doping) and dedoping to the neutral state. In order to ascertain that relaxation effects, caused by ion transport into and out of the film during the redox process, are minimized, we will use the onset of the oxidation process. At this point the polymer just starts to be oxidized and ion transport in the film will not cause large changes in the film structure. The onset potentials ( $E'_{\text{ox}}$ ) were estimated from the intersection of the two tangents drawn at the rising oxidation current and background current in the cyclic voltammograms. The reversibility of the process (the same electrical charge in the oxidation and reduction cycles) indicates that no electrochemical degradation takes place and the onset of the oxidation potential can be related to the ionization potential.

To transpose the measured redox behavior into estimates for the ionization potential and electron affinity, it is necessary to relate the electrochemical potentials to the vacuum level relative to which IP and EA are defined. It is convenient to refer the potential values ( $E$ ) to the standard hydrogen electrode (SHE), in the sequence correcting them to the vacuum level reference. We will assume, for practical purposes, that the liquid junction potential between the aqueous KCl and the organic solution can be neglected. The conversion of the SHE to the vacuum scale can be accomplished by theoretical and experimental means with relaxation of thermodynamic rigor. In that case, one obtains an energy value corresponding to  $E$  for SHE at about  $-4.6 \pm 0.1$  eV on the zero vacuum-level scale [10]. It is important to consider that values obtained by various authors slightly differ [11], but the average is 4.6 eV [12].

Assuming the validity of the difference value, expressing the potentials in volts we can write:



**Fig. 2.** Cyclic voltammograms for PPy, PMeT and PHT films. Electrolyte: 0.1 mol L<sup>-1</sup> solution of Me<sub>4</sub>NBF<sub>4</sub> in acetonitrile;  $v = 30$  mV s<sup>-1</sup>

$$E_{\text{SHE}} \approx E_{\text{vac}} + 4.6 \quad (1)$$

where  $E_{\text{SHE}}$  is the standard hydrogen electrode potential and  $E_{\text{vac}}$  the vacuum potential. Taking into account the correction for the case that Ag/AgCl is used as the reference electrode, the potential is expressed as:

$$E_{\text{Ag/AgCl}} \approx E_{\text{SHE}} - 0.2 \approx E_{\text{vac}} + 4.4 \quad (2)$$

It is then possible, having the oxidation potential onset  $E'_{\text{ox}}$  relative to Ag/AgCl, to calculate the oxidation potential onset relative to the vacuum level:

$$E_{\text{ox}} = E'_{\text{ox}} + E_{\text{Ag/AgCl}} \approx E'_{\text{ox}} + E_{\text{vac}} + 4.4 \quad (3)$$

Assuming  $E_{\text{vac}} \equiv 0$ , we can calculate the ionization potential, i.e.  $\text{IP} = eE_{\text{ox}}$  ( $e$  is the elementary charge), which permits location of the HOMO level in an energy diagram, correlating the energies with other useful quantities like metal and transparent conducting oxide electrode work functions. In a similar way, EA can be obtained if  $E'_{\text{red}}$  (reduction potential onset) can be experimentally determined.

The potentials measured at the onset of oxidation of the polymers investigated in this work are given in Table 1, referred to the Ag/AgCl reference electrode, and the application of Eq. 3 yields the corresponding IP values.

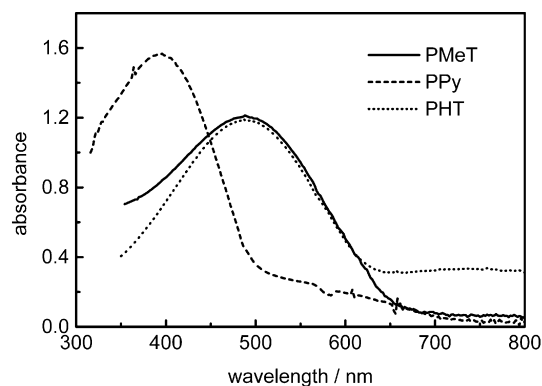
Comparison of the determined onset potential with the literature data for PPy oxidation reveals that there is a small variation of the onset oxidation potential (0.1 V) with variation of the solvent, electrolyte and electrode material [13, 14, 15]. Therefore, the deviation in the estimation of the onset potential would be within 0.1 V, which is reasonable taking into account the easy handling of the method proposed. The value of the estimated IP is again affected by uncertainties related to the determination of the onset potentials.

The IP value for PPy estimated theoretically using the VEH approximation is 4.0 eV [16], close to the estimated experimental value obtained from the onset of the oxidation potential (see Table 1).

In the absence of a direct measurement of the reduction potential, it has been common practice to estimate EA by subtraction of the energy gap [6]. Figure 3 shows the absorption spectra of the conducting polymers. The absorption onsets rather than peak maxima should be taken as corresponding to  $E_g$ . Table 1 shows

**Table 1.** The onset potentials for the electrochemical oxidation ( $E'_{\text{ox}}$ ), the ionization potentials (IP), absorption onsets ( $\lambda'$ ) and energy gap ( $E_g$ ) values for the conducting polymers PPy, PMeT and PHT

	PPy	PMeT	PHT
$E'_{\text{ox}}$ (V vs. Ag/AgCl)	-0.4	0.5	0.8
IP (eV)	4.0	4.9	5.2
$\lambda'$ (nm)	516	654	627
$E_g$ (eV)	2.4	1.9	2.0
EA (eV)	1.6	3.0	3.2

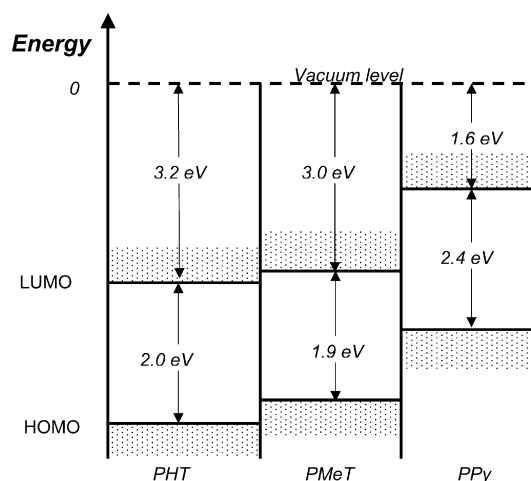


**Fig. 3.** Absorption spectra of PPy, PMeT and PHT films at the respective polarizations of  $-1.2$ ,  $-0.2$  and  $0.2$  V vs. Ag/AgCl. Electrolyte:  $0.1 \text{ mol L}^{-1}$  solution of  $\text{Me}_4\text{NBF}_4$  in acetonitrile

the values of the absorption onset ( $\lambda'$ ) that yield the  $E_g$  values. These values agree with some experimental values reported in the literature for PMeT [17], PPy [18] and PHT [19]. The EA values (Table 1) were obtained by taking the difference between the other two parameters.

Based on these results it was possible to construct the energy level diagrams for PPy, PMeT and PHT (Fig. 4). For PHT, the location of the HOMO that corresponds to the IP is similar to that evaluated by photoelectron spectroscopy ( $5.2 \text{ eV}$ ) [19]. Our results agree reasonably well with those reported by Miyauchi et al. [20] concerning the stabilization displacement of the HOMO level of PMeT when compared to PPy, which was found to be  $0.8 \text{ eV}$  [21]. For PMeT, the energy diagram is displaced by  $\sim 0.4 \text{ eV}$  from that obtained by flat band measurements from the electrolyte/polymer interface [22] and by electrical measurements using suitable solid-state devices [23, 24]. The displacement observed for PMeT in solid-state device-based measurements suggests that the charge injection of positive charge carriers into PMeT occurs throughout the same polymer segments responsible for the low-energy tail in the PMeT absorption spectrum and for the low-voltage tail in the PMeT voltammogram: longer effective conjugation length segments or segments with energy levels inside the gap due to enhanced energetic disorder. In this case, the charge injection into PMeT would occur preferentially through these energetically more favorable sites, effectively reducing the energy barrier. The major contribution from the material to the absorption spectrum, or to the voltammogram, however, does not originate from this material fraction. Assuming that these sites occur at low concentration (as is the case when the distribution of HOMO and LUMO levels is of a Gaussian type), eventually at specific interfaces they are expected to be more important at low charge injection levels, when local current densities would not be too high.

Another important point to be considered is that the solid-state stabilization is due, in part, to the polarization of the neighboring molecules. At the polymer/elec-



**Fig. 4.** Energy level diagram schemes for PPy, PMeT and PHT

trode interface, symmetry is broken, so that there may be a molecular energy level shift of the molecules at the interface, when compared to molecules in the bulk, modifying the energy barrier for charge injection. This contribution is more important in techniques that evaluate energy levels by measuring an energy difference to a reference level at the interface, as is the case in solid-state devices: the polymer energy levels are determined through the determination of the energy barrier height between metal and polymer, adding again the metal work function. Polarization effect contributions would make this value different from those values determined by other methods.

## Conclusions

We have demonstrated that, by simple and non-cost-intensive electrochemical and optical measurements, we can estimate important parameters such as the ionization potential and the energy gap of conducting polymers.

There are several uncertainties associated in the conversion of the reference electrode potential to the vacuum scale and there are also uncertainties in determining the onset of the oxidation potential due to the structural relaxation during electrochemical oxidation of the polymeric films. In spite of these uncertainties, the method seems very convenient owing to the easy handling and low cost. However, to validate further the method, other measurements are in course in our laboratory and the results will be the subject of a future communication.

Using the values for IP and  $E_g$  estimated using the method, we have constructed energy level diagrams for PPy, PMeT and PHT, exemplifying the procedure.

**Acknowledgements** The authors would like to thank PADCT/CNPq (project 62.0081/97-0 CEMAT) and FUNPAR for financial support. I.A.H. acknowledges CNPq for a research fellowship.

F.C.N. acknowledges financial support from FAPESP and CNPq.

---

## References

- Scrosati B (1993) Applications of electroactive polymers, Chapman & Hall, London, p 43
- Gazotti WA, Nogueira AF, Girotto EM, Micaroni L, Martini M, das Neves S, De Paoli M-A (2001) Optical devices based on conductive polymers. In Nalwa HS (ed) Handbook of advanced electronic and photonic materials and devices, vol 10. Academic Press, London, p 54
- Scrosati B (1988) Prog Solid State Chem 18:1
- Pei Q, Yang Y, Yu G, Cao Y, Heeger AJ (1997) Synth Met 85:1229
- Onoda M, Tada K, Zakhidov AA, Yoshino K (1998) Thin Solid Films 331:76
- Eckhardt H, Shacklette LW, Jen KY, Elsenbaumer RL (1989) J Chem Phys 91:1303
- Janietz S, Bradley DDD, Grell M, Giebeler C, Inbasekaran M, Woo EP (1998) Appl Phys Lett 73:2453
- Roman LS, Hümmelgen IA, Nart FC, Péres LO, de Sá EL (1996) J Chem Phys 105:10614
- Spaepen H, Campbell IH, Smith DL (2001) Physics of organic devices. In Ehrenreich F (ed) Solid state physics – advances in research and applications, vol 55. Academic Press, London, p 1
- Bard AJ, Faulkner LR (1980) Electrochemical methods – fundamentals and applications, Wiley, New York, p 634
- Trasatti SJ (1983) Electroanal Chem 150:1
- Bockris JO'M, Khan SUM (1983) Surface electrochemistry – a molecular level approach. Plenum Press, New York, p 78
- Lee H, Yang H, Juhyoun K, (1999) J Electroanal Chem 468:104
- Xie Q, Kuwabata S, Yoneyama H (1997) J Electroanal Chem 420:219
- Fermin DJ, Teuel H, Scharaifker BR (1996) J Electroanal Chem 401:207
- Bredas JL (1986) Electronic structure of highly conducting polymers. In: Skotheim TA (ed) Handbook of conducting polymers, vol 2. Dekker, New York, p 860
- Stöckert D, Kessel R, Schultze JW (1991) Synth Met 41–43:1295
- Kaneto K, Takeda S, Yoshino K (1985) Jpn J Appl Phys 24:L553
- Onoda M, Manda Y, Morita S, Yoshino K (1992) Jpn J Appl Phys 31:2265
- Miyauchi S, Goto Y, Tsubata I, Sorimachi Y (1991) Synth Met 41–43:1051
- Valaski R, Ayoub S, Micaroni L, Hümmelgen IA (2001) Thin Solid Films 388:171
- Micaroni L, Fonseca CP, Decker F, De Paoli M-A (2000) Sol Energy Mater Sol Cells 60:27
- Valaski R, Bozza AF, Micaroni L, Hümmelgen IA (2000) J Solid State Electrochem 4:390
- Valaski R, Moreira LM, Micaroni L, Hümmelgen IA (2002) J Appl Phys (in press)